SHORT COMMUNICATIONS

Combination of Tris(pentafluorophenyl)borane and Trialkylsilyl Triflate as an Efficient Catalyst System for the Group Transfer Polymerization of Acrylates

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Group transfer polymerization (GTP) is a convenient method to prepare polymethacrylates and polyacrylates with narrow molecular weight distributions (MWDs) at room temperature.[1,2] For the GTP of methacrylates nucleophilic catalysts[3] and polar solvents are most suitable for achieving a living polymerization. On the other hand, Lewis acid catalysts and nonpolar solvents are preferred for the GTP of acrylates. The use of nucleophilic catalysts and polar solvents in acrylate GTP leads to broad MWDs.[2,4] Examples of Lewis acid catalysts include zinc halides and dialkylaluminum halides. The drawback of these catalysts is that large amounts of catalysts (*e.g.*, zinc halides), usually 10 mol% based on monomer, or low temperatures (*e.g.*, dialkylaluminum halides) are required. Although HgI_2 catalysis can overcome this limitation,[5,6] toxic reaction mixtures are inconvenient to handle. Trifluoromethanesulfonate (triflate) salts of lanthanides [$La(OTf)_3$, $Sm(OTf)_3$, $Y(OTf)_3$] are also claimed to be effective as Lewis acid catalysts for acrylate GTP.[7] However, the catalytic activity of lanthanide triflates seems to be lower than that of HgI_2.

Dicker has disclosed that a trialkylsilyl compound such as $(CH_3)_3SiI$ or $(CH_3)_3SiOTf$ catalyzes GTP of acrylates preferably in the presence of a Lewis acid such as HgI_2 or zinc halides.[8] Zhuang and Müller have reported that the HgI_2-catalyzed GTP of *n*-butyl acrylate is drastically accelerated in the presence of $(CH_3)_3SiI$.[9-11] The HgI_2-$(CH_3)_3SiI$ system is so efficient that methyl crotonate can be homopolymerized in a quantitative yield.[12,13] Interestingly, this GTP shows high stereospecificity leading to the formation of disyndiotactic poly(methyl crotonate).[13] These findings prompted us to explore the combination of Lewis acid (*e.g.*, alkylaluminum bis(2,6-di-*tert*-butylphenoxide)) and silylating agent (*e. g.*, trialkylsilyl triflate, R_3SiOTf) as a catalyst system for the GTP of acrylic monomers.[14,15]

Here we report very efficient GTP of acrylates promoted by $B(C_6F_5)_3$ and R_3SiOTf. The amounts of $B(C_6F_5)_3$ and R_3SiOTf required for the catalysis are 0.01 —0.1 mol% and 0—0.001 mol%, respectively, relative to monomer. A variety of organic reactions employing $B(C_6F_5)_3$ as the Lewis acid catalyst have been studied by Ishihara and co-workers.[16,17] Sugimoto and co-workers demonstrated that $B(C_6F_5)_3$ accelerates the living polymerization of methyl methacrylate with methylaluminum tetraphenylporphyrin.[18] $(CH_3)_3SiOTf$ is also known to catalyze aldol-type condensation of enol silyl ethers and acetals.[19,20] However, no study has been reported on the synergetic effects of $B(C_6F_5)_3$ and R_3SiOTf.

The GTP of ethyl acrylate was initiated by adding a CH_2Cl_2 solution of 1-methoxy-1-(triethylsiloxy)-2-methyl-1-propene (1) to the mixture of ethyl acrylate, catalysts, and CH_2Cl_2. As shown in Table I, both $B(C_6F_5)_3$ and $(C_2H_5)_3SiOTf$ were found effective as catalysts for the GTP. Particularly, $B(C_6F_5)_3$ is useful because only a small amount is needed to attain a practical rate of polymerization. The $B(C_6F_5)_3$-catalyzed GTP, in which 1 mol% initiator and 0.1 mol% $B(C_6F_5)_3$ were used, proceeded rapidly at 20°C to give poly(ethyl acrylate) with a narrow MWD (yield 91%, polymerization for 1 h). When 0.001 mol% $(C_2H_5)_3SiOTf$ was added to the $B(C_6F_5)_3$-catalyzed GTP, polymerization proceeded more rapidly and completed within 1 h. M_n of the resulting polymer as determined by ^1H NMR end-group analysis agreed well with the expected value, indicating nearly 100% initiator efficiency. It was thus possible to control M_n by the feed ratio of monomer to initiator in the $B(C_6F_5)_3$-catalyzed GTP with $(C_2H_5)_3SiOTf$.

