Self-catalyzed Living Radical Polymerization Using Quaternary-Ammonium-Iodide Containing Monomers

Chen-Gang Wang,[‡] *Xin Yi Oh,*[‡] *Xu Liu, and Atsushi Goto**

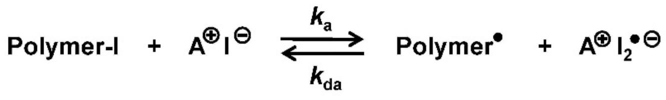
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

Abstract. Self-catalyzed living radical polymerization using quaternary ammonium iodide (QAI)-containing monomers is reported. The monomer contains a polymerizable methacrylate or acrylate moiety and QAI as a catalytic moiety at the side chain. Several (functional) methacrylates and acrylates were successfully co-polymerized with QAI-containing monomers without additional catalysts, generating QAI-containing copolymers. The obtained QAI-containing polymers were further used as catalytic macroinitiators, enabling self-catalyzed block polymerizations of various monomers without additional catalysts. This self-catalyzed living radical polymerization was also used to prepare a QAI-containing polymer brush on a solid surface. This technique is attractive for its wide range of amenable monomers and metal-free nature. The obtained QAI-containing polymers may find biomedical and antibacterial applications.

INTRODUCTION

Self-catalysis is a unique process in which a reactant carries a reacting group and also a catalytic group to trigger a reaction.[1–4] The reactant is self-catalyzed to convert to the product without need for additional catalysts. Self-catalysis offers simple purification processes (no need for the catalyst removal), which is advantageous in practical applications.

Living radical polymerization (LRP), also known as reversible-deactivation radical polymerization, is widely used for synthesizing well-defined polymers with controlled molecular weights and narrow molecular weight distributions.[5–8] Our research group has developed an organocatalyzed LRP using an alkyl iodide (R–I) as an initiator (Scheme 1).[9–15] The catalysts include iodide anion (I^-),[11–13] and I^- is used in the form of quaternary ammonium iodide (QAI) such as tetrabutylammonium iodide ($Bu_4N^+I^-$). Mechanistically, the polymer-iodide dormant species (polymer–I) coordinates the catalyst (I^-) *via* halogen bonding to form a complex (polymer–I···catalyst). The complex reversibly generates a propagating radical (Polymer$^\bullet$). We termed this polymerization reversible complexation mediated polymerization (RCMP).[10,11] The use of non-special capping agents and non-metal catalysts are attractive features of RCMP.



$$\text{Polymer-I} + A^{\oplus}I^{\ominus} \underset{k_{da}}{\overset{k_a}{\rightleftarrows}} \text{Polymer}^{\bullet} + A^{\oplus}I_2^{\bullet\ominus}$$

Scheme 1. Reversible Activation in RCMP.

In material chemistry, polymers possessing quaternary ammonium halides such as QAI at the side chains are widely used for functional materials due to their hydrophilic, antifouling, and antibacterial properties.[16–19] Their structures such as block, comb-shaped and brush structures have successfully been controlled *via* LRP.[20–25] In many cases, polymers containing tertiary amino groups are first prepared by LRP, and the subsequent quaternization using alkyl halides generates polymers with quaternary ammonium halides.[20,21] Despite the successful synthesis, the removal of metallic catalysts or odorous capping agents and the time-consuming post-quaternization may pose possible issues in further applications.

Herein we report self-catalyzed RCMP using QAI-containing monomers (Figure 1). The monomer contains a polymerizable methacrylate or acrylate moiety and also QAI as a catalytic moiety, offering self-catalyzed RCMP. The monomer is termed as catalytic monomer (CM) in this paper. The self-catalyzed RCMP directly yields QAI-containing polymers without post-quaternization. Furthermore, the obtained QAI-containing polymer can be used as a catalytic macroinitiator in subsequent block polymerization, offering self-catalyzed block polymerizations of (meth)acrylates in the absence of additional catalysts. Self-catalyzed RCMP was further exploited to prepare QAI-containing polymer brushes on a solid surface. Self-catalysis was used in other polymerizations (ring-opening polymerizations) and polymer degradation.[26–28] In the field of LRP, self-photo-catalytic initiators (not catalytic "monomers") were successfully used.[29,30] In the present work, we report the first use of CMs for self-catalyzed LRP.

