Regiospecific Radical Polymerization of Vinyl Methacrylate in the Presence of Lewis Acids into Soluble Polymers with Pendent Vinyl Ester Substituents

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ABSTRACT: The regiospecific radical polymerization of vinyl methacrylate (VMA), a divinyl compound with two different radically polymerizable double bonds, was investigated in the presence of Lewis acids, such as $SnCl_4$, Et_nAlCl_{3-n}, and $R_nAl(ODBP)_{3-n}$ [R = Me, Et, *i*-Bu; ODBP = 2,6-di-*tert*-butylphenoxy]. The polymerization with α,α-azobis(isobutyronitrile) (AIBN) in the presence of aluminum-based Lewis acids gave soluble polymers, in which the methacryloyl group was selectively polymerized, while insoluble polymer gels were obtained without Lewis acids or with $SnCl_4$. When using monoalkylaluminum bulky diphenoxides [$RAl(ODBP)_2$], the highly regiospecific radical polymerization significantly proceeded with a high conversion (>85%) to give soluble polymers with quantitatively remaining vinyl ester pendants and a relatively high molecular weight ($M_n \geq 10^4$). The copolymerization of VMA with methyl methacrylate in the presence of $EtAl(ODBP)_2$ induced the simultaneous consumption of both monomers at almost the same rate to directly give soluble random pendant-functionalized copolymers with vinyl ester moieties. The NMR analysis of the mixture of VMA and $EtAl(ODBP)_2$ showed a 1:1 complexation with a relatively high association constant ($K_{assn} = 59.6\ M^{-1}$) via the coordination of the aluminum Lewis acid to the carbonyl moiety. The ruthenium-catalyzed living radical polymerization of VMA was also possible in the presence of $EtAl(ODBP)_2$ and an iodide initiator to give soluble polymers with controlled molecular weights.

Introduction

An unconjugated diene monomer is generally employed as a cross-linking agent for the formation of gels[1] but can be a prosperous monomer for functional or high-performance polymers because it may give linear polymers with vinyl groups remaining in the side chain via selective polymerization of one of the vinyl groups or may afford rigid cyclic structures in the main-chain via ring-closing cyclopolymerization.[2,3] However, the homopolymerization of a divinyl compound usually results in cross-linked insoluble polymers, especially by conventional radical polymerizations due to the uncontrolled or random propagation of the growing radical species to both double bonds. In contrast to almost no substantial selective radical polymerizations, which lead to linear soluble polymers with one of the two vinyl groups remaining unreacted, relatively large numbers of studies on the selective radical cyclopolymerization of divinyl compounds have been reported.[2,3] Most of these studies were directed to diallylammonium, dialkylmethacrylamide, or related divinyl compounds, the common feature of which is that the corresponding monovinyl compounds do not efficiently homopolymerize due to the stability of the allyl radicals or due to the bulkiness of the dialkylmethacrylamide monomer. In contrast, these divinyl versions can undergo a ring-closing cyclopolymerization via selective intramolecular cyclization, which affords less stable or less bulky primary radical species followed by its addition to the vinyl group of another molecule, and thus form soluble polymers consisting of 5- or 6-membered rings in the main chain.

Vinyl methacrylate (VMA), a divinyl compound with both methacryloyl and vinyl ester groups, usually gives insoluble cross-linked products by radical polymerizations because both C=C double bonds participate in the radical propagation (Scheme 1).[4,5] Although previous papers reported soluble product formation by the radical polymerization of VMA, there were several problems including limited yields or conversions (≤20%), highly dilute conditions, and mixed ill-defined structures consisting of both the remaining vinyl ester and methacryloyl groups in addition to the cyclic structures.[6] This is due to the lack of a high selectivity during the propagation of the two vinyl groups although their model vinyl compounds such as methyl methacrylate (MMA) and vinyl acetate (VAc) show quite different monomer reactivity ratios ($r_1 \sim 20$, $r_2 \sim 0.05$; M_1 = methyl methacrylate, M_2 = vinyl acetate; $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, where k_{ij} is the rate constant for a propagating chain ending in M_i adding to monomer M_j).[7] This means that the differences in the reactivities of the two double bonds are not large enough to induce either of the selective propagations, which may generate linear polymers with pendent vinyl groups or to lead to selective cross-propagation that may result in cyclopolymerization. A possible solution for the highly selective polymerization is to change the reactivity of the two vinyl groups or to alter the selectivity of the derived radical species using some additives that can give drastic effects on them. Although anionic and group transfer polymerization can generate the linear polymers with the remaining vinyl ester groups due to the fact that the vinyl ester group is intact to the anionic species, it requires stringent conditions such as a low-temperature and/or anhydrous condition.[6,8,9]

