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Stereocontrol in Radical Polymerization of Acrylic Monomers

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Summary: A clear effect of Lewis acids, such as scandium trifluoromethanesulfonate [Sc(OTf)$_3$], on stereocontrol during the radical polymerization of a designed monomer, benzyl α-(methoxymethyl)acrylate was found. This Lewis acid also influenced the stereochemistry in the radical polymerization of methyl methacrylate giving a less syndiotactic and more isotactic polymer, although many Lewis acids were not effective. A catalytic amount of Lewis acids, such as Y(OTf)$_3$ and Yb(OTf)$_3$, also significantly enhanced isotactic-specificity during the radical polymerization of acrylamide and its derivatives, *N*-isopropylacrylamide (NIPAM) and *N,N*-dimethylacrylamide. Obvious solvent and temperature effects on tacticity were observed in these polymerizations, and poly(NIPAM) with >80% triad isotactic content has been obtained in the presence of Lewis acids.

Introduction

Stereocontrol of radical polymerization is important because it has been widely used for the production of many industrially important polymers and polymer properties are often significantly affected by main-chain tacticity. We recently found that the stereochemistry of the polymerization of vinyl esters and methacrylates is strongly influenced by fluoroalcohols used as reaction solvents.[1, 2] On the other hand, it is well known that Lewis acids significantly affect the monomer reactivity and stereochemistry during the radical copolymerization.[3, 4] However, until very recently, influence of Lewis acids on the stereochemistry during radical homopolymerization had not been reported,[5] probably because no effect on tacticity had been observed. Here, we report our recent work on the stereoregulation in the radical homopolymerization of acrylic

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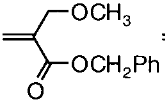
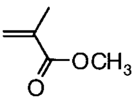
monomers including methacrylates and acrylamides in the presence of Lewis acids.



BMMA



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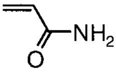
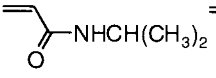
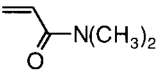


AM



NIPAM



DMAM

Results and Discussion

The radical polymerization of a designed monomer, benzyl α-(methoxymethyl)acrylates (BMMA), was performed in the presence of various Lewis acids (Table 1). It is known that atactic polymers are generally obtained in the radical polymerization of α-(alkoxymethyl)acrylates without a Lewis acid.[6] The polymerization systems in the presence of $ZnBr_2$ and scandium trifluoromethanesulfonate [$Sc(OTf)_3$] [initiator: $(i\text{-}PrOCO_2)_2$, 30 °C] produced syndiotactic- and isotactic-rich poly(BMMA)s, respectively (entries 2 and 3).[7-9] When amino alcohols were added to the polymerization system with $ZnBr_2$, heterotactic-rich polymer was obtained (entry 4). Therefore, the synthesis of syndiotactic-, isotactic-, and heterotactic-rich polymers was attained to a certain

Table 1. Radical polymerization of BMMA in the presence of various Lewis acids at 30°C for 48h in CH_2Cl_2.[a]

entry	Lewis acid ([Lewis acid]$_0$)	yield[b] %	DP[c] (M_w/M_n)	triad tacticity[d] *mm / mr / rr*
1	none	96[e]	63 (2.5)	30 / 48 / 22
2	$ZnBr_2$ (0.10M)[f]	90	110 (3.2)	9 / 40 / 51
3	$Sc(OTf)_3$ (0.12M)	77	92 (1.9)	50 / 38 / 12
4	$ZnBr_2$-AE[g] (0.10M)	83	83 (2.4)	21 / 57 / 22

[a] Initiator = $(i\text{-}PrOCO_2)_2$, $[BMMA]_0$ = 1.0 M, $[BMMA]_0 / [initiator]_0$ = 30.
[b] Methanol-insoluble part.
[c] Determined by SEC (polystyrene standard).
[d] Determined by ^{13}C NMR analysis.
[e] Hexane-insoluble part.
[f] Solvent = toluene.
[g] 2-Aminoethanol.