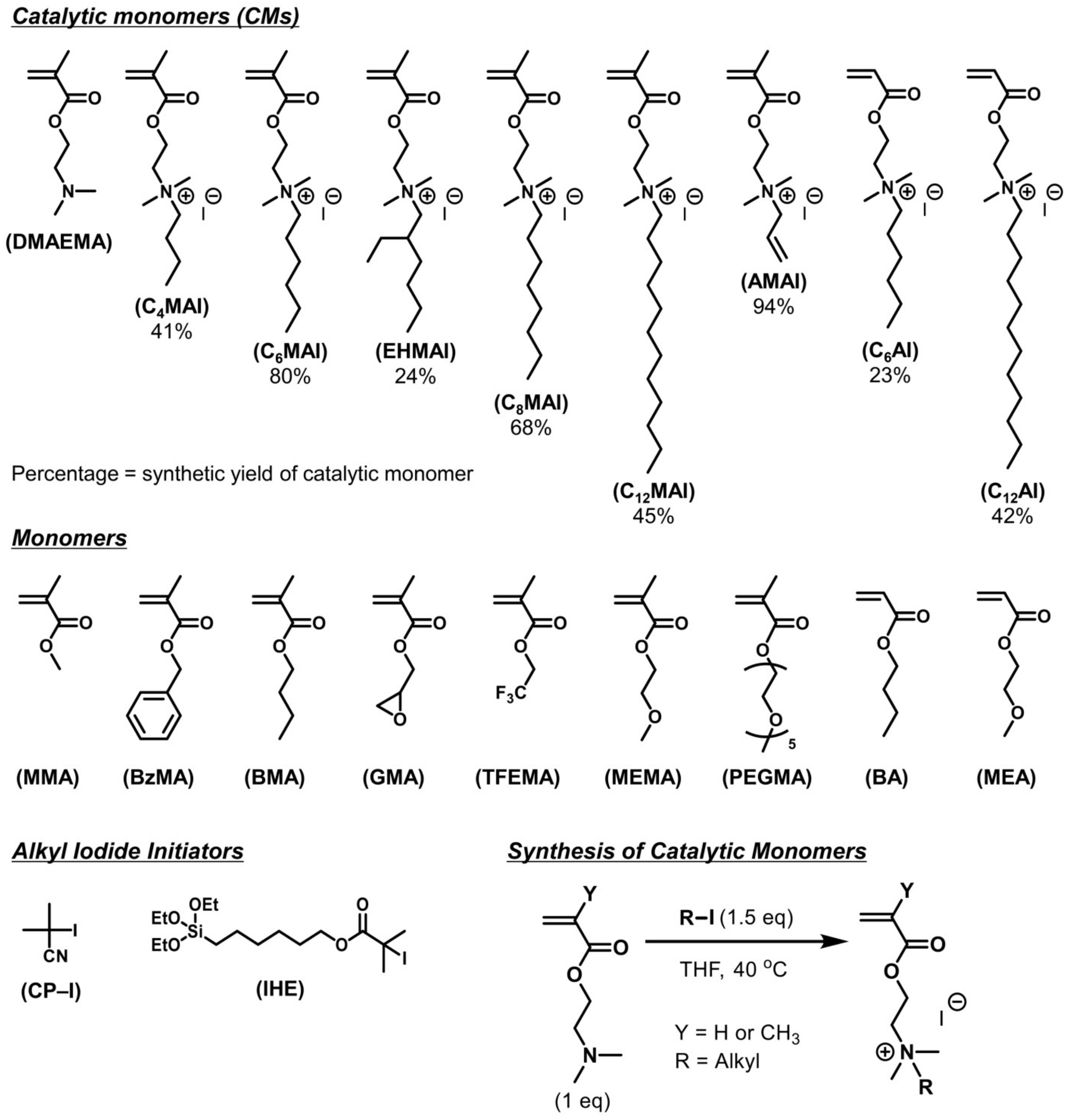


Figure 1. Structures of catalytic monomers (CMs), monomers, alkyl iodides used in this work and the synthesis of catalytic monomers.

RESULTS AND DISCUSSION

Synthesis of catalytic monomers (CMs) containing quaternary ammonium iodide (QAI). The QAI-containing catalytic monomers (Figure 1) were synthesized *via* Menshutkin reaction in high yields (up to 94%) in a simple manner. 2,2-(Dimethylamino)ethyl methacrylate (DMAEMA) (1 eq) or 2,2-(dimethylamino)ethyl acrylate (1 eq) was reacted with an alkyl iodide (1.5 eq) in tetrahydrofuran (THF) at 40 °C for 24 h to generate the corresponding CM. Several CMs with different alkyl chains were synthesized for tuning the solubility of CMs in monomers and solvents. The structures and abbreviations of the studied CMs are given in Figure 1. A 90 gram scale synthesis of C_6MAI (Figure 1) was achieved using DMAEMA and hexyl iodide (C_6H_{13}–I), for example. The purification was simple; namely, the solid C_6MAI was rinsed with cold THF, giving an 80% yield after purification in the mentioned 90 gram synthesis. The use of 1.1 eq of hexyl iodide gave a lower yield (57%) than that of 1.5 eq (yield = 80%). The scalable synthesis and facile purification are beneficial for practical use.

Self-catalyzed RCMP of MMA and C_6MAI. We carried out self-catalyzed RCMP using methyl methacrylate (MMA) as a main monomer and C_6MAI as a co-monomer with different ratios of $[\mathrm{MMA}]_0/[\mathrm{C_6MAI}]_0$ ranging from 99/1 to 75/25 (Table 1, entries 1–4). We heated a mixture of the two monomers (100 eq in total) and 2-iodo-2-methylpropionitrile (CP–I (Figure 1)) initiator (1 eq) at 70 °C. The QAI moiety of C_6MAI plays a catalytic role to generate propagating radicals from CP–I and polymer–I. Ethylene carbonate (EC) was used as a solvent to dissolve C_6MAI for the high C_6MAI-content systems ($[\mathrm{MMA}]_0/[\mathrm{C_6MAI}]_0$ = 90/10 and 75/25).

Figure 2a shows the time-evolution of the conversions of MMA (squares) and C_6MAI (triangles) for $[\mathrm{MMA}]_0/[\mathrm{C_6MAI}]_0$ = 90/10 (Table 1, entry 3). The rate of the monomer consumption was very similar for MMA (monomer 1) and C_6MAI (monomer 2), meaning that the reactivity ratios (r_1 and r_2) are nearly 1. The nearly unity reactivity ratios are reasonable because both monomers are methacrylates (the same type of monomer). The polymerization was relatively fast; the total monomer conversion reached 69% for 4 h. The number-average molecular weight (M_n) well matched with the theoretical value, and the dispersity ($Đ = M_w/M_n$) was low (1.17–1.34) from an early stage of polymerization (Figure 2b), where M_w is the weight-average molecular weight. This result shows a good catalytic activity of C_6MAI.

