

Article

Macromolecular Architectures Designed by Living Radical Polymerization with Organic Catalysts

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Abstract: Well-defined diblock and triblock copolymers, star polymers, and concentrated polymer brushes on solid surfaces were prepared using living radical polymerization with organic catalysts. Polymerizations of methyl methacrylate, butyl acrylate, and selected functional methacrylates were performed with a monofunctional initiator, a difunctional initiator, a trifunctional initiator, and a surface-immobilized initiator.

Keywords: living radical polymerization; organic catalysts; block copolymers; triblock copolymers; star polymers; polymer brushes

1. Introduction

Living radical polymerization (LRP) has attracted increased attention as it allows for the rational design of polymer architectures with predictable molecular weights and narrow molecular weight distributions [1–3]. LRP can offer, not only well-defined linear homopolymers, but also diblock copolymers, triblock copolymers, star polymers, and surface-grated brush polymers with sophisticated structures, which have many useful applications.

LRP is based on the reversible activation of a dormant species (Polymer-X) to a propagating radical (Polymer•) (Scheme 1a). A sufficiently large number of activation-deactivation cycles are required for low polydispersity [4–7]. Examples of the capping agent (X) include nitroxides, dithioesters, tellurides, and halogens [8–15]. Halogens are combined with transition metal catalysts [13–15].

We recently developed new LRP systems using iodine as a capping agent and organic molecules as catalysts. We developed two mechanistically different systems referred to as reversible chain transfer catalyzed polymerization (RTCP) [16–23] and reversible coordination mediated polymerization (RCMP) [24–27].

RTCP uses a reversible chain transfer of Polymer-I with a catalyst radical to generate Polymer• and a catalyst (deactivator) (Scheme 1b). RTCP consists of a dormant species, a catalyst (deactivator), and a radical source that supplies Polymer•. The catalysts include germanium, phosphorus, nitrogen, oxygen, and carbon-centered iodides including *N*-iodosuccinimide (NIS) (Figure 1) [17] used in the present work.

RCMP utilizes a reversible coordination of Polymer-I with a catalyst (activator) to generate Polymer• and a catalyst-iodine complex. RCMP consists of a dormant species and a catalyst (activator). The catalysts include amines and organic salts such as tetrabutylammonium iodide (BNI) (Figure 1) [27] and methyltributylphosphonium iodide (BMPI) (Figure 1) [27] used in the present work.

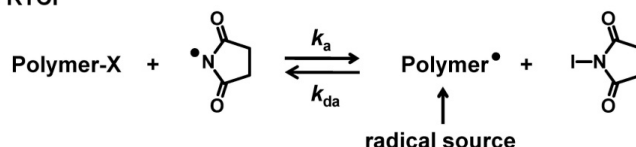
The attractive features of RTCP and RCMP include no use of special capping agents or metals. The catalysts are inexpensive, relatively non-toxic, easy to handle, and amenable to a wide range of monomers including styrenes, methacrylates, acrylates, acrylonitrile, and those with various functional groups. RTCP and RCMP can be facile and pervasive methodologies for various applications.

Scheme 1. Reversible activation: (a) General scheme; (b) RTCP; and (c) RCMP.

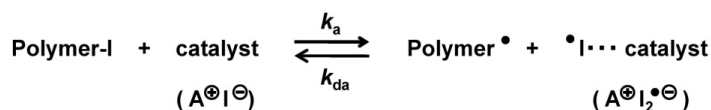
(a) Reversible activation (general scheme)