extent by choosing Lewis acid catalysts without changing the other polymerization conditions and monomer structure. The Lewis acids seem to catalytically change the conformations of the propagating radicals through the coordination of the polar substituents (ether or ester group) of the monomer and polymer ω-end during the polymerization.[10]

$Sc(OTf)_3$ also influenced the stereochemistry during the radical polymerization of the conventional monomer, methyl methacrylate (MMA), although many Lewis acids including $ZnBr_2$ hardly changed the stereoregularity (Table 2).[11] The radical polymerization of MMA in the presence of $Sc(OTf)_3$ in toluene (initiator: AIBN, 60 °C) produced a polymer with a less syndiotacticity and more isotacticity (*mm* / *mr* / *rr* = 14 / 46 / 40) (entry 2) than those of the polymer prepared in the normal radical method (entry 1). This effect of the Lewis acid was significant in nonpolar solvents, such as toluene and $CHCl_3$, and in bulk (entry 3). The increase of the isotacticity and heterotacticity of PMMA was also observed during the polymerization with a catalytic amount of $Yb(OTf)_3$ and $HfCl_4$ (entries 4 and 5), although these effects were much smaller than that of $Sc(OTf)_3$. The monomer-Lewis acid interaction also seems to be involved in the

Table 2. Radical polymerization of MMA in the presence of various Lewis acids at 60°C for 24h in toluene.[a)]

entry	Lewis acid ([Lewis acid]$_0$)	yield[b)] %	$M_n \times 10^4$[c)] (M_w/M_n)	triad tacticity[d)] *mm* / *mr* / *rr*
1	none	79	3.46 (1.61)	3 / 33 / 64
2	$Sc(OTf)_3$ (0.20M)	>99	5.23 (2.23)	14 / 46 / 40
3[e)]	$Sc(OTf)_3$ (0.90M)	91	11.3 (5.42)	16 / 45 / 39
4[f)]	$Yb(OTf)_3$ (0.24M)	83	3.01 (1.97)	10 / 36 / 54
5	$HfCl_4$ (0.20M)	>99	6.11 (4.74)	6 / 36 / 58

a) Initiator = AIBN, $[MMA]_0$ = 2.4 M, $[AIBN]_0$ = 0.02 M.
b) Methanol-insoluble part.
c) Determined by SEC in THF (polystyrene standard).
d) Determined by ^{1}H NMR analysis.
e) Bulk, $[MMA]_0$ = 9.35M, time = 12h.
f) Solvent = chloroform.

stereochemical mechanism of the polymerization, based on the NMR analysis of a mixture of $Sc(OTf)_3$, MMA, and PMMA.[11]

The effect of Lewis acids was clearly found during the radical polymerization of *N*-isopropylacrylamide (NIPAM) (Table 3).[12] The diad tacticity of poly(NIPAM) obtained in the polymerization with a catalytic amount of $Y(OTf)_3$ in methanol (initiator: AIBN, 60 °C) was 80% (entry 4), while the polymer prepared by the normal radical method was slightly rich in sindiotacticity (entry 1). This effect of the Lewis acids was strongly dependent on the polymerization conditions, such as solvent and temperature, whereas, in the absence of Lewis acid, the tacticity of poly(NIPAM) is only slightly influenced by the polymerization conditions. The isotactic content of the polymer obtained in the presence of $Y(OTf)_3$ in methanol at lower temperature (–20 °C) remarkably increased and reached to 92% (entry 8), when 0.2 equivalent of Lewis acid to the monomer was used. This value of the isotacticity may be the highest one for the homogeneous radical polymerization of