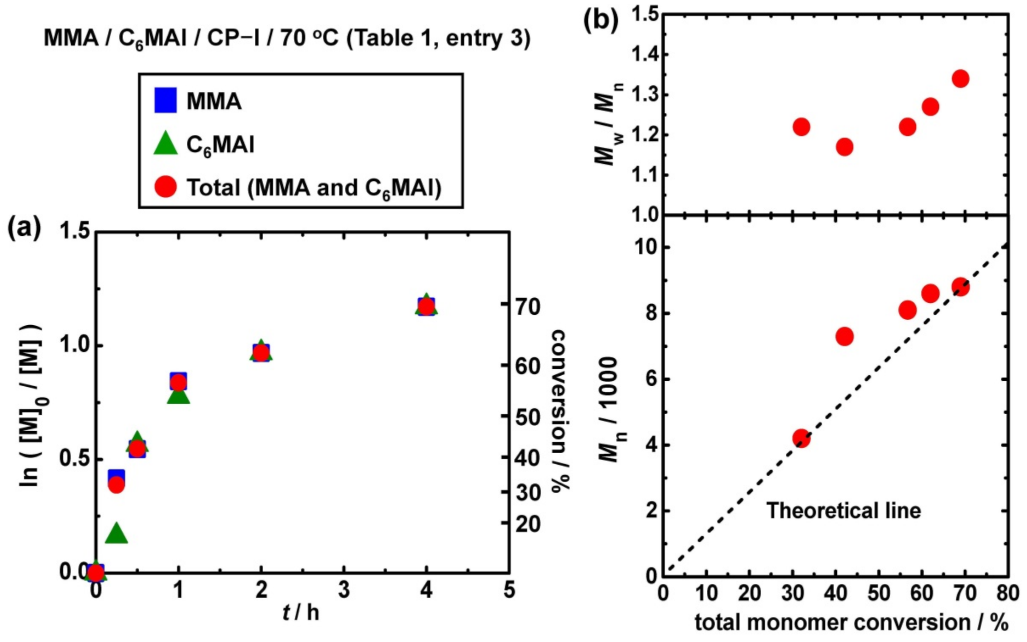


Figure 2. Plots of (a) ln([M]$_0$/[M]) vs t and (b) M_n and M_w/M_n vs conversion for the MMA/CP−I/C_6MAI system (70 ^{o}C): [MMA]$_0$ = 7200 mM; [CP−I]$_0$ = 80 mM; [C_6MAI]$_0$ = 800 mM. The M_n and M_w/M_n values are obtained by PMMA-calibrated GPC. The symbols are indicated in the Figure.

Figure 3 shows the ^{1}H NMR spectrum of the random copolymer (PMMA-*r*-PC$_6$MAI) obtained at 4 h (M_n = 8800 and $Đ$ = 1.34) after purification. The methyl (*d* in Figure 3) and methylene (c and e) protons of the quaternary amino group in the C$_6$MAI unit clearly appeared at 3.53 (*d*), 3.73 (*e*), and 4.15 (*c*) ppm, emphasizing the existence of C$_6$MAI moieties in the copolymer. From the peak areas of the methyl proton (*a*) in the MMA unit and the ethylene proton (*c*) in the C$_6$MAI unit, the polymer composition (MMA/C$_6$MAI) was calculated to be 92/8, which matched the feed monomer composition (90/10) and the nearly unity reactivity ratio. This result means that the fraction of C$_6$MAI in the copolymer can be manipulated in a predictable manner by simply tuning the feed MMA/C$_6$MAI monomer ratio. Thus, the self-catalyzed RCMP using QAI-containing monomer offers a facile access for preparing well-defined QAI-containing polymers.

In the preset work, methyl (*a* in Figure 3) protons in the MMA units are overlapped with the methyl (*d*) and methylene (e) protons in the C$_6$MAI units, and therefore we are not able to clearly observe the terminal monomer unit or evaluate the iodide-chain-end fidelity. Nevertheless, high chain-end fidelity was clearly demonstrated in the block copolymerizations, as shown below. Namely, the QAI-containing polymers were used as macroinitiators in the block copolymerizations, and a large fraction of the macroinitiator chains extended to block copolymers. This result demonstrated the high chain-end fidelity of the QAI-containing polymers.

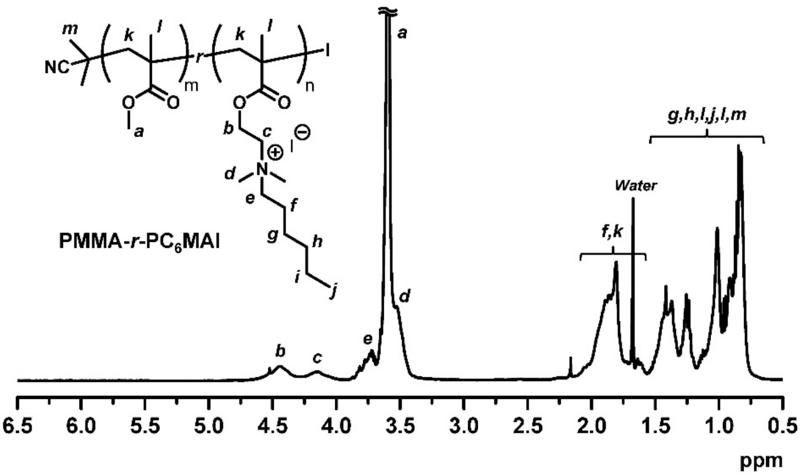


Figure 3. ^{1}H NMR spectrum of PMMA-*r*-PC$_6$MAI (Table 1, entry 3) after purification (400 MHz, 298 K, CDCl$_3$).