The effects of $(C_2H_5)_3SiOTf$ were more pronounced in the $B(C_6F_5)_3$-catalyzed GTP at 0°C. The $B(C_6F_5)_3$-catalyzed GTP in the presence of $(C_2H_5)_3SiOTf$ afforded poly(ethyl acrylate) with a narrow MWD ($M_w/M_n = 1.18$), whereas that in the absence of $(C_2H_5)_3SiOTf$ gave poly(ethyl acrylate) with a somewhat broad MWD ($M_w/M_n = 1.52$). The latter polymer had a large M_n as compared with the former whose M_n was close to the predicted value (Table I).

Though its mode of action is not known with certainty, $(C_2H_5)_3Si^+$ species produced by the reaction of $(C_2H_5)_3SiOTf$ with $B(C_6F_5)_3$ should be responsible for the cooperative catalysis in this GTP. Since the GTP proceeds even in the absence of $(C_2H_5)_3SiOTf$, a catalytic amount of $(C_2H_5)_3Si^+$ species is supposed to be formed directly from ketene triethylsilyl acetals (initiator and the growing site of a polymer chain) through the action of $B(C_6F_5)_3$.

The living nature of this GTP was affected by the structure of trialkylsilyl groups in the initiator and cata-

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**Table I.** Group transfer polymerization of ethyl acrylate catalyzed by B(C$_6$F$_5$)$_3$ and (C$_2$H$_5$)$_3$SiOTf in CH$_2$Cl$_2$ [a]

Initiator [b]	B(C$_6$F$_5$)$_3$	(C$_2$H$_5$)$_3$SiOTf	Temp	Time	Yield		M_n		M_w [c]
μmol	μmol	μmol	°C	h	%	calcd [c]	NMR [d]	SEC [e]	M_n
200	0	100	0	24	74	3800		3200	2.35
200	10	0	0	1	100	5100		7500	1.52
200	10	0.10	0	1	100	5100	5300	6800	1.18
100	10	0	20	1	91	9200		12600	1.13
100	10	0.10	20	1	100	10100	10500[f]	15100	1.14
50	10	0.10	20	4	100	20100	21700	36000	1.16

[a] Ethyl acrylate 10 mmol, CH$_2$Cl$_2$ 4.0 mL. [b] Initiator **1**, (CH$_3$)$_2$C=C(OCH$_3$)OSi(C$_2$H$_5$)$_3$. [c] Calculated from the yield and the feed ratio of monomer to initiator at 100% initiator efficiency. [d] Determined by ^{1}H NMR end-group analysis (based on the relative intensity of the OCH$_2$ resonances at 4.01—4.21 ppm to the terminal OCH$_3$ resonances at 3.60—3.68 ppm, measured in CDCl$_3$ at 55°C and 500 MHz). [e] Determined by size exclusion chromatography calibrated against standard PMMAs (two PLgel Mixed-C columns 7.5×300 mm; eluent, tetrahydrofuran). [f] Diad tacticity determined by ^{1}H NMR, m / r = 36 / 64.