Table 3. Radical polymerization of NIPAM in the presence of Lewis acids.[a)]

entry	Lewis acid	solvent	temp	yield[b)]	tacticity[c)]
			°C	%	*m* / *r*
1	none	$CHCl_3$	60	65	45 / 55
2	$Yb(OTf)_3$	$CHCl_3$	60	39	58 / 42
3	$Y(OTf)_3$	$CHCl_3$	60	75	62 / 38
4	$Y(OTf)_3$	CH_3OH	60	94	80 / 20
5	$Y(OTf)_3$	H_2O	60	94	57 / 43
6	none	CH_3OH	–20	61	44 / 56
7	$Y(OTf)_3$	CH_3OH	–20	85	90 / 10
8	$Y(OTf)_3$[d)]	CH_3OH	–20	72	92 / 8

a) $[NIPAM]_0 = 2.4$ M, $[\text{Lewis acid}]_0 = 0.2$ M, initiator: AIBN (entries 1–4), AIBN with UV irradiation (entries 6–8), $Na_2SO_3 + K_2S_2O_8$ ($[\text{initiator}]_0 =$ 0.02 M), time = 3h (entries 1–5), 24h (entries 6–8).

b) Hot water-insoluble part.

c) Determined by ^1H NMR measurement in DMSO-d_6 at 170°C .

d) $[\text{Lewis acid}]_0 = 0.5$ M

conventional vinyl monomers. Methanol seems to be the best solvent for the isotactic-specific polymerization, and even in water, the effect was observed to some extent (entry 5). However, the polymerization in dimethyl sulfoxide (DMSO) hardly showed an effect of Lewis acid. DMSO may very tightly coordinate to $Y(OTf)_3$ and prevent the interaction of the monomer with the Lewis acid.

The isotactic-specific effect of the Lewis acids was also observed for the polymerization of acrylamide (AM) and *N,N*-dimethylacrylamide (DMAM) in methanol (initiator: AIBN or AIBN with UV irradiation) (Table 4).[12] Poly(AM) has been industrially produced by the radical method in water. The polymer is atactic with a tacticity, *mm* : *mr* : *rr* = 18 : 49 : 33.[13] It is very difficult to change its stereoregularity by the conventional polymerization methods. The polymer obtained with $Yb(OTf)_3$ at 0 °C was rich in isotacticity (*mm* = 65%) (entry 3), indicating that this method using Lewis acids must be significantly useful. $Sc(OTf)_3$ and $Y(OTf)_3$ were less iso-specific in this system. On the other

Table 4. Radical polymerization of AM and DMAM in the presence of various Lewis acids for 24h in methanol.[a)]

entry	monomer	Lewis acid	yield[b)]	tacticity[c)]
			%	*m* / *r* (*mm* / *mr* / *rr*)
1	AM	none	60	46 / 54 (22 / 49 / 29)
2		$Sc(OTf)_3$	71	62 / 38 (40 / 43 / 17)
3		$Yb(OTf)_3$	50	80 / 20 (65 / 29 / 6)
4		$Y(OTf)_3$	91	75 / 25 (58 / 33 / 9)
5	DMAM	none	73	46 / 54
6		$Sc(OTf)_3$	76	78 / 22
7		$Yb(OTf)_3$	86	84 / 16
8		$Y(OTf)_3$	90	84 / 16

a) $[Monomer]_0$ = 1.0 M, $[Lewis\ acid]_0$ = 0.1 M, initiator: AIBN or AIBN with UV irradiation, $[AIBN]_0$ = 0.02 M, temp. = 0°C for AM and 60°C for DMAM.

b) Polymers were purified by dialysis with cellophane in water.

c) Determined by ^{13}C NMR measurement in D_2O at 80°C for AM, and ^1H NMR measurement in DMSO-d_6 at 170°C for DMAM.

hand, the *m* content of poly(DMAM) was increased by 38% using $Yb(OTf)_3$ or $Y(OTf)_3$ at 60 °C (entries 7 and 8). The polymer with $m = 88\%$ was obtained in the polymerization with $Yb(OTf)_3$ at 0 °C.

Conclusion

The efficient stereocontrolled radical polymerization of acrylic monomers, such as methacrylates and acrylamide derivatives was accomplished by using a catalytic amount of Lewis acids. The effect was strongly dependent on the polymerization conditions, such as the Lewis acid, solvent, and temperature, as well as the monomer structure. These results suggest that even a higher level of stereocontrol would be realized by optimizing the polymerization conditions as has been successfully done in ionic and coordination polymerizations.

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