(b) RTCP

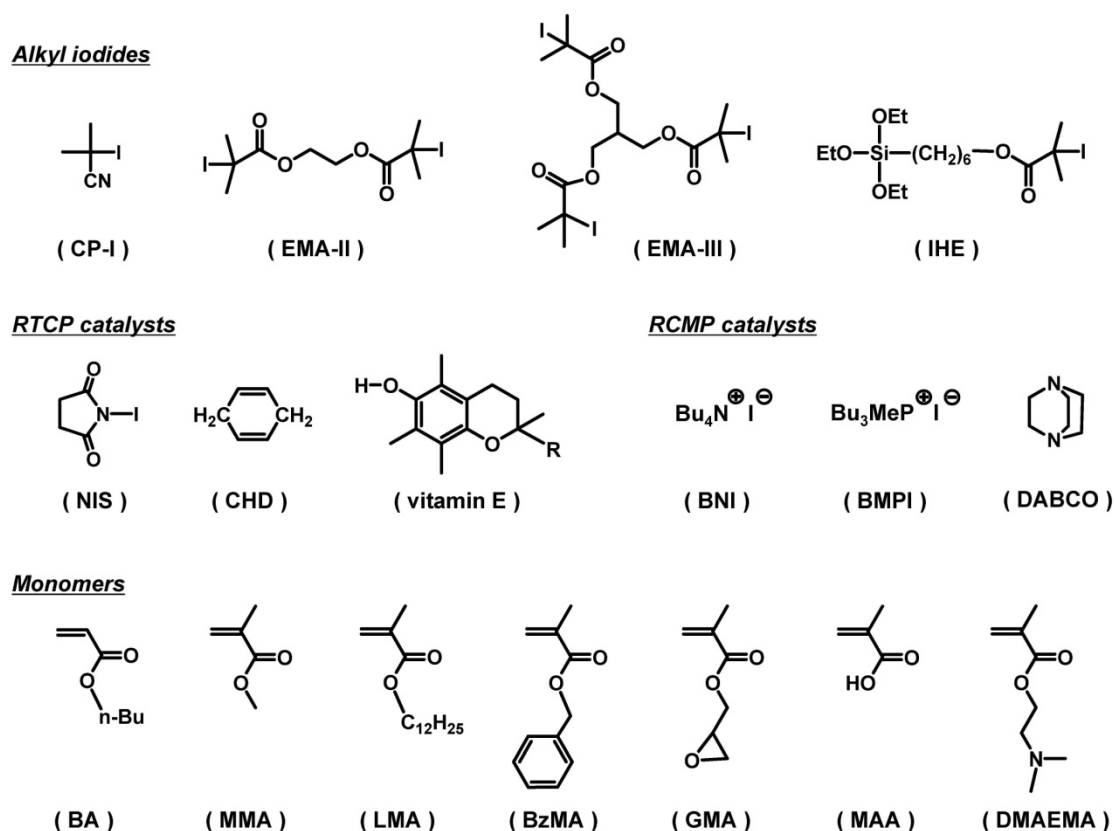


(c) RCMP



We previously reported the use of RTCP and RCMP in preparing well-defined linear polymers including homopolymers, random copolymers, and diblock copolymers [16–27]. In this paper, we report new examples of diblock copolymers and summarize the diblock copolymers prepared in previous and current works. We also report the syntheses of triblock copolymers, 3-arm star polymers, and surface-grafted brush polymers. Macromolecular designs of diblock, triblock, star, and brush architectures are important to widen the range of RTCP and RCMP applications. The structures and abbreviations of the studied monomers, catalysts, and initiating alkyl iodides (dormant species) are provided in Figure 1.

Figure 1. Structures and abbreviations of studied alkyl iodides (initiators), catalysts, and monomers.



2. Experimental Section

2.1. Materials

Methyl methacrylate (MMA) (99%, Nacalai Tesque, Kyoto, Japan), glycidyl methacrylate (GMA) (97%, Aldrich, St. Louis, MI, USA), 2-(dimethylamino)ethyl methacrylate (DMAEMA) (99%, Wako Pure Chemical, Osaka, Japan), methacrylic acid (MAA) (99%, Nacalai), lauryl methacrylate (LMA) (Aldrich, 96%), benzyl methacrylate (BzMA) (96%, Aldrich), and butyl acrylate (BA) (99%, Nacalai) were purified on an alumina column. 2-cyanopropyl iodide (CP-I) [99%, Tokyo Chemical Industry (TCI), Tokyo, Japan (contract service)], I_2 (98%, Wako), NIS (98%, Wako), 1,4-cyclohexadiene (CHD) (98%, TCI), vitamin E (99.5%, Wako), BNI (98%, TCI), BMPI (96%, Wako), azobis(isobutyronitrile) (AIBN) (98%, Wako), 2,2'-azobis(2,4-dimethyl valeronitrile) (V65) (95%, Wako), 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70) (95%, Wako), sodium iodide (NaI)

(99.5%, Wako), 2-bromoisobutryl bromide (98%, TCI), ethylene glycol (99.5%, Wako), glycerol (99%, Wako), and pyridine (99.5%, Kishida Chemical, Osaka, Japan) were used as received.

2.2. GPC Measurements

Gel permeation chromatography (GPC) analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) or dimethyl formamide (DMF) with a flow rate of 0.8 mL/min (40 °C). Sample detection and quantification were conducted using a Shodex differential refractometer RI-101 calibrated with known polymer concentrations in solvent. The monomer conversion was determined from the GPC peak area. The column system was calibrated using standard poly(methyl methacrylate)s (PMMA)s. For the homopolymerizations of BA and LMA and the homopolymerization of MMA from a trifunctional initiator, the samples were also detected using a Wyatt Technology DAWN EOS multiangle laser light-scattering (MALLS) detector (Santa Barbara, CA, USA) equipped with a Ga-As laser ($\lambda = 690$ nm). The refractive index increment dn/dc was determined with a Wyatt Technology OPTILAB DSP differential refractometer ($\lambda = 690$ nm).

2.3. Preparation of Ethylene Glycol Bis(2-iodoisobutyrate) (EMA-II)

Ethylene glycol (5.0 g: 80 mmol) and pyridine (13.9g: 176 mmol) were stirred in dichloromethane (25 mL). The mixture was slowly added to 2-bromoisobutryl bromide (44.1 g: 192 mmol) in dichloromethane 15 mL and stirred for an hour. This white suspension was washed with aqueous HBr (5%), saturated aqueous Na_2SO_3 , and water and dried over MgSO_4 . Removal of the solvent under reduced pressure afforded the crude ethylene glycol bis(2-bromoisobutyrate) (EMA-BB), which was used in the subsequent reaction without further purification. ^1H NMR (400 MHz, CDCl_3): 1.92 (s, 12H, CCH_3), 4.42 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$). EMA-BB (25.5 g: 71 mmol), and NaI (50.9 g: 340 mmol), were stirred in dry acetonitrile (110 mL) at 80 °C for 8 h. The reaction mixture was filtered off to remove NaBr. The solution was concentrated under reduced pressure and diluted with dichloromethane. The mixture was washed with saturated aqueous Na_2SO_3 solution and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (ethyl acetate/hexane) to afford pure EMA-II in a 35% yield. ^1H NMR (400 MHz, CDCl_3): 2.08 (s, 12H, CCH_3), 4.39 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$).

2.4. Preparation of Glycerol Tris(2-iodoisobutyrate) (EMA-III)

EMA-III was obtained from the same process as EMA-II. Glycerol was used instead of ethylene glycol to afford pure EMA-III in a 35% yield. ^1H NMR (400 MHz, CDCl_3): 2.08 (m, 18H, CCH_3), 4.33 (dd, 2H, OCHHCHCHHO), 4.48 (dd, 2H, OCHHCHCHHO), and 5.37 (m, 1H, OCHHCHCHHO).