With an increase in the C$_6$MAI fraction (ranging the $[\mathrm{MMA}]_0/[\mathrm{C6MAI}]_0$ ratio from 99/1 to 75/25 (Table 1, entries 1–4), the polymerization rate reasonably increased because of the higher catalyst (C$_6$MAI) concentration. The total monomer conversion reached 72% for a short time of 3 h for $[\mathrm{MMA}]_0/[\mathrm{C_6MAI}]_0 = 75/25$ (Table 1, entry 4). The homopolymerization of C$_6$MAI was also performed at 80 °C for 8 h to give PC$_6$MAI with 73% monomer conversion (Table 1, entry 5 and Figure S27). However, the obtained polymer was not able to analyze with gel permeation chromatography (GPC), because the polymer tended to be adsorbed on the GPC columns. Non-quaternized DMAEMA (Figure 1) with a tertiary amine also served as a CM to copolymerize with MMA (Table 1, entry 6). Tertiary amines are known to work as moderately efficient RCMP catalysts.[10] However, compared with QAI-containing C$_6$MAI (Table 1, entry 3), DMAEMA provided a 3 times slower polymerization (64% total monomer conversion for 12 h) and a higher *Đ* value (1.46) because of the lower catalytic activity.

Table 1. Self-catalyzed RCMP of Methacrylates and Acrylates with Catalytic Monomers.

Entry	M[a]	CM[b]	Solvent[c]	$[\mathrm{M}]_0/[\mathrm{CM}]_0/[\mathrm{CP{-}I}]_0$	T (°C)	t (h)	Conv (M/CM, %)[d]	M_n[e] ($M_\mathrm{n,theo}$[f])	$Đ$[e]
1	MMA	C_6MAI	none	7920/80/80	70	12	62/59	7800 (6400)	1.28
2	MMA	C_6MAI	none	7800/200/80	70	8	72/76	11000 (7300)	1.29
3	MMA	C_6MAI	EC	7200/800/80	70	4	69/68	8800 (8700)	1.34
4	MMA	C_6MAI	EC	6000/2000/80	70	3	66/89	8700 (7500)	1.24
5	none	C_6MAI	EC	0/8000/80	80	8	−/73	NA[g] (27000)	NA[g]
6	MMA	DMAEMA	none	7200/800/80	70	12	64/59	6700 (6700)	1.46
7	MMA	C_4MAI	EC	7200/800/80	70	8	61/95	5500 (8700)	1.26
8	MMA	C_8MAI	EC	7200/800/80	70	8	60/93	8300 (9700)	1.25
9	MMA	EHMAI	EC	7200/800/80	70	7	81/81	8000 (11000)	1.28
10	MMA	C_{12}MAI	EC	7200/800/80	70	6	70/66	6300 (11000)	1.33
11	MMA	AMAI	EC	7200/800/80	70	8	37/37	5300 (4500)	1.19
12	BMA	C_6MAI	EC	7200/800/80	70	10	51/55	8000 (8600)	1.39
13	GMA	C_6MAI	EC	7200/800/80	70	4	82/55	16000 (13000)	1.35
14	BzMA	C_6MAI	EC	7200/800/80	70	8	70/69	18000 (14000)	1.37
15	MEMA	C_6MAI	none	7200/800/80	70	7	52/57	6500 (7900)	1.32
16	PEGMA	C_6MAI	none	7200/800/80[h]	60	10	56/98	9900 (10000)	1.40
17	DMAEMA	C_6MAI	none	7200/800/80[i]	50	3	93/94	12000 (16000)	1.39
18	BA	C_{12}AI	none	7200/800/80[j]	110	48	40/60	8300 (7400)	1.17
19	MEA	C_6AI	none	7200/800/80	110	24	66/72	8100 (10000)	1.18
20[k]	MMA	C_6MAI	EC	7200/800/8	60	8	19/15	20000 (25000)	1.27

[a] Main monomer. [b] Catalytic monomer. The structures and abbreviations are given in Figure 1 [c] EC means dilution with 25wt% ethylene carbonate (EC). [d] ^{1}H NMR calculated monomer conversion. [e] PMMA-calibrated THF-GPC values for entries 1−3, 7−15, 18, and 19. PMMA-calibrated DMF-GPC values for entries 4, 6, 16, 17, and 20. [f] Theoretical M_n calculated with $[\mathrm{M}]_0$, $[\mathrm{CM}]_0$, $[\mathrm{CP{-}I}]_0$, and monomer conversion. [g] The polymer tended to be adsorbed on columns in THF and DMF eluents and was not able to analyze with GPC. [h] Addition of V65 (160 mM). [i] Addition of V65 (40 mM). [j] Addition of I_2 (5 mM). [k] Surface-initiated RCMP.

Polymerization of MMA and other CMs. Besides C_6MAI, CMs possessing different alkyl chains (Figure 1), *i.e.*, butyl (C_4MAI), 2-ethylhexyl (EHMAI), octyl (C_8MAI), dodecyl (C_{12}MAI), and allyl (AMAI) chains, were effective for the MMA polymerizations (Table 1, entries 7−11), yielding low dispersity polymers ($Đ$ = approximately 1.3). The use of AMAI successfully provided functional allyl groups in the copolymer chain (Table 1, entry 11, and Figure S28 in Supporting Information). We also observed that the length of alkyl chains largely affected the hydrophobicity of QAI-containing polymers. While PMMA-*r*-PC_6MAI (M_n = 8800 and $Đ$ = 1.34, Table 1, entry 3) (5.0wt%) was dissolved in an acetone/water (40/60) mixture, PMMA-*r*-PC_{12}MAI with a longer alkyl chain (M_n = 6300 and $Đ$ = 1.33, Table 1, entry 10) (5.0wt%) was precipitated even in a more acetone-containing mixture (acetone/water = 46/54). This observation demonstrates that the hydrophobicity of QAI-containing polymers is tunable through the side chains in CMs. The facile synthesis and functionalization of CMs is highly beneficial for practical use and design of functional polymers.