Table II. Group transfer polymerization catalyzed by the Lewis acid - silylating agent (SA) system [a]

Monomer	Initiator [b]	B(C$_6$F$_5$)$_3$	SA	Solvent	Temp	Time	M_n [c]	M_w [c]
	μmol	μmol	μmol		°C	h		M_n
Ethyl acrylate	2	10.0	(CH$_3$)$_3$SiOTf	CH$_2$Cl$_2$	20	1	14700	1.26
	100		0.10					
Ethyl acrylate	2	1.0	(CH$_3$)$_3$SiOTf	CH$_2$Cl$_2$	0	1	15300	1.15
	100		0.010					
Ethyl acrylate	2	5.0	(CH$_3$)$_3$SiOTf	Toluene	0	4	17300	1.12
	100		0.10					
Methyl methacrylate	1	200	(C$_2$H$_5$)$_3$SiI	CH$_2$Cl$_2$	0	2	12100	1.06
	100		50					
Methyl methacrylate	1	200	(C$_2$H$_5$)$_3$SiI	CH$_2$Cl$_2$	−40	24	7400[d]	1.12
	200		100					

[a] Monomer 10 mmol, solvent 4.0 mL. A quantitative yield of polymer was obtained. [b] Initiator: **1**, (CH$_3$)$_2$C=C(OCH$_3$)OSi(C$_2$H$_5$)$_3$; **2**, (CH$_3$)$_2$C=C(OCH$_3$)OSi(CH$_3$)$_3$. [c] Determined by size exclusion chromatography calibrated against standard PMMAs. [d] Triad tacticity determined by ^{1}H NMR: mm / mr / rr = 0 / 12 / 88.
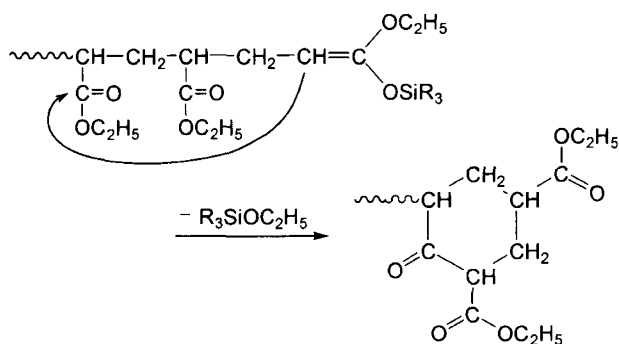
Scheme 1. Self-termination of living poly(ethyl acrylate) through cyclization.

lyst. At a polymerization temperature of 20°C, the use of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (**2**) as the initiator and B(C$_6$F$_5$)$_3$-(CH$_3$)$_3$SiOTf as the catalyst resulted in the formation of polymers with broader MWDs than those prepared by the corresponding (C$_2$H$_5$)$_3$Si- system (Table II). The ketene trimethylsilyl acetal at the chain-end of growing polymer would be more liable to deactivation, probably through intramolecular cyclization (Scheme 1).[21] A similar tendency has been observed in the HgI$_2$-catalyzed GTP of methyl crotonate.[13]

The (CH$_3$)$_3$Si- system gave poly(ethyl acrylate) with a narrow MWD when the GTP was carried out at 0°C using far less amounts of catalysts (0.01 mol% B(C$_6$F$_5$)$_3$ and 0.0001 mol% (CH$_3$)$_3$SiOTf) (Table II). Obviously, the (CH$_3$)$_3$Si- system is superior to the (C$_2$H$_5$)$_3$Si- system in

reactivity. However, the GTP by the (CH$_3$)$_3$Si- system was sensitive to a minor change in the polymerization conditions such as the amount of **2**, B(C$_6$F$_5$)$_3$, or (CH$_3$)$_3$SiOTf, leading to erratic results with respect to the yield and MWD of the polymer. Further study on the polymerization by the (CH$_3$)$_3$Si- system is now under way. The use of toluene instead of CH$_2$Cl$_2$ as the solvent slowed down the rate of polymerization significantly (Table II).

