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Stereocontrol Using Lewis Acids in Radical Polymerization

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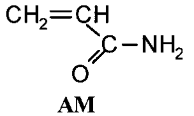
Summary: The radical polymerization of various (meth)acrylamides in the presence of Lewis acids such as $Yb(OTf)_3$ and $Y(OTf)_3$ was carried out. The polymerization with Lewis acids led to highly isotactic polymers, while the polymers synthesized without Lewis acids were atactic or syndiotactic. The dependence of the polymer properties on the tacticity was also demonstrated.

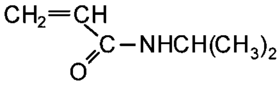
Keywords: isotactic; radical polymerization

Introduction

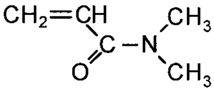
The control of the stereochemistry during radical polymerization is very important, because the tacticity of a polymer often influences the polymer properties and functions, and the radical polymerization process has been widely used in industry. However, an effective and facile method of stereocontrol during radical polymerization has been rarely found. Recently, we reported that Lewis acids such as $Sc(OSO_2CF_3)_3$ [$Sc(OTf)_3$] were effective in enhancing the isotactic-selectivity during the radical polymerization of α-(alkoxymethyl)acrylate[1,2] and methyl methacrylate.[3] Furthermore, during the radical polymerization of acrylamides[4] and methacrylamides,[5] Lewis acids significantly increased the isotacticity of the obtained polymers. Here, we report our recent results on the isotactic-specific radical polymerization of various (meth)acrylamides, such as *N*-isopropylacrylamide (NIPAM), acrylamide (AM), *N,N*-dimethylacrylamide (DMAM), *N*-methylmethacrylamide (MMAM), and *N*-isopropylmethacrylamide (IPMAM), with Lewis acids.



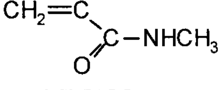
AM



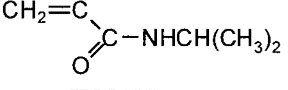
NIPAM



DMAM



MMAM



IPMAM

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Results and Discussion

In the presence of various Lewis acids, the radical polymerization of NIPAM was carried out in methanol at 60°C (Table 1). The polymerization without Lewis acids produced an almost atactic polymer (m = 45%). The polymerizations using a catalytic amount of Lewis acids ([monomer]/[Lewis acid] = 12/1) proceeded in an isotactic-specific manner, and rare earth metal triflates except for $Sc(OTf)_3$ and $La(OTf)_3$ resulted in the meso diad of more than 80%. The rare earth metal chlorides were less effective in enhancing the isotactic-selectivity of the polymerization than the corresponding triflates. Table 2 shows the result of the NIPAM polymerization in the presence of

Table 1. Effect of Lewis acid on NIPAM polymerization in methanol[a]

entry	Lewis acid	yield[b] %	diad tacticity[c] m / r
1	none	82	45 / 55
2	$Sc(OTf)_3$	86	62 / 38
3	$Y(OTf)_3$	94	80 / 20
4	$La(OTf)_3$	98	76 / 24
5	$Pr(OTf)_3$	96	81 / 19
6	$Sm(OTf)_3$	87	81 / 19
7	$Ho(OTf)_3$	98	83 / 17
8	$Tm(OTf)_3$	97	84 / 16
9	$Lu(OTf)_3$	97	84 / 16
10	$ScCl_3$	85	57 / 43
11	$YbCl_3$	95	67 / 33

[a] $[NIPAM]_0 = 2.40$ M, $[Lewis acid]_0 = 0.20$ M, $[AIBN]_0 = 0.02$ M. Temp. = 60°C. Time = 3hr.

[b] Hot water-insoluble part.

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

Table 2. Solvent effect on NIPAM polymerization in the presence of $Y(OTf)_3$[a]

entry	solvent	Lewis acid	yield[b] %	diad tacticity[c] m / r
1	methanol	none	82	45 / 55
2	methanol	$Y(OTf)_3$	94	80 / 20
3	ethanol	$Y(OTf)_3$	90	73 / 27
4	isopropanol	$Y(OTf)_3$	92	64 / 36
5	H_2O	$Y(OTf)_3$	94	57 / 43
6	THF	$Y(OTf)_3$	66	67 / 33
7	$CHCl_3$	$Y(OTf)_3$	75	62 / 38
8	DMSO	$Y(OTf)_3$	96	47 / 53

[a] $[NIPAM]_0 = 2.40$ M. $[Lewis acid]_0 = 0.20$ M. Initiator: AIBN (entries 1-4, 6-8), Na_2SO_3+$K_2S_2O_8$ (entry 5) ($[initiator]_0 = 0.02$ M). Temp. = 60°C. Time = 3h.