Polymerization of Functional Methacrylates and Acrylates. QAI-containing monomers were compatible with various functional methacrylates and acrylates (Figure 1). The polymerization results of butyl methacrylate (BMA), glycidyl methacrylate (GMA), benzyl methacrylate (BzMA), 2-methoxyethyl methacrylate (MEMA), poly(ethylene glycol) methyl ether methacrylate (PEGMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with C_6MAI are summarized in Table 1 (entries 12–17). QAI-containing copolymers with low-dispersity ($Đ \leq 1.40$) was successfully synthesized. The relatively slow polymerization of BMA could be attributed to the low solubility of C_6MAI in the highly hydrophobic BMA (Table 1, entry 12). While 70 ^{o}C was used for hydrophobic monomers (Table 1, entries 1–4 and 6–15), a milder temperature (50–60 °C) was used for hydrophilic PEGMA and DMAEMA monomers to suppress a side reaction (elimination of HI from the polymer chain end to generate a dead polymer, which is enhanced in polar media) (Table 1, entries 16 and 17). In the two systems, an azo initiator (2,2'-azobis(2,4-dimethyl-valeronitrile) (V65)) was added to increase the polymerization rate. Azo initiators are often used to decrease the deactivator concentration and hence increase the polymerization rate in RCMP and other LRP systems.[31]

Table 1 (entries 18 and 19) shows the polymerizations of acrylates. Two QAI-containing acrylates, *i.e.*, C_{12}AI and C_6AI (Figure 1), were used to polymerize butyl acrylate (BA) and 2-methoxyethyl acrylate (MEA) (Figure 1), respectively, yielding low-dispersity polymers ($Đ$ = 1.17–1.18). (C_{12}AI exhibited a good solubility in the hydrophobic BA.) RCMP of acrylates requires highly active catalysts because of the stronger secondary alkyl C−I bond in an acrylate polymer than the tertiary alkyl C−I bond in a methacrylate polymer. The successful polymerizations of the acrylates demonstrate the high catalytic activities of the QAI-containing monomers.

Quaternary ammonium halide containing polymers are of great interest in antibacterial applications. The introduction of QAI in the biocompatible polymers, *i.e.*, MEMA, PEGMA, and MEA polymers, can significantly increase their antibacterial properties.[32,33] The self-catalyzed RCMP is a metal-free, odor-free, and straightforward synthetic route for QAI-containing copolymers with quantitative quaternization. The technique does not require post-quaternization or time-consuming removal of unreacted quaternizing agents from the polymers.

Self-catalyzed Block Polymerization. The obtained QAI-containing polymers were used as macroinitiators to generate block copolymers in the absence of additional catalysts. The polymerization is a self-catalyzed system, because the macroinitiator possesses catalysts. Using a purified PMMA-*r*-PC$_6$MAI (M_n = 1600 and $Đ$ = 1.15) as a macroinitiator, the polymerizations of several methacrylates, *i.e.*, MMA, BzMA, and 2,2,2-trifluoroethyl methacrylate (TFEMA), were performed, yielding low-dispersity block copolymers with M_n = 9600–16000 and $Đ \leq 1.10$ (Table 2, entries 1−3). A large fraction of the macroinitiator extended to block copolymers, meaning the high block-efficiency (Figure 4 (a−c)). This macroinitiator was also successfully used for an acrylate (MEA) polymerization, yielding a methacrylate-acrylate block copolymer (Table 2, entry 4 and Figure 4d). More hydrophobic PBzMA-*r*-PC$_6$MAI (M_n = 2800 and $Đ$ = 1.22) and more hydrophilic PMEMA-*r*-PC$_6$MAI (M_n = 1300 and $Đ$ = 1.20) macroinitiators were used for MMA polymerizations, giving block copolymers with M_n = 5100−9200 and $Đ$ = 1.23−1.31 (Table 2, entries 5 and 6, and Figure 4 (e and f)). These results demonstrate the versatility in macroinitiators and monomers and the accessibility to a range of block copolymers.

Table 2. Self-catalyzed block copolymerization.

Entry	Macroinitiator	Monomer	[Monomer]$_0$/[Macroinitiator]$_0$ (mM)	T (°C)	t (h)	Conv (%)[a]	M_n[b] ($M_{n,theo}$[c])	$Đ$[b]
1	PMMA-*r*-PC$_6$MAI[d]	MMA	8000/80	70	6	78	9600 (9400)	1.10
2	PMMA-*r*-PC$_6$MAI[d]	BzMA	8000/80	70	6	62	11000 (12000)	1.05
3	PMMA-*r*-PC$_6$MAI[d]	TFEMA	8000/80	70	4	94	16000 (17000)	1.02
4	PMMA-*r*-PC$_6$MAI[d]	MEA	8000/80	110	48	49	7200 (7900)	1.08
5	PBzMA-*r*-PC$_6$MAI[e]	MMA	8000/80	70	8	68	9200 (9600)	1.31
6	PMEMA-*r*-PC$_6$MAI[f]	MMA	8000/80	70	5	45	5100 (6800)	1.23

[a] ^{1}H NMR calculated conversion. [b] PMMA-calibrated THF-GPC values. [c] Theoretical M_n calculated with [Monomer]$_0$, [Macroinitiator]$_0$, and monomer conversion. [d] M_n = 1600 and $Đ$ = 1.15 (MMA/C$_6$MAI = 86/14). [e] M_n = 2800 and $Đ$ = 1.22 (BzMA/C$_6$MAI = 88/12). [e] M_n = 1300 and $Đ$ = 1.20 (MEMA/C$_6$MAI = 91/9).