To demonstrate the living nature of the B(C$_6$F$_5$)$_3$-(C$_2$H$_5$)$_3$SiOTf-catalyzed GTP, block copolymerization was carried out by polymerizing ethyl acrylate first and adding n-butyl acrylate subsequently. Both the first stage polymerization of ethyl acrylate and the second stage polymerization of n-butyl acrylate proceeded quantitatively to give poly(ethyl acrylate)-*block*-poly(n-butyl acrylate). Figure 1 shows size exclusion chromatograms of the block copolymer and the poly(ethyl acrylate) prepared in a similar manner as the first stage polymerization. The block copolymer had a narrow MWD without noticeable tailing to the lower molecular weight region, indicating quantitative initiation of the second stage polymerization by living poly(ethyl acrylate).

It should be mentioned that B(C$_6$F$_5$)$_3$-catalyzed GTP is also useful for the preparation of polymethacrylates with narrow MWDs. (C$_2$H$_5$)$_3$SiI seems to be more effective than (C$_2$H$_5$)$_3$SiOTf as the co-catalyst for this polymerization. PMMA obtained by the GTP at −40°C was predominantly syndiotactic (rr = 88%) (Table II). Though optimized conditions are under investigation, the results imply the possibility of copolymerization of acrylate and
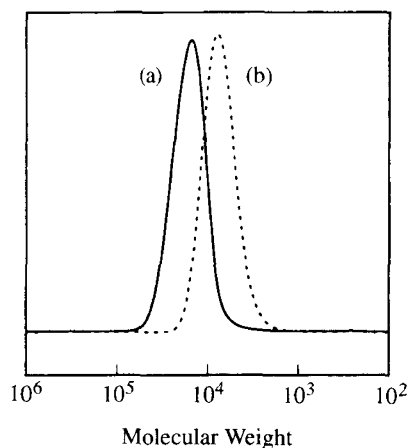
Figure 1. Size exclusion chromatograms of poly(ethyl acrylate)-*block*-poly(*n*-butyl acrylate) (a) and poly(ethyl acrylate) (b) obtained by $B(C_6F_5)_3$-$(C_2H_5)_3SiOTf$-catalyzed GTP in CH_2Cl_2 at $0°C$. The block copolymer (a) was prepared by adding *n*-butyl acrylate to the living poly(ethyl acrylate) ([*n*-butyl acrylate]$_0$ / [ethyl acrylate]$_0$ = 1.0 mol/mol) formed under the following conditions: ethyl acrylate, 10 mmol ; 1-methoxy-1-(triethylsiloxy)-2-methyl-1-propene, 200 μ mol; $B(C_6F_5)_3$, 10 μ mol; $(C_2H_5)_3SiOTf$, 0.10 μ mol; CH_2Cl_2, 4 mL; polymerization time, 1 h. The block copolymerization was carried out for 2 h after the addition of *n*-butyl acrylate. The homopolymer (b) was obtained in a quantitative yield by quenching the living poly(ethyl acrylate) described above. Molecular weight was calibrated against standard PMMA samples: (a) $M_n = 15000$, $M_w/M_n = 1.19$; (b) $M_n = 6800$, $M_w/M_n = 1.18$.

methacrylate.

Living or controlled polymerization of *n*-alkyl acrylates other than GTP has been reported for the polymerization with aluminum porphyrin initiators,[22] organolanthanides,[23] diphenylmethyllithium / polydentate lithium alkoxide,[24] and *t*-butyllithium / ethylaluminum bis(2,6-di-*tert*-butylphenoxide) systems,[25] and for the atom transfer radical polymerization using CuBr / multidentate amine systems.[26,27] The advantage of the GTP described in this communication would be its easiness. Living poly(*n*-alkyl acrylate)s with M_n exceeding 20000 can be prepared at room temperature $(20°C)$ in a reasonable reaction time. This GTP proceeds with very small amounts of $B(C_6F_5)_3$ and $(C_2H_5)_3SiOTf$ as catalysts, both of which are commercially available. Further, the ketene triethylsilyl acetal initiator is readily obtained by the $[(C_6H_5)_3P]_3RhCl$-catalyzed hydrosilylation of methyl methacrylate with triethylsilane.[28]

The combination of Lewis acid and silylating agent opens the possibility for advanced control (*e.g.*, stereospecificity) and higher efficiency of GTP.

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