For changing the monomer reactivity ratios, alkylaluminum chlorides were first employed for the radical copolymerizations of acrylonitrile and propylene and enhanced the copolymerizability between the electron acceptor and donor monomers, which resulted in the alternating copolymers.[10] Later studies revealed that other Lewis acids, including a wide variety of metal halides (MCl_n; M = Al, Zn, Ti, B, Sn, etc.), are also effective for increasing the alternating sequences of various combinations of the electron acceptor and donor monomers by the selective cross-propagation.[11,12] Recently, these alternating copolymerizations were combined with living radical polymerizations to give

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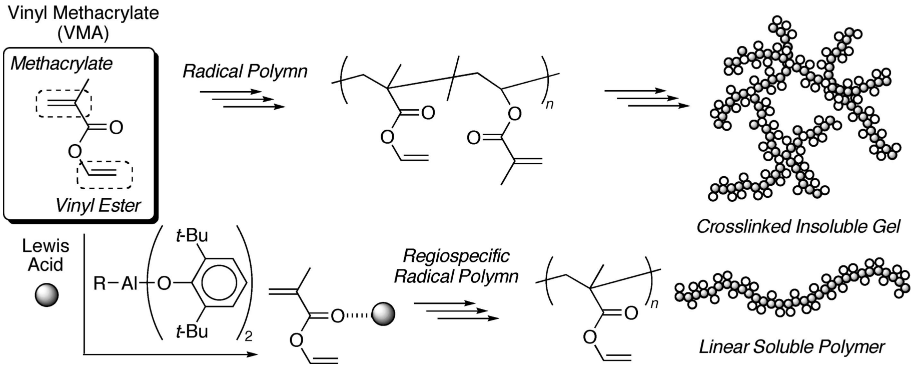
Scheme 1. Radical Polymerization of Vinyl Methacrylate in the Presence of Lewis Acids



the alternating copolymers with controlled molecular weights.[13,14] However, there are no reports on the effects of Lewis acids on the radical copolymerizations of methacrylates and vinyl esters.

This study is thus directed to the possible selective radical polymerizations of VMA using Lewis acid additives to obtain linear soluble polymers with well-defined main-chain structures and either one of the vinyl groups remaining. We employed a series of alkylaluminum bulky phenoxides that can strongly interact with carbonyl moieties.[15] Bulky aluminum phenoxides have been employed for the anionic polymerizations of (meth)-acrylates to accelerate the reactions and/or inducing controlled stereospecific propagations via coordination to monomers and/or growing species.[16–19] Their use for the radical polymerizations was also reported for the ruthenium-catalyzed living radical polymerization of MMA, in which a rate enhancement was observed.[20] Another use was also reported for the initiator-free radical polymerization of acrylate and styrene, in which they act as initiators or catalysts to induce fast radical polymerizations.[21]

This paper will reveal that the bulky aluminum phenoxides afford the linear soluble polymers of VMA with complete retention of the vinyl ester groups and high molecular weights ($M_n > 10^4$) up to almost quantitative conversions (>90%) without any remaining methacryloyl groups as well as cyclic structures. The further combination with the ruthenium-catalyzed living radical polymerization can generate soluble polymers with controlled molecular weights.