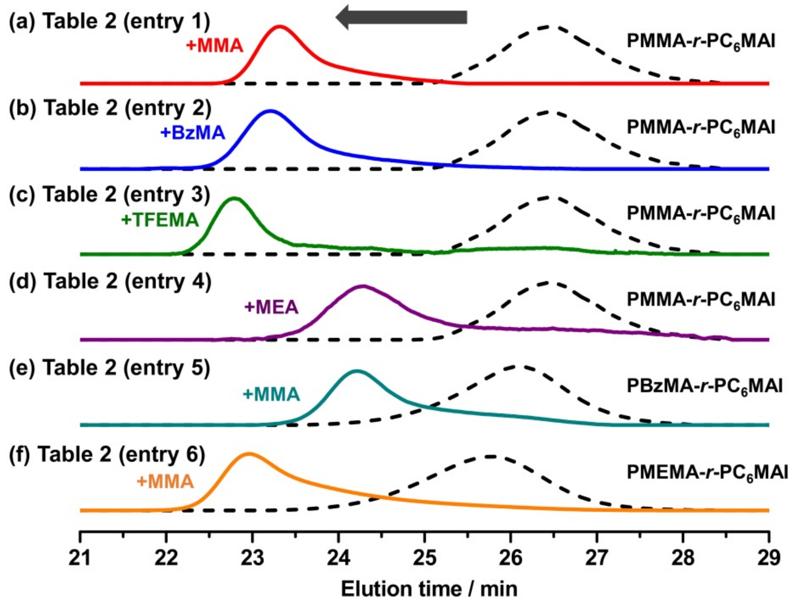


Figure 4. GPC chromatograms before (dashed lines) and after (solid lines) the block polymerizations in Table 2.

Synthesis of QAI-containing polymer brushes *via* surface-initiated RCMP. Quaternary ammonium halide containing polymer brushes on surfaces have been synthesized *via* post-quaternization and extensively studied for biological applications.[34–36] Such polymer brushes are obtainable *via* self-catalyzed RCMP in a simple manner. We performed a one-step synthesis of a polymer brush using MMA as a main monomer and C_6MAI as a CM *via* surface-initiated RCMP (Figure 5a). 6-(2-Iodo-2-isobutyryloxy)hexyltriethoxysilane (IHE, Figure 1) was immobilized on a silicon wafer. The IHE-immobilized silicon wafer was immersed in a mixture of MMA, C_6MAI, a non-immobilized free initiator CP−I, and EC (solvent) and heated at 60 °C to give a QAI-containing polymer brush (Table 1, entry 20). The M_n and $Đ$ of the free polymers generated from the free initiators are generally in good agreement with those of the graft polymers.[37] The M_n and $Đ$ of the free polymer were 20000 and 1.27, respectively. The dry thickness of the

PMMA-*r*-PC$_6$MAI copolymer brush was measured to be 6 nm using atomic force microscopy (AFM) (Figure S2). Assuming an identical M_n value for the graft and free polymers, the graft density (σ) was calculated to 0.21 chains/nm^2, and the surface occupancy (σ^*) was 12%. This surface occupancy is located in the concentrated brush region ($\sigma^* > 10\%$).[38] The polymer brush was analyzed with X-ray photoelectron spectroscopy (XPS) (Figure 5 (b–d)). The I 3d (617 and 628 eV) peaks were clearly observed. The observed N 1s peak at 402 eV (Figure 5d) supports the existence of a quaternary ammonium, because a non-quaternary amine (DMAEMA) has a different binding energy around 399 eV.[36] The abundance of iodide and quaternary ammonium confirms the successful synthesis of a QAI-containing polymer brush *via* self-catalysis.

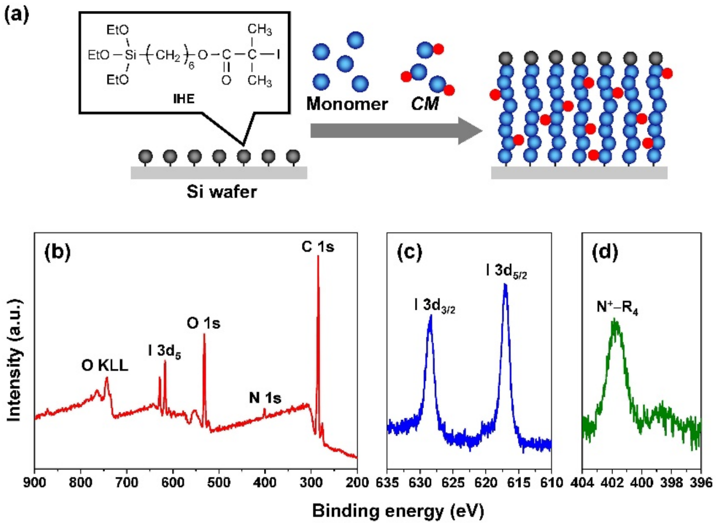


Figure 5. Synthesis of PMMA-*r*-PC$_6$MAI brush *via* surface-initiated self-catalyzed RCMP. (a) Schematic illustration. XPS (b) survey spectrum, (c) high resolution spectra of I 3d$_5$ signal, and (d) N 1s signal of PMMA-*r*-PC$_6$MAI brush.