2.5. Preparation of 6-(2-iodo-2-isobutyloxy)Hexyltriethoxysilane (IHE)

6-(2-bromo-2-isobutyloxy)hexyltriethoxysilane (BHE) was prepared according to the literature [28]. BHE (6.2 g: 15 mmol) and NaI (11.23 g: 75 mmol) were stirred in dry acetone (100 mL) at 50 °C for

two days, and the reaction mixture was evaporated to dryness. Dry chloroform (300 mL) was subsequently added. The precipitated NaI, which contained NaBr, was filtered off. The solvent was evaporated, yielding IHE in a 98% yield. ^1H NMR (CDCl_3): 0.64 (t, 2H, CH_2Si), 1.23 (t, 9H, $\text{CH}_3\text{CH}_2\text{OSi}$), 1.32–1.54 and 1.60–1.75 (broad, 8H, CH_2), 2.08 (s, 6H, CCH_3), 3.81 (q, 6H, $\text{SiOCH}_2\text{CH}_3$), and 4.15 (t, $J = 6.8$ Hz, 2H, OCH_2).

2.6. Polymerization

In a typical run, a Schlenk flask containing a mixture of MMA (3 mL), CP-I, and a catalyst was heated at 60 °C under an argon atmosphere with magnetic stirring. For block copolymerization, the second monomer was subsequently added, and the solution was heated under an argon atmosphere with magnetic stirring. After the polymerization, the solution was quenched to room temperature, diluted with THF to a known concentration, and analyzed by GPC.

2.7. Preparation of Poly(methyl methacrylate) Iodide (PMMA-I)

A 100-mL round-bottom flask containing a mixture of MMA [(20 mL (8 M))], CP-I (80 mM), and BMPI (40 mM) was heated at 60 °C for 2.75 h under an argon atmosphere with magnetic stirring. After purification by reprecipitation from cold hexane twice, PMMA-I with $M_n = 5100$ and $\text{PDI} = 1.15$ was isolated. The polymer was then used as a macroinitiator for block copolymerizations (entries 1, 4, 7, and 8, in Table 1).

2.8. Preparation of Poly(butyl acrylate) Iodide (PBA-I)

A 100-mL round-bottom flask containing a mixture of BA [20 mL (8 M)], CP-I (80 mM), and BNI (320 mM) was heated at 110 °C for 16 h under an argon atmosphere with magnetic stirring. After purification by reprecipitation from water/methanol (9:1) twice, PBA-I with $M_n = 10,000$ and $\text{PDI} = 1.33$ was isolated. The polymer was used as a macroinitiator for block copolymerization (entry 10 in Table 1).

2.9. Surface-Initiated Polymerization

Silicon wafers (Ferrotec Corp., Tokyo, Japan, chemically/mechanically polished on one side, thickness 525 μm) were cleaned by successive sonication in acetone, water, and 1,2-dichloroethane for 8 min each and dried in a stream of nitrogen gas followed by evaporation under reduced pressure prior to use. The silicon wafer was immersed in an ethanol solution containing IHE (1 wt%) and 28% aqueous NH_3 (5 wt%) for 12 h at room temperature under darkness to immobilize the initiating group and then washed with ethanol. For graft polymerization of MMA, the IHE-immobilized wafer was immersed in a solution containing MMA [3 mL (8 M)], CP-I (20 mM), NIS (5 mM), and AIBN (20 mM) in a Schlenk flask and subsequently heated at 70 °C for 4 h under an argon atmosphere. After polymerization, the solution was diluted with THF to a known concentration and analyzed using GPC. The substrate was copiously rinsed with methanol to remove physisorbed free polymers and impurities. The thickness of the brush layer in the dry state was determined using a rotating compensator spectroscopic ellipsometer (M-2000UTM, J.A. Woolam, Lincoln, NE, USA) equipped with D_2 and QTH lamps with a polarizer angle of 45 degrees and an incident angle of 70 degrees.

3. Results and Discussion

3.1. Diblock Copolymers

Table 1 summarizes examples of diblock copolymerization, including previously reported [18,27] and new results as indicated.

Table 1 (entries 1–3) shows the block copolymerizations of MMA and GMA. The polymerizations were conducted using three methods. The first method involved polymerization from a purified macroinitiator (polymer-iodide) (entry 1). We prepared the PMMA-I macroinitiator in the bulk RCMP of MMA (8 M) using CP-I (80 mM) as an initiating dormant species and BMPI (40 mM) as a catalyst at 60 °C for 2.75 h. After purification from hexane, we obtained a purified PMMA-I macroinitiator with $M_n = 5500$ and PDI = 1.15. The iodine elemental analysis indicated that this macroinitiator included a high fraction (95%) of active polymer possessing iodine at the chain end (with $\pm 5\%$ experimental error). Such high chain-end fidelity of this macroinitiator can lead to high block efficiency for the subsequent block copolymerizations. Using this macroinitiator, the RCMP of GMA yielded a well-defined diblock copolymers with $M_n = 17,000$ and PDI = 1.23 at 90% monomer conversion for 6 h at 60 °C.

The second method involved successive addition of two monomers starting from a purified low-mass dormant species (entry 2). When CP-I was used as a low-mass dormant species, a low-polydispersity diblock copolymer (PDI = 1.34) was obtained. Toluene was used as a solvent to prevent solidification of the first block solution, which facilitated mixing with the second monomer. To overcome the slow polymerization due to dilution, a small amount of an azo compound (V65) was added in the first block. V65 can supply Polymer• and, thus, increase the polymerization rate R_p . Azo compounds have often been used to increase R_p in other LRP systems [4–7]. The R_p was sufficiently increased (90% monomer conversion over 6 h) without causing significant broadening of the molecular weight distribution. Because the amount of V65 was approximately 0.15 equivalents compared with CP-I, the obtained block copolymer could include approximately 15% of dead first-block homopolymer.