Results and Discussion

1. Radical Polymerization of VMA in the Presence of Various Lewis Acids. VMA was first polymerized with α,α-azobis(isobutyronitrile) (AIBN) in toluene at 60 °C without Lewis acids. The polymerization mixture was homogeneous with a low conversion and then gelated when the conversion reached around 40% (Table 1). The addition of $SnCl_4$ (200 mM; 20 mol % to VMA) did not lead to any improvements in the formation of insoluble products, which is similar to no substantial effects of $ZnCl_2$ on the structure of poly(VMA) as already reported.[22]

However, Et_2AlCl, an alkylaluminum-based Lewis acid, prevented the gelation to give completely soluble polymers until the polymerization ceased (>70%) irrespective of the low molecular weight of the products [number-average molecular weight (M_n) ~ 1000]. Similar soluble products with a low molecular weight were also obtained with another dialkylaluminum compound containing the bulky phenoxy group, $Et_2Al(ODBP)$ (ODBP = 2,6-di-*tert*-butylphenoxy). The suppression of gelation is probably due to the interaction of the Lewis acidic aluminum part with the carbonyl groups of the monomer, while the low molecular weight may suggest chain transfer or initiation by the dialkylaluminum compounds.

Table 1. Effect of Lewis Acid on Radical Polymerization of Vinyl Methacrylate (VMA)[a]

entry	Lewis acid	time, h	conv, %	M_n[b]	M_w/M_n[b]	reaction mixture
1	none	3	28	11 000	6.5	solution
2	none	3.5	37	16 000[c]	11.7[c]	gelation
3	$SnCl_4$	4	33	20 000[c]	13.0[c]	gelation
4	Et_2AlCl	36	74	1 200	7.5	solution
5	$Et_2Al(ODBP)$	32	52	2 000	3.6	solution
6	$MeAl(ODBP)_2$	24	81	20 000	8.4	solution
7	$EtAl(ODBP)_2$	5	83	46 000	3.3	solution
8	*i*-$BuAl(ODBP)_2$	1	75	91 000	5.4	solution
9	ATPH	4	62	43 000[c]	12.2[c]	gelation

[a] Polymerization conditions: $[VMA]_0/[α,α\text{-azobis(isobutyronitrile)}]_0/[\text{Lewis acid}]_0 = 1000/2.5/200$ mM in toluene at 60 °C. [b] The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) were determined on size-exclusion chromatography in tetrahydrofuran. [c] Soluble part.

Further progress was attained using a monoalkylaluminum bulky diphenoxide, $MeAl(ODBP)_2$, which resulted in soluble polymers with a higher molecular weight (M_n = 19 000) and a higher conversion (>85%). Upon increasing the alkyl group on the aluminum additive [$EtAl(ODBP)_2$, *i*-$BuAl(ODBP)_2$], the molecular weights further increased without forming insoluble products up to high conversions. With the isobutylaluminum compound, soluble polymers with much higher molecular weights (M_n = 91 000) were especially obtained. In contrast, a bulkier triphenoxyaluminum compound [aluminum tris(2,6-diphenylphenoxide) (ATPH)] led to gelation around a 60% monomer conversion.

The obtained polymers were then analyzed by ^{1}H NMR spectroscopy (Figure 1). The products obtained in the absence of Lewis acids just before gelation showed relatively large peaks of the remaining vinyl ester protons (c and d) in addition to small peaks due to methacrylate vinyl protons (h) (Figure 1A). All of the resonances are broadened, which suggested that the cross-linking has already started even for the apparently soluble products. Thus, the conventional radical polymerization of VMA without Lewis acids mainly proceeds via propagation of the methacrylate unit along with the minor consumption of the vinyl ester moiety, which then results in insoluble products due to cross-linking. In contrast, the polymers obtained with $EtAl(ODBP)_2$ showed sharp resonances of the remaining vinyl ester protons in addition to the main-chain methylene (a) and methyl (b) protons typical for polymethacrylates without remaining methacrylate vinyl protons (Figure 1B). The resonance intensity ratios of the vinyl ester (d) to the main-chain methylene protons (a) were 1.07, which indicates that the vinyl ester moieties are completely intact during the radical polymerizations. Therefore, the radical polymerization of VMA in the presence of $EtAl(ODBP)_2$ proceeds via the highly selective propagation of the methacrylate moieties to give linear soluble polymers with vinyl ester pendants.