CONCLUSION

Self-catalyzed RCMP using QAI-containing CMs was developed. QAI-containing CMs are easy to synthesize, which is attractive for large scale use. The amenable monomers encompassed MMA, BA, and several functional methacrylates and acrylates. The system does not require additional catalysts and generates QAI-containing polymers without post-quaternization. The obtained QAI-containing polymers further worked as catalytic macroinitiators, enabling self-catalyzed block polymerizations without additional catalysts. The self-catalyzed RCMP was also used to prepare a QAI-containing polymer brush. The high versatility in amenable monomers and CMs and the metal-free nature are beneficial aspects, and the obtained polymers may find biomedical and antibacterial applications.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

Materials, measurement, experimental procedures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: agoto@ntu.edu.sg

Author Contributions

‡These authors contributed equally. (C.-G. Wang and X. Y. Oh)

ORCID

C.-G Wang: 0000-0001-6986-3961

A. Goto: 0000-0001-7643-3169

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was partly supported by Academic Research Fund (AcRF) Tier 2 from Ministry of Education in Singapore (MOE2017-T2-1-018).

REFERENCES

(1) The description of self-catalysis here is different from autocatalysis. In autocatalysis, the reaction products serve as the catalysts to accelerate the reactions.

(2) Krawczyk, H. Self-Catalytic Michael Reaction, An Efficient Route to 2-Cyanoalkanoic Acids *Synth. Commun.* **2000**, *30*, 657−664.

(3) Bachmann, J.; Zierold, R.; Chong, Y. T.; Hauert, R.; Sturm, C.; Schmidt-Grund, R.; Rheinländer, B.; Grundmann, M.; Gösele, U.; Nielsch K. A. Practical, Self‐Catalytic, Atomic Layer Deposition of Silicon Dioxide. *Angew. Chem. Int. Ed.* **2008**, *47*, 6177−6179.

(4) MacLeod, P. D.; Li, Z.; Li C.-J. Self-catalytic, solvent-free or in/on water protocol: aza-Friedel–Crafts reactions between 3,4-dihydroisoquinoline and 1- or 2-naphthols. *Tetrahedron* **2010**, *66*, 1045−1050.

(5) Matyjaszewski, K. Advanced Materials by Atom Transfer Radical Polymerization. *Adv. Mater.* **2018**, *30*, 1706441.

(6) Keddie, D. J.; Moad, G.; Rizzardo, E.; Thang, S. H. RAFT Agent Design and Synthesis. *Macromolecules* **2012**, *45*, 5321-5342.

(7) Matyjaszewski, K.; Tsarevsky, N. V. Macromolecular engineering by atom transfer radical polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 6513−6533.

(8) Nicolas, J.; Guillaneuf, Y.; Lefay, C.; Bertin, D.; Gigmes, D.; Charleux, B. Nitroxide-mediated polymerization. *Prog. Polym. Sci.* **2013**, *38*, 63−235.

(9) Goto, A.; Zushi, H.; Hirai, N.; Wakada, T.; Tsujii, Y.; Fukuda, T. Living Radical Polymerizations with Germanium, Tin, and Phosphorus Catalysts − Reversible Chain Transfer Catalyzed Polymerizations (RTCPs). *J. Am. Chem. Soc.* **2007**, *129*, 13347−13354.

(10) Goto, A.; Suzuki, T.; Ohfuji, T.; Tanishima, M.; Fukuda, T.; Tsujii, Y.; Kaji, H. Reversible Complexation Mediated Living Radical Polymerization (RCMP) Using Organic Catalysts. *Macromolecules* **2011**, *44*, 8709−8715.

(11) Goto, A.; Ohtsuki, A.; Ohfuji, H.; Tanishima, M.; Kaji, H. Reversible Generation of a Carbon-Centered Radical from Alkyl Iodide Using Organic Salts and Their Application as Organic Catalysts in Living Radical Polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 11131−11139.

(12) Ohtsuki, A.; Lei, L.; Tanishima, M.; Goto, A.; Kaji, H. Photocontrolled Organocatalyzed Living Radical Polymerization Feasible over a Wide Range of Wavelengths. *J. Am. Chem. Soc.* **2015**, *137*, 5610−5617.

(13) Wang, C.-G.; Goto, A. Solvent-Selective Reactions of Alkyl Iodide with Sodium Azide for Radical Generation and Azide Substitution and Their Application to One-Pot Synthesis of Chain-End-Functionalized Polymers. *J. Am. Chem. Soc.* **2017**, *139*, 10551−10560.

(14) Wang, C.-G.; Hanindita, F.; Goto, A. Biocompatible Choline Iodide Catalysts for Green Living Radical Polymerization of Functional Polymers. *ACS Macro Lett.* **2018**, *7*, 263−268.

(15) Wang, C.-G.; Chen, C.; Sakakibara, K.; Tsujii, Y.; Goto, A. Facile Fabrication of Concentrated Polymer Brushes with Complex Patterning by Photocontrolled Organocatalyzed Living Radical Polymerization. *Angew. Chem. Int. Ed.* **2018**, *57*, 13504−13508.

(16) Konai, M. M.; Bhattacharjee, B.; Ghosh S.; Haldar, J. Recent Progress in Polymer Research to Tackle Infections and Antimicrobial Resistance. *Biomacromolecules* **2018**, *19*, 1888−1917.

(17) Jiao, Y.; Niu, L.; Ma, S.; Li, J.; Tay, F. R.; Chen, J. Quaternary Ammonium-based Biomedical Materials: State-of-the-art, Toxicological Aspects and Antimicrobial Resistance. *Prog. Polym. Sci.* **2017**, *71*, 53−90.