[b] Hot water-insoluble part.

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

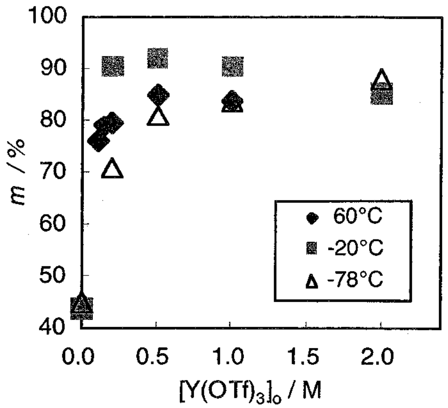

Figure 1. Relationship between the concentration of $Y(OTf)_3$ and the meso content of the obtained polymers. $[NIPAM]_o$=2.4M.

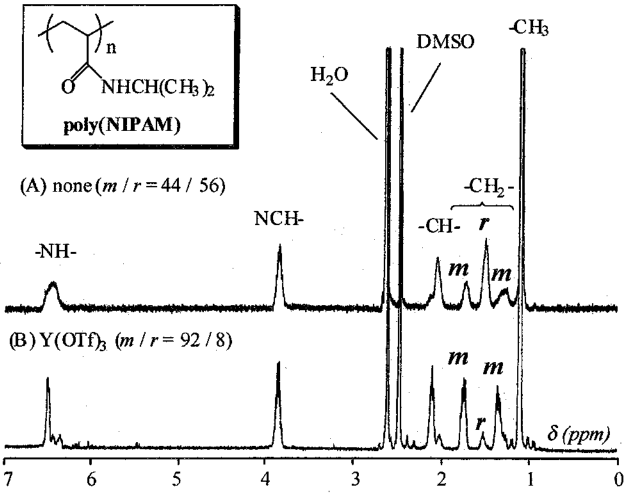

Figure 2. ^1H NMR spectra of poly(NIPAM)s prepared (A) in the absence and (B) presence of $Y(OTf)_3$ (0.5 M) in methanol at -20°C [400MHz, DMSO-d_6, 170°C].

$Y(OTf)_3$ in various solvents at 60°C. The effect of $Y(OTf)_3$ depended on the polymerization solvent, and the highest isotacticity-enhancing effect was observed for methanol. This effect decreased in the order of methanol, ethanol, and isopropanol. The effect of $Y(OTf)_3$ was also observed in THF, chloroform, and even in water, but disappeared in DMSO, which may tightly interact with the Lewis acids to prevent the interaction with the monomer. On the other hand, the polymerization in the absence of

Table 3. Polymerization of acrylamides in the presence of Lewis acids in methanol[a]

entry	monomer	Lewis acid	temp. °C	yield[b] %	tacticity[c] m / r (mm / mr / rr)
1	AM	none	0	60	46 / 54 (22 / 49 / 29)
2	AM	Sc(OTf)$_3$	0	71	62 / 38 (40 / 43 / 17)
3	AM	Yb(OTf)$_3$	0	50	80 / 20 (65 / 29 / 6)
4	AM	Y(OTf)$_3$	0	91	75 / 25 (58 / 33 / 9)
5	DMAM	none	60	73	46 / 54
6	DMAM	Sc(OTf)$_3$	60	76	78 / 22
7	DMAM	Yb(OTf)$_3$	60	86	84 / 16
8	DMAM	none	0	81	49 / 51
9	DMAM	Yb(OTf)$_3$	0	76	88 / 12

[a] $[\mathrm{Monomer}]_0$ = 1.0~1.6 M. $[\mathrm{Lewis\ acid}]_0$ = 0.1 M. Initiator: AIBN (60°C) or AIBN with UV irradiation (0~-20°C) ($[\mathrm{AIBN}]_0$ = 0.01~0.02 M). Time = 24h.

[b] Polymers were purified by dialysis with a cellophane tube in water (entries 1-4). Methanol-insoluble part (entries 5-9).

[c] Determined by ^{13}C NMR in D_2O at 80°C (entries 1-4), and by ^{1}H NMR in DMSO-d_6 at 170°C (entries 5-9).