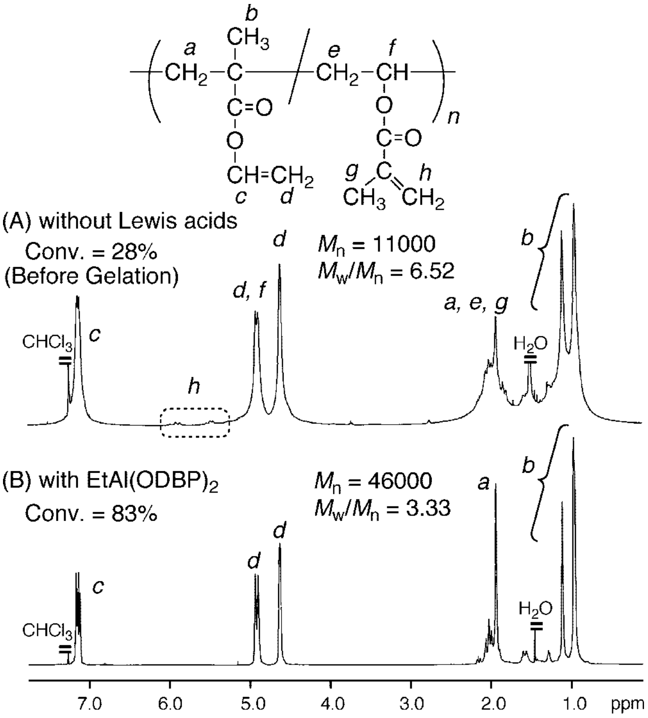


Figure 1. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 50 °C) of poly(vinyl methacrylate) obtained without Lewis acids (entry 1, Table 1 in the main text) (A) and with $EtAl(ODBP)_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) (entry 7, Table 1 in the main text) (B).

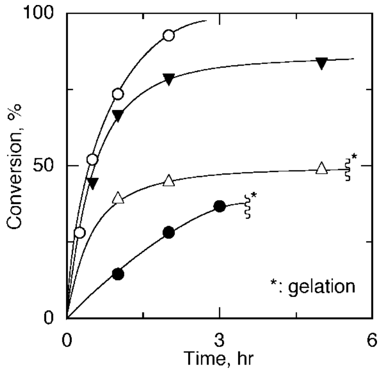


Figure 2. Radical polymerization of vinyl methacrylate (VMA) ($[VMA]_0$ = 1.0 M) at varying the concentrations of $EtAl(ODBP)_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) in toluene at 60 °C; $[EtAl(ODBP)_2]_0/[VMA]_0$ = 0 (●), 0.05 (△), 0.20 (▼), 0.40 (○).

The effects of the added Lewis acid amounts were investigated for the radical polymerization and $EtAl(ODBP)_2$ with varying concentrations ($[EtAl(ODBP)_2]_0$ = 0−400 mM; 0−40 mol %) (Figure 2). Even a smaller amount of $EtAl(ODBP)_2$ (5.0 mol %) accelerated the polymerization while gelation occurred around a 50% conversion to result in insoluble products.

As shown in Figure 3A, the products obtained just before gelation in the presence of 5.0 mol % of $EtAl(ODBP)_2$ showed relatively sharp peaks, but there were a very small amount of remaining methacryloyl groups in comparison to those obtained without the Lewis acid (Figure 1A), which will result in cross-linking. A larger amount of the Lewis acid (40 mol %) was more effective for the rate enhancements, higher conversions of monomers (>90%) (Figure 2), inhibition of gelation, and soluble polymer formation without the unreacted methacryloyl groups (Figure 3B). These results indicate that $EtAl(ODBP)_2$ coordinates the carbonyl groups of the monomer and increases the reactivity of the methacryloyl C=C double bond over the vinyl esters to enhance the propagation of the methacrylate unit.