The third method involved successive addition of two monomers starting from molecular iodine (I_2) and an azo compound ($R-N=N-R$) (entry 3). An alkyl iodide ($R-I$) formed *in situ* in the polymerization serves as the initiating dormant species. This I_2 /azo method was originally invented by Lacroix-Desmazes *et al.* for iodide-mediated LRP [29,30]. This method was also effective for RTCP [17,18] and RCMP [25,27]. A low-polydispersity diblock copolymer (PDI = 1.39) was obtained (entry 3).

Table 1. Syntheses of diblock copolymers.

First block/ second block	Entry	Polymerization	Monomer (equiv to [R-I])	R-I	In ^a	Cat	[M] ₀ /[R-I] ₀ /[In] ₀ / [cat] ₀ ^b (mM)	T (°C)	t (h)	Conv. (%)	M _n ^c (M _{n,theo})	PDI ^c	Ref. ^d
MMA/GMA	1	2nd block	GMA (200 eq)	PMMA-I ^e	–	BMPI	8000/80/80	60	6	90	17,000 (17,000)	1.23	[27]
	2	1st block	MMA (100 eq)	CP-I	V65	BMPI	8000/80/15/80 ^f	60	6	91	8300 (9100)	1.13	–
		2nd block	GMA (100 eq)	–	–	–	+8000	60	+6	200	17,000 (24,000)	1.34	–
	3	1st block	MMA (100 eq)	I ₂	V70/V65	BMPI	8000/40/(60/15)/80 ^f	60	6	89	8200 (8900)	1.12	–
		2nd block	GMA (100 eq)	–	–	–	+8000	60	+6	200	17,000 (24,000)	1.39	–
MMA/DMAEMA	4	2nd block	DMAEMA (100 eq)	PMMA-I ^e	V70	BMPI	8000/80/10/10	50	2	95	18,000 (19,000)	1.32	–
	5	1st block	MMA (100 eq)	CP-I	V65	BMPI	8000/80/15/80 ^f	60	6	91	8300 (9100)	1.25	–
		2nd block	DMAEMA (100 eq)	–	V70	–	+8000/15	50	+4	178	21,000 (23,000)	1.29	–
	6	1st block	MMA (100 eq)	I ₂	V70/V65	BMPI	8000/40/(60/15)/80 ^f	60	6	89	8200 (8900)	1.12	–
		2nd block	DMAEMA (100 eq)	–	V70	–	+8000/15	50	+4	172	21,000 (23,000)	1.29	–
MMA/(MMA/MAA)	7	2nd block	MMA/MAA (24/16 eq)	PMMA-I ^e	V70	CHD	8000/160/80/5	40	2	80	6600 (5700)	1.31	[18]
MMA/BA	8	2nd block	BA (100 eq)	PMMA-I ^e	–	BNI	8000/80/320	110	24	65	15,000 (16,000)	1.31	[27]
	9	1st block	MMA (100 eq)	CP-I	–	BMPI	8000/80/80	60	5	83	8400 (8300)	1.10	[27]
		2nd block	BA (100 eq)	–	–	BNI	8000/320	110	24	155	18,000 (18,000)	1.32	[27]
BA/MMA	10	2nd block	MMA (100 eq)	PBA-I ^e	–	BNI	8000/80/320 ^g	110	5	86	16,000 (20,000)	1.31	[27]
	11	1st block	BA (100 eq)	CP-I	–	BNI	8000/80/320	110	22	82	13,000 (11,000)	1.28	[27]
		2nd block	MMA (100 eq)	–	–	–	+8000 ^{f,g}	110	5	170	27,000 (21,000)	1.39	[27]

^a In = conventional azo radical initiator, V65 = 2,2'-azobis(2,4-dimethyl valeronitrile), and V70 = 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile). ^b M = monomer. ^c Determined by GPC with a multiangle laser light-scattering detector (MALLS) for the first block of entry 11 and PMMA-calibration for others. ^d Hyphen denotes this work. ^e PMMA-I (*M_n* = 5100 and PDI = 1.15) for entries 1 and 8, PMMA-I (*M_n* = 2700 and PDI = 1.15) for entries 4 and 7, and PBA-I (*M_n* = 10,000 and PDI = 1.33) for entry 10. ^f Diluted in toluene (40% toluene and 60% MMA for the first block of entries 2, 3, 5, and 6) and (50% toluene and 50% MMA for the second block of entry 11). ^g With the addition of I₂ (4 mM).

In the three cases studied (entries 1–3), the total polymerization time for the first and second blocks was below 12 h. Figure 2 provides the full molecular weight distributions (GPC chromatograms). A large fraction of the first block polymers was extended to block copolymers in all three cases, confirming the high block efficiency due to the high chain-end fidelity demonstrated above.

RTCP and RCMP provide a variety of diblock copolymers, including amphiphilic diblock copolymers consisting of water-insoluble and water-soluble segments. Table 1 shows amphiphilic diblock copolymers with MMA and DMAEMA (water-soluble basic) segments (entries 4–6) and MMA and MMA/MAA (water-soluble acidic) segments (entry 7). The second segment in entry 7 is a random copolymer of MMA (60%) and MAA (40%), which is water soluble at this monomer composition. Both the basic and acidic segments are accessible as water-soluble segments.

Table 1 (entries 8–11) shows diblock copolymerizations of MMA and BA. We can start with both MMA and BA (as the first block) to obtain well-defined diblock copolymers. In certain LRP systems, the synthetic order of the two blocks is crucial when two different monomer families are used. Thus, the lack of restriction in the synthetic order of the two blocks in the present system is of interest. Figure 3 shows the GPC chromatograms, confirming high block efficiency. These examples demonstrate the high accessibility of RTCP and RCMP to a variety of block copolymers.