Table 4. Polymerization of methacrylamides in the presence of Lewis acids[a]

entry	monomer	Lewis acid ($[\mathrm{Lewis\ acid}]_0$)	temp. °C	yield[b] %	tacticity[c] mm / mr / rr
1	MMAM	none	60	90	7 / 40 / 53
2	MMAM	Yb(OTf)$_3$ (0.20 M)	60	90	32 / 50 / 18
3	MMAM	none	60	97	2 / 29 / 69
4	MMAM	Sc(OTf)$_3$ (0.19 M)	60	92	28 / 55 / 17
5	MMAM	Y(OTf)$_3$ (0.19 M)	60	91	46 / 40 / 14
6	MMAM	Yb(OTf)$_3$ (0.20 M)	60	89	46 / 44 / 10
7	IPMAM	none	60	50	1 / 31 / 68
8	IPMAM	Yb(OTf)$_3$ (0.10 M)	60	77	58 / 37 / 5
9	IPMAM	none	20	16	~0 / 20 / 80
10	IPMAM	Yb(OTf)$_3$ (0.10 M)	20	54	63 / 33 / 4

[a] $[\mathrm{Monomer}]_0$ = 2.0 M (entries 1-6), 1.0 M (entries 7-10). Initiator: AIBN (0.02 M). Time = 24 hr.

[b] THF-insoluble part (entries 1-6), hot water-insoluble part (entries 7-10).

[c] Determined by ^{1}H NMR in DMSO-d_6 at 170°C (entries 1-6), ^{13}C NMR in DMSO-d_6 at 80°C (entries 7-10).

Y(OTf)$_3$ produced atactic poly(NIPAM)s (m = 42~46%) in these solvents.

The effect of the Lewis acids was influenced by their concentration and the polymerization temperature (Figure 1). The Lewis acids catalytically influenced the stereochemistry of the polymerization. A catalytic amount of Y(OTf)$_3$, 5-20 mol% of the monomer, was enough to control the stereoregularity of the obtained polymer. The effect of the Lewis acids was higher at -20°C than that at -78 and 0°C. The polymerization at -20°C using 20 mol% of Y(OTf)$_3$ to the monomer produced the polymer having the highest isotacticity (m = 92%). Figure 2 shows the ^{1}H NMR spectra of the isotactic poly(NIPAM) and the atactic one.

Table 3 shows the results of the polymerization of AM and DMAM in the presence of Lewis acids. During the AM polymerization, the Lewis acids increased the isotacticity of the obtained polymers, and $Yb(OTf)_3$ was more effective than $Sc(OTf)_3$ and $Y(OTf)_3$. The polymerization of AM with $Yb(OTf)_3$ at 0°C gave a polymer having the tacticity of mm/mr/rr = 65/29/6. In the DMAM polymerization, isotactic polymers were obtained in the presence of Lewis acids similar to the AM polymerizations.

The polymerizations of MMAM and IPMAM were also examined in the presence of Lewis acids (Table 4). Although the polymerization of MMAM and IPMAM in the absence of Lewis acids produced syndiotactic-rich polymers, isotactic polymers were obtained in the presence of Lewis acids. During the IPMAM polymerization in methanol at 20°C with $Yb(OTf)_3$, the mm value of the produced polymer increased by 63% and the rr value decreased by 76%.

The cloud points of the poly(IPMAM) solution in water were influenced by the main-chain tacticity. Figure 3 shows the transmittance change in the water solution of poly(IPMAM)s having two different tacticities, syndiotacticity (rr = 80%) and isotacticity (mm = 67%), at 500nm at 20-45°C. During both the heating and cooling processes, the solution of the isotactic polymer had lower cloud points than those of the syndiotactic one.

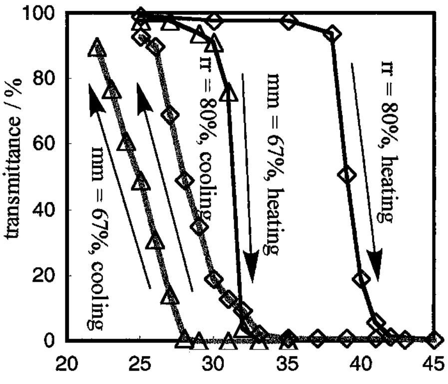

Figure 3. The change of transmittane of a poly(IPMAM) solution in water at 500nm (2 mg/ml).

Conclusion

During the radical polymerization of NIPAM, AM, DMAM, MMAM, and IPMAM in methanol, the Lewis acids such as $Yb(OTf)_3$ and $Y(OTf)_3$ increased the isotacticity of the obtained polymers. The difference in the tacticity clearly influenced the properties such as the cloud points of the poly(NIPAM) solution in water. This method of the stereocontrol catalyzed by Lewis acids should be widely applicable to various polar vinyl monomers.

Acknowledgment

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