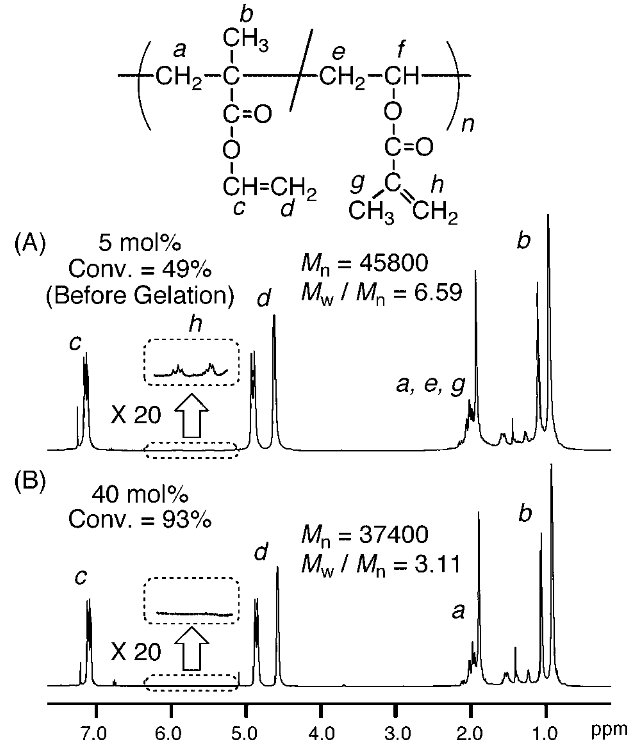


Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 50 °C) of poly(vinyl methacrylate) obtained at varying the concentrations of $EtAl(ODBP)_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) in toluene at 60 °C; $[EtAl(ODBP)_2]_0$/[vinyl methacrylate]$_0$ = 0.05 (A), 0.40 (B).

2. Copolymerization of VMA with MMA in the Presence of Aluminum Compounds. Although the above-mentioned studies suggest that the polymerization of VMA in the presence of aluminum compounds most probably proceeds via a radical mechanism, the contribution of anionic polymerizations, which may be induced by the aluminum compound, cannot be completely eluded. We thus investigated the copolymerization of VMA and MMA in the presence of $EtAl(ODBP)_2$ and checked the monomer reactivities because MMA is more reactive than VMA in the anionic polymerizations.[9]

The copolymerization of an equimolar mixture of VMA and MMA was carried out in toluene at 20 °C with 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in the presence of $EtAl(ODBP)_2$. Both monomers were almost simultaneously consumed to give the soluble products without gelation, in which VMA was polymerized slightly faster than MMA (Figure 4). This strongly suggests that the copolymerization in the presence of the aluminum compound proceeds via a radical mechanism and not an anionic one.

The ^{1}H NMR analysis of the products showed the presence of almost equal contents of each unit (VMA/MMA = 54/46) with a moderately high molecular weight (M_n = 15 000; M_w/M_n = 6.13) (Figure 5). In addition to this, no remaining methacrylate C=C double bonds were observed, which again indicates that the copolymerization proceeds via the selective polymerization of methacrylate units in the VMA. This also indicates the effective direct introduction of the vinyl ester pendent groups into the poly(methacrylates), i.e., the direct synthesis of the pendent-functionalized polymers, which can be applicable as gelation reagents, only by the radical copolymerization of the methacrylates with VMA in the presence of the aluminum compounds.