Figure 2. GPC chromatograms for MMA/GMA diblock copolymerizations for entries 1–3 in Table 1: (a) entry 1; (b) entry 2; (c) entry 3.

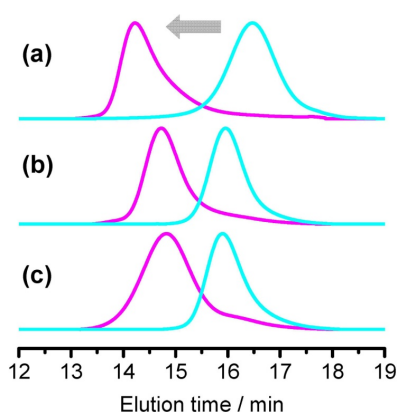
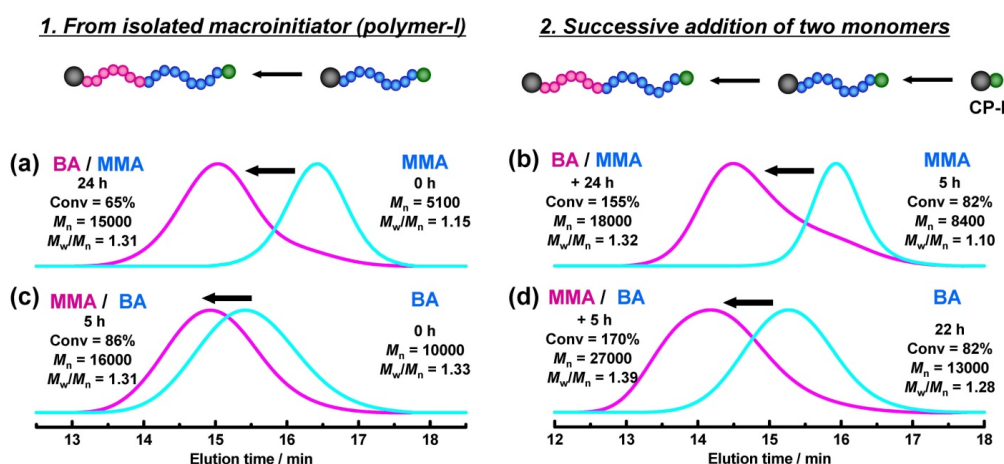


Figure 3. GPC chromatograms for BA/MMA and MMA/BA diblock copolymerizations for entries 8–11 in Table 1: (a) entry 8; (b) entry 9; (c) entry 10; (d) entry 11.



3.2. Triblock Copolymers

We attempted to use a difunctional initiator in addition to the above-described monofunctional initiator. We synthesized a difunctional initiator, EMA-II, with two methacrylate-type chain ends (Figure 1). Figure 4 shows the polymerizations of MMA with EMA-II. Low polydispersity polymers of predetermined molecular weight were obtained in both the RTCP with NIS at 40 °C and the RCMP with BMPI at 80 °C. Figure 5 shows the polymerizations of BA. Again, low polydispersity polymers of predetermined molecular weight were obtained in the RCMP with BNI at 110 °C. These results demonstrate the high initiation efficiency of EMA-II for both MMA and BA polymerizations.

The high initiation efficiency of EMA-II and the aforementioned lack of restricted synthetic order for the two blocks encouraged the preparation of two different types of triblock copolymers of MMA and BA, *i.e.*, BA-MMA-BA and MMA-BA-MMA triblock copolymers [Table 2 (entries 1–3)]. Starting with MMA (as the first block), we obtained a low-polydispersity BA-MMA-BA triblock copolymer (PDI = 1.31), and starting with BA, we obtained a low-polydispersity MMA-BA-MMA triblock copolymer (PDI = 1.3–1.4). The accessibility of two different types of triblock copolymers is an attractive feature.

The MMA-BA-MMA triblock copolymer is a hard-soft-hard triblock copolymer with a variety of applications including use in elastomers. We also prepared a well-defined MMA-LMA-MMA triblock copolymer [Table 2 (entry 4)] as another hard-soft-hard triblock copolymer. This copolymer is an all-methacrylate copolymer and was easier to prepare with a shorter polymerization time (12 h) than the MMA-BA-MMA copolymer (21–27 h).

Figure 4. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/EMA-II/catalyst systems: $[MMA]_0 = 8$ M; $[EMA-II]_0 = 80$ mM; $[BMPI]_0 = 80$ mM in 50% toluene at 80 °C and $[MMA]_0 = 8$ M; $[EMA-II]_0 = 40$ mM; $[V70]_0 = 10$ mM; $[NIS]_0 = 2$ mM in 50% diglyme at 40 °C. The symbols are indicated in the figure.