(18) Xue, Y.; Xiao, H.; Zhang, Y. Antimicrobial Polymeric Materials with Quaternary Ammonium and Phosphonium Salts. *Int. J. Mol. Sci.* **2015**, *16*, 3626−3655.

(19) Jaeger, W.; Bohrisch, J.; Laschewsky, A. Synthetic Polymers with Quaternary Nitrogen Atoms − Synthesis and Structure of the Most Used Type of Cationic Polyelectrolytes. *Prog. Polym. Sci.* **2010**, *35*, 511−577.

(20) Lenoir, S.; Pagnoulle, C.; Detrembleur, C.; Galleni, M.; Jérôme, R. New Antibacterial Cationic Surfactants Prepared by Atom Transfer Radical Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1214−1224.

(21) Murata, H.; Koepsel, R. R.; Matyjaszewski, K.; Russell, A. J. Permanent, Non-leaching Antibacterial Surfaces − 2: How High Density Cationic Surfaces Kill Bacterial Cells. *Biomaterials* **2007**, *28*, 4870−4879.

(22) Li, Y.; Armes, S. P.; Jin, X.; Zhu, S. Direct Synthesis of Well-defined Quaternized Homopolymers and Diblock Copolymers via ATRP in Protic Media. *Macromolecules* **2003**, *36*, 8268−8275.

(23) Kobayashi, M.; Terada, M.; Terayama, Y.; Kikuchi, M.; Takahara, A. Direct Synthesis of Well-Defined Poly[{2-(methacryloyloxy)ethyl}trimethylammonium chloride] Brush via Surface-Initiated Atom Transfer Radical Polymerization in Fluoroalcohol. *Macromolecules* **2010**, *43*, 8409−8415.

(24) Roy, D.; Knapp, J. S.; Guthrie, J. T.; Perrier, S. Antibacterial Cellulose Fiber via RAFT Surface Graft Polymerization. *Biomacromolecules* **2008**, *9*, 91–99.

(25) Siegwart, D. J.; Oh, J. K.; Matyjaszewski, K. ATRP in the Design of Functional Materials for Biomedical Applications. *Prog. Polym. Sci.* **2012**, *37*, 18−37.

(26) Tagoshi, H.; Endo, T. Syntheses and Properties of Polymers that Undergo No Shrinkage on Cross-linking by Self-catalyst. *J. Appl. Polym. Sci.* **1991**, *43*, 1933−1939.

(27) Truong, N. P.; Jia, Z.; Burges, M.; McMillan, N. A. J.; Monteiro, M. J. Self-Catalyzed Degradation of Linear Cationic Poly(2-dimethylaminoethyl acrylate) in Water. *Biomacromolecules* **2011**, *12*, 1876−1882.

(28) Liu, L.; Chen, L.; Fang, Y. Self-Catalysis of Phthaloylchitosan for Graft Copolymerization of ε-Caprolactone with Chitosan. *Macromol. Rapid Commun.* **2006**, *27*, 1988−1994.

(29) Xu, J.; Shanmugam, S.; Boyer, C. Organic Electron Donor – Acceptor Photoredox Catalysts: Enhanced Catalytic Efficiency toward Controlled Radical Polymerization. *ACS Macro Lett.* **2015**, *4*, 926−932.

(30) Zeng, G.; Liu, M.; Jiang, R.; Huang, Q.; Huang, L.; Wan, Q.; Dai, Y.; Wen, Y.; Zhang, X.; Wei, Y. Self-catalyzed Photo-initiated RAFT Polymerization for Fabrication of Fluorescent Polymeric Nanoparticles with Aggregation-induced Emission Feature. *Mater. Sci. Eng. C* **2018**, *83*, 154−159.

(31) Goto, A.; Fukuda, T. Kinetics of Living Radical Polymerization. *Prog. Polym. Sci.* **2004**, *29*, 329−385.

(32) Sellenet, P. H.; Allison, B.; Applegate, B. M.; Youngblood, J. P. *Biomacromolecules* **2007**, *8*, 19−23.

(33) Han, H.; Wu, J.; Avery, C. W.; Mizutani, M.; Jiang, X.; Kamigaito, M.; Chen, Z.; Xi, C.; Kuroda, K. *Langmuir* **2011**, *27*, 4010–4019.

(34) Zoppe, J. O.; Ataman, N. C.; Mocny, P.; Wang, J.; Moraes J.; Klok, H.-A. Surface-initiated Controlled Radical Polymerization: State-of-the-art, Opportunities, and Challenges in Surface and Interface Engineering with Polymer Brushes. *Chem. Rev.* **2017**, *117*, 1105−1318.

(35) Krishnamoorthy, M.; Hakobyan, S.; Ramstedt, M.; Gautrot, J. E. Surface-initiated Polymer Brushes in the Biomedical Field: Applications in Membrane Science, Biosensing, Cell Culture, Regenerative Medicine and Antibacterial Coatings. *Chem. Rev.* **2014**, *114*, 10976−11026.

(36) Yang, W. J.; Neoh, K.-G.; Kang, E.-T.; Teo, S. L.-M.; Rittschof, D. Polymer Brush Coatings for Combating Marine Biofouling. *Prog. Polym. Sci.* **2014**, *39*, 1017−104.

(37) Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. Structure and Properties of High-density Polymer Brushes Prepared by Surface-initiated Living Radical Polymerization. *Adv. Polym. Sci.* **2006**, *197*, 1−45.

(38) Yao, C.; Li, X.; Neoh, K.-G.; Shi, Z.; Kang, E.-T. Surface Modification and Antibacterial Activity of Electrospun Polyurethane Fibrous Membranes with Quaternary Ammonium Moieties. *J. Membrane Sci.* **2008**, *320*, 259–267.

for Table of Contents use only