We also investigated the copolymerization of MMA with VAc in the presence of $EtAl(ODBP)_2$ to investigate effects of the

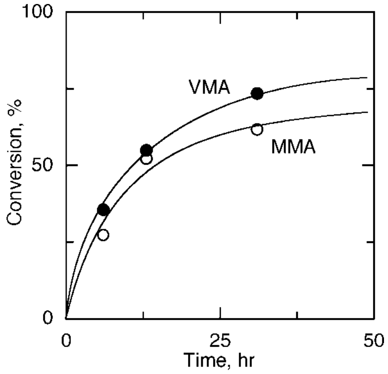


Figure 4. Copolymerization of vinyl methacrylate (VMA) (●) and methyl methacrylate (MMA) (○) in the presence of EtAl(ODBP)$_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) in toluene at 20 °C; [VMA]$_0$/[MMA]$_0$/[EtAl(ODBP)$_2$]$_0$/[2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)]$_0$ = 1000/1000/100/2.5 mM.

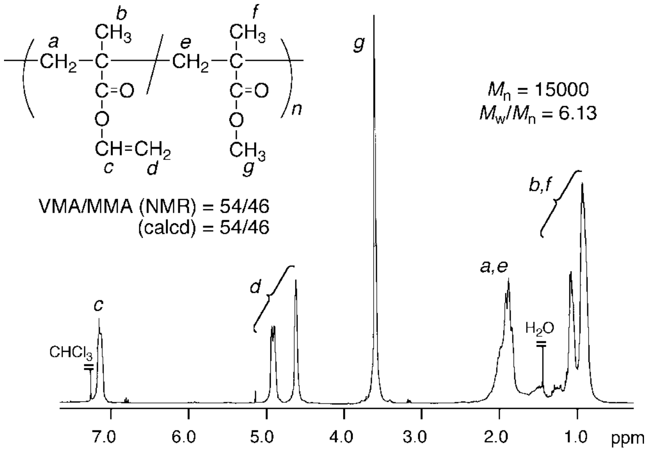


Figure 5. ^{1}H NMR spectra (400 MHz, CDCl$_3$, 50 °C) of copolymers obtained in the copolymerization of vinyl methacrylate (VMA) and methyl methacrylate (MMA) in toluene at 20 °C in 31 h.

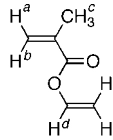
aluminum compound on the copolymerizability of the two monomers ([MMA]$_0$/[VAc]$_0$/[AIBN]$_0$/[EtAl(ODBP)$_2$]$_0$ = 250/1000/2.5/0 or 100 mM) in toluene at 60 °C. The copolymerizations proceeded irrespective of the presence or absence of EtAl(ODBP)$_2$ while the content of the VAc unit in the copolymers was decreased with the aluminum compound (VAc/MMA = 14/86 vs 25/75). This again shows the increased monomer reactivity of the methacryloyl group in comparison to the vinyl ester moiety by the coordination of the aluminum compound.

3. Interaction between VMA and EtAl(ODBP)$_2$. A possible interaction between VMA and the aluminum additive was investigated by ^{1}H and ^{13}C NMR analyses of the mixture in toluene-d_8 at 60 °C (Tables 2A,B). Upon the addition of an equimolar amount of EtAl(ODBP)$_2$ to VMA, two methacryloyl vinyl protons (a and b) shifted to a lower magnetic field, which indicates a decrease in the electron density of the vinyl group by coordination of the aluminum compound. As for the ^{13}C NMR spectra, relatively large shifts to a lower magnetic field (ca. +4 ppm) were seen not only for the carbonyl carbon but also for the methylene carbon of the vinyl ester group. This suggests that the aluminum compound coordinates to the carbonyl carbon and further results in some reactivity depletion of the vinyl ester moiety.

A combination of ethyl methacrylate (EMA), which does not possess the vinyl ester moiety, with EtAl(ODBP)$_2$ was similarly analyzed by NMR spectra. Similar chemical shift changes were observed in the ^{1}H NMR spectrum while adverse chemical shift changes were observed in the ^{13}C NMR spectra of a and e (Tables 3A,B). These may indicate some special interactions between the aluminum part and the vinyl ester moiety of VMA.