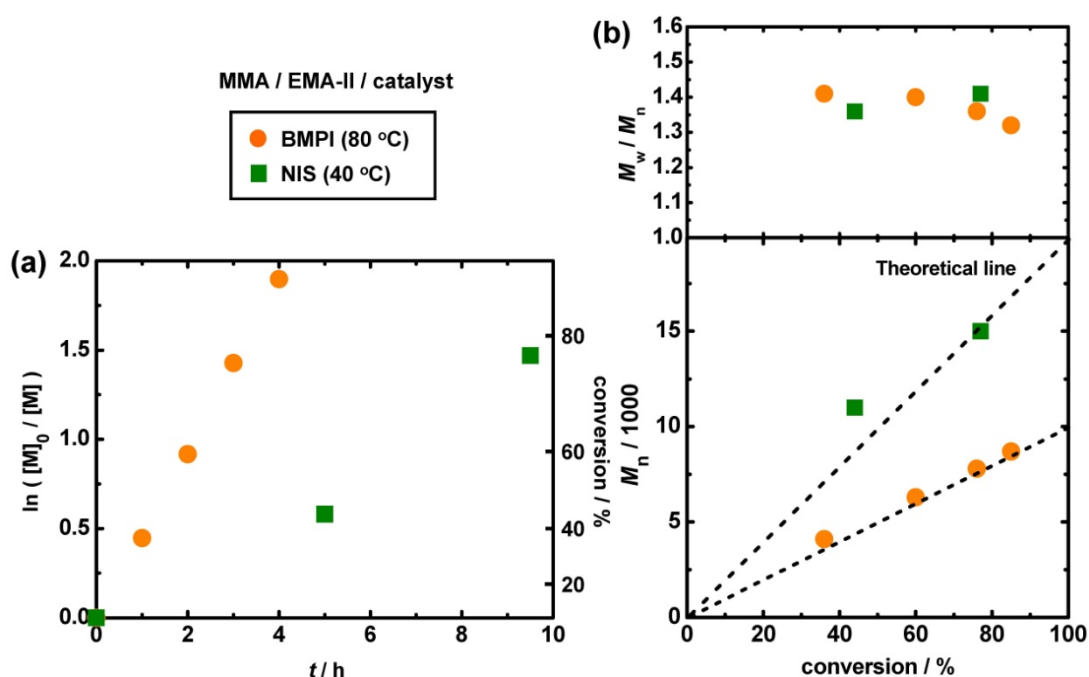
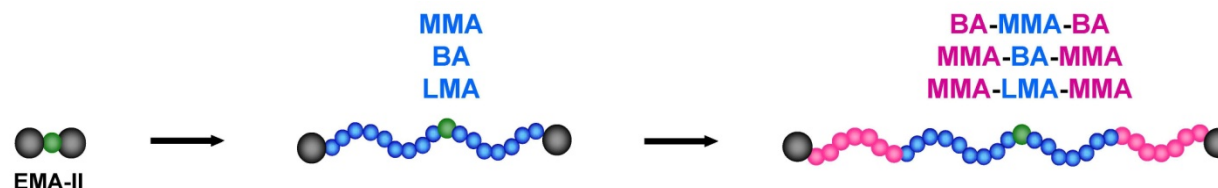


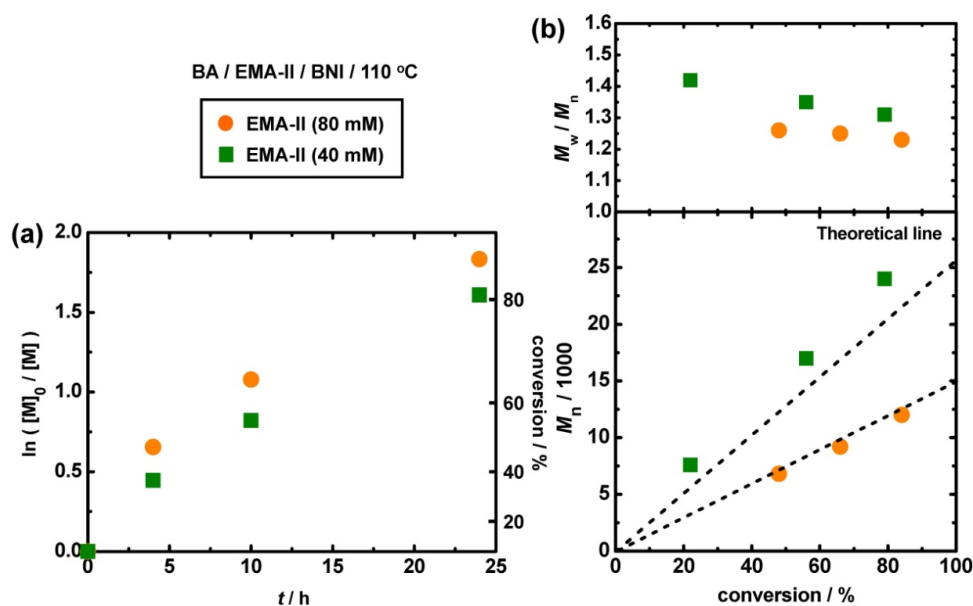
Table 2. Syntheses of triblock copolymers.



ABA block	Entry	Polymerization	Monomer (equiv to [R-I])	R-I	In ^a	Cat	[M] ₀ /[R-I] ₀ /[In] ₀ / [cat] ₀ ^b (mM)	T (°C)	t (h)	Conv. (%)	M _n ^c (M _{n,theo})	PDI ^c
BA/MMA/BA	1	1st block	MMA (100 eq)	EMA-II	—	BMPI	8000/80/80 ^d	80	6	85	8800 (8500)	1.32
		2nd block	BA (100 eq)	—	—	BNI	+8000/320	110	+24	154	17,000 (18,000)	1.31
MMA/BA/MMA	2	1st block	BA (100 eq)	EMA-II	—	BNI	8000/80/320	110	23	89	13,000 (11,000)	1.21
		2nd block	MMA (100 eq)	—	—	—	+ 8000 ^{d,e}	110	+5	186	23,000 (21,000)	1.33
	3	1st block	BA (100 eq)	EMA-II	—	BNI/DABCO	8000/80/(320/15)	110	16	87	14,000 (11,000)	1.37
		2nd block	MMA (100 eq)	—	—	—	+8000 ^d	110	+5	176	25,000 (20,000)	1.39
MMA/LMA/MMA	4	1st block	LMA (100 eq)	EMA-II	V65	BMPI	8000/80/15/80 ^d	60	6	84	17,000 (21,000)	1.31
		2nd block	MMA (100 eq)	—	V65	—	8000/10	60	+6	162	24,000 (29,000)	1.33

^a In = conventional azo radical initiator, and V65 = 2,2'-azobis(2,4-dimethyl valeronitrile). ^b M = monomer. ^c Determined by GPC with a multiangle laser light-scattering detector (MALLS) for the first block of entries 2-4 and PMMA-calibration for others. ^d Diluted in toluene (50% toluene and 50% MMA for the first block of entries 1 and the second block of entries 2 and 3 and 40% *N,N*-dimethyl 2-methoxyethylamide and 60% LMA for the first block of entry 4). ^e With the addition of I₂ (4 mM).

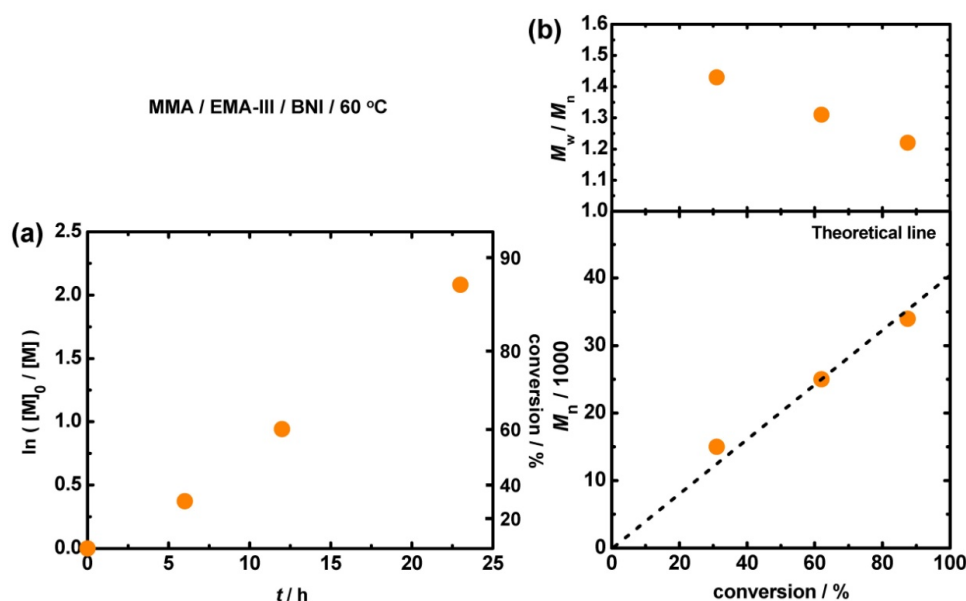
Figure 5. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the BA/EMA-II/BNI systems in bulk (110 °C): $[BA]_0 = 8$ M; $[EMA-II]_0 = 80$ or 40 mM; $[BNI]_0 = 320$ mM. The symbols are indicated in the figure.



3.3. Three-Arm Star Polymer

In addition to linear polymers, we also prepared a 3-arm star polymer from a trifunctional initiator. We synthesized EMA-III as a trifunctional initiator (Figure 1). Figure 6 shows the RCMP of MMA from EMA-III with BNI at 60 °C. The molecular weights were determined by GPC-MALLS. The M_n was in good agreement with the theoretical value and PDI was about 1.2 at a later stage of polymerization. A 3-arm star polymer with $M_n = 34,000$ and PDI = 1.22 was obtained as an example.

Figure 6. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/EMA-III/BNI system (60 °C): $[MMA]_0 = 8$ M; $[EMA-III]_0 = 20$ mM; $[BNI]_0 = 80$ mM in 25% toluene.

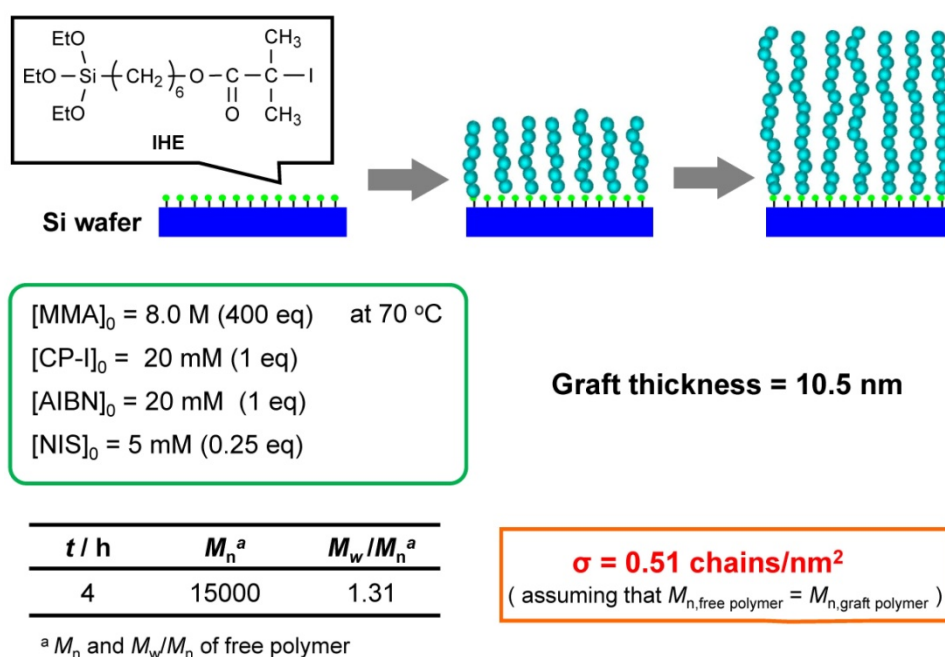


3.4. Surface-Initiated Polymerization—Concentrated Polymer Brush

A surface of material plays a crucial role in many important properties such as mechanical, thermodynamic, and chemical properties; thus, surface modification is an important issue [31–33]. Surface-initiated graft polymerization is among the most effective surface modification methods. Fukuda and Tsujii *et al.* [31,34] were the first to use LRP in graft polymerization to obtain a polymer brush with a surface density that was one order of magnitude higher than those of conventional brushes. The surface occupancy reached 40%. This so-called concentrated polymer brush takes a highly extended conformation, with extension up to 80% of all-trans conformation length in good solvents [31]. Such an extended conformation affords many new properties not attainable by conventional semi-dilute and dilute brushes, such as high elasticity, ultra-low friction, and excellent repellency of proteins and cells. Therefore, concentrated brushes may have useful applications [31–33].