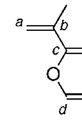
Table 2. (A) ^{1}H and (B) ^{13}C NMR Chemical Shifts (δ, ppm) of Vinyl Methacrylate (VMA)[a]

(A)



	a	*b*	*c*	*d*	*e*	*f*
none	5.19	5.97	1.69	7.27	4.70	4.25
EtAl(ODBP)$_2$	5.24	6.18	1.57	7.19	4.66	4.25
Δδ	+0.05	+0.21	−0.08	−0.08	−0.04	0.00

(B)

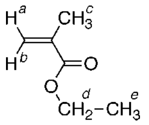


	a	*b*	*c*	*d*	*e*
none	126.74	136.23	164.15	142.29	97.56
EtAl(ODBP)$_2$	125.90	139.22	168.91	142.40	101.57
Δδ	−0.84	+2.99	+4.76	+0.11	+4.01

[a] [VMA]$_0$ = 500 mM, [EtAl(ODBP)$_2$ (ODBP = 2,6-di-*tert*-butylphenoxy)]$_0$ = 500 mM in toluene-d_8 at 60 °C.

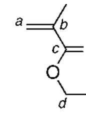
Table 3. (A) ^{1}H and (B) ^{13}C NMR Chemical Shifts (δ, ppm) of Ethyl Methacrylate (EMA)[a]

(A)



	a	*b*	*c*	*d*	*e*
none	5.17	5.97	1.75	3.91	0.96
EtAl(ODBP)$_2$	5.23	6.14	1.57	3.91	0.80
Δδ	+0.06	+0.17	−0.18	0.00	−0.16

(B)



	a	*b*	*c*	*d*	*e*
none	124.73	137.90	167.02	60.83	14.77
EtAl(ODBP)$_2$	125.85	139.50	172.79	66.53	14.12
Δδ	+1.12	+1.60	+5.77	+5.70	−0.65

[a] [EMA]$_0$ = 500 mM, [EtAl(ODBP)$_2$ (ODBP = 2,6-di-*tert*-butylphenoxy)]$_0$ = 500 mM in toluene-d_8 at 60 °C.

To investigate the interaction between VMA and EtAl(ODBP)$_2$ in more detail, two series of ^{1}H NMR measurements were examined: in one series, the total concentration of the two compounds was kept constant ([VMA] + [EtAl(ODBP)$_2$] = 100 mM) while varying each amount between 0 and 100 mM. Figure 6A shows the Job plot for this series of experiments, which indicates the clear 1:1 interaction between them. In another series of experiments, the concentration of VMA was kept constant ([VMA] = 100 mM), while the concentration of EtAl(ODBP)$_2$ was increased from 0 to 400 mM (Figure 6B). Upon increasing