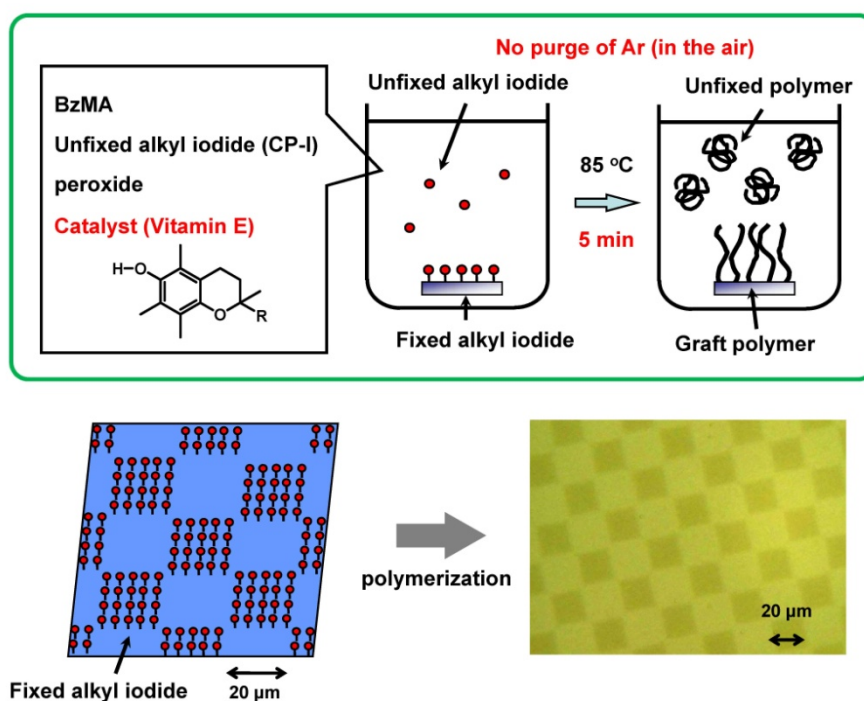
Given these results, surface-initiated RTCP was studied. We synthesized a surface-immobilizing initiator IHE (Figure 1) consisting of an alkyl iodide (initiating) moiety and a triethoxysilyl (TEOS) group. IHE was synthesized from BHE (the previously reported corresponding bromide) [28] via a halogen exchange reaction with NaI. IHE was fixed on a silicon wafer through the TEOS group. The IHE-immobilized silicon wafer was immersed in a mixture of MMA, a non-immobilized free initiator CP-I, a catalyst NIS, and a radical source AIBN, and heated at 70 °C for 4 h for polymerization (Figure 7). The free initiator CP-I was added because its addition can improve control over M_n and PDI of the immobilized graft polymer [31–33]. The M_n and PDI of the free polymers generated from free initiators, which are usually in good agreement with those of the immobilized graft polymers [31–33], were 15,000 and 1.31, respectively. The thickness of the graft polymer was measured to be 10.5 nm using ellipsometry. Assuming the same M_n for the graft and free polymers, the surface density of the graft polymer was calculated to be 0.51 chains/nm². This density is high and located in a concentrated polymer brush region [31], indicating the successful controlled synthesis of a concentrated polymer brush.

Figure 7. Surface-initiated RTCP of MMA. The experimental conditions are indicated in the figure.



Another example of the graft polymerization is depicted in Figure 8, in which IHE was fixed on the surface in a patterned manner. For demonstration purposes, we carried out an RTCP of BzMA, using a non-toxic catalyst vitamin E, without *a priori* purge of inert gas for the short time of 5 min at 85 °C. After the polymerization, the polymer brushes were observed as black square spots (Figure 8), demonstrating patterning and a robust and quick polymer brush synthesis.

Figure 8. Surface-initiated RTCP of BzMA: $[BzMA]_0 = 8.0 \text{ M}$; $[CP-I]_0 = 60 \text{ mM}$; $[di(4\text{-}t\text{-butylcyclohexyl}) \text{ peroxydicarbonate}]_0 = 60 \text{ mM}$; $[Vitamin \text{ E}]_0 = 10 \text{ mM}$; IHE-immobilized wafer (85 °C); in 25% toluene for 5 min. The conversion was 80%. The M_n and PDI of the free polymer were 13,000 and 1.45, respectively. The surface density was estimated to be 0.48 chains/nm^2 . The figure in the right-bottom part shows a microscope image of polymer brush patterned on surface.



4. Conclusions

Diblock copolymers were synthesized using a purified macroinitiator and the successive addition of two monomers. Well-defined triblock and star polymers and concentrated polymer brushes on solid surfaces were synthesized from difunctional, trifunctional, and surface-immobilized initiators. We prepared two different types of triblock copolymers using MMA and BA: MMA-BA-MMA and BA-MMA-BA copolymers. Access to a variety of macromolecular architectural designs may be beneficial to a variety of applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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