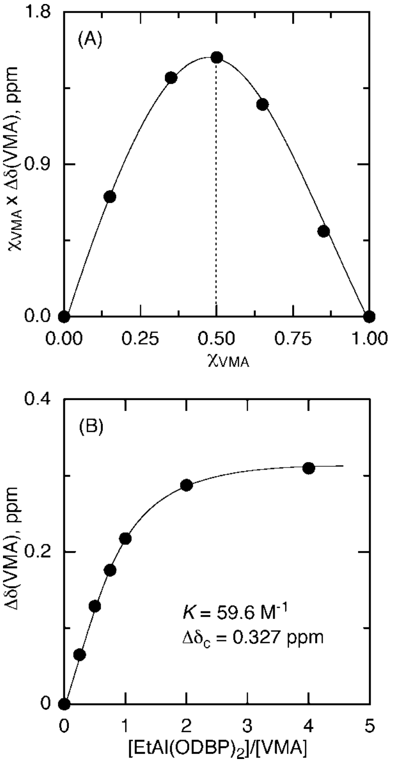


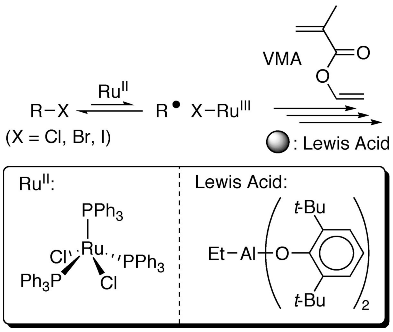
Figure 6. Job plots for the association of vinyl methacrylate (VMA) with EtAl(ODBP)$_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) from the changes in chemical shift (ppm) of the methacryloyl proton [$CH_2{=}C(CH_3)CO{-}$] of VMA ($[VMA]_0 + [EtAl(ODBP)_2]_0 = 100$ mM) (A) and NMR titration from the changes in the methacryloyl proton chemical shifts of VMA in the presence of EtAl(ODBP)$_2$ ($[VMA]_0 = 100$ mM) (B) in toluene-d_8 at 20 °C.

the amount of the aluminum compound, the ^{13}C NMR chemical shift of the carbonyl carbon moved to a lower magnetic field, indicating the increased concentration of the VMA-EtAl(ODBP)$_2$ complex. The equilibrium constant was thus calculated to be 59.6 M^{-1}. This value is relatively high in comparison to a similar complex between *N*-isopropylacrylamide (NIPAM) and metal triflates [$K = 39.3$ M^{-1} for NIPAM and Sc(OTf)$_3$ and 5.3 M^{-1} for NIPAM and Y(OTf)$_3$], which is effective for the stereospecific radical polymerization via coordination.[23] These results indicate that the strong coordination of the bulky aluminum compound to VMA enhances the selective methacryloyl polymerization of VMA.

4. Regiospecific Ruthenium-Catalyzed Radical Polymerization of VMA. The aluminum-induced regiospecific radical polymerization of VMA was then combined with the controlled/living radical polymerization for the simultaneous control of the regiospecificity and molecular weight. We then investigated the RuCl$_2$(PPh$_3$)$_3$-catalyzed radical polymerization of VMA with in the presence of EtAl(ODBP)$_2$. The choice of the ruthenium complex for the combination with the aluminum aryloxide was based on the first report of the RuCl$_2$(PPh$_3$)$_3$-catalyzed living radical polymerization of MMA in the presence of EtAl(ODBP)$_2$.[20] A series of halide initiators [R−X: Me$_2$C(CO$_2$Me)-CH$_2$C(CO$_2$Me)(Me)Cl [(MMA)$_2$−Cl], Me$_2$C(CO$_2$Et)Br (EMA−Br), and Me$_2$C(CO$_2$Et)I (EMA−I)] were thus employed in conjunction with the ruthenium catalyst (Scheme 2).

The ruthenium-catalyzed radical polymerization of VMA occurred very fast in the presence of EtAl(ODBP)$_2$ in toluene at 20 °C that reached over an 80% conversion within 20 min independent of the halogens in the initiators (Figure 7A). The ruthenium catalyst did not lose its activity for the radical polymerization of VMA even in the presence of the aluminum compound while EtAl(ODBP)$_2$ showed a similar drastic acceleration even for the ruthenium-catalyzed radical polymerization. The obtained polymers were completely soluble, and the ^1H NMR spectrum was quite similar to that obtained with AIBN. These showed the regiospecific radical polymerization by EtAl(ODBP)$_2$ also proceeded in the ruthenium-catalyzed system.

Scheme 2. Ru-Catalyzed Radical Polymerization of Vinyl Methacrylate in the Presence of Lewis Acids



As shown in Figure 7B, the M_n of the polymers obtained with the iodide initiator increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of EMA−I generates one living polymer chain. In contrast, the chloride and bromide initiators resulted in almost constant molecular weights (M_n = 8000−10 000), which were higher than the calculated values at the early stage of the polymerization but were finally close to those at higher conversions. The M_w/M_n were around 2−3 and independent of the halides and conversions. These results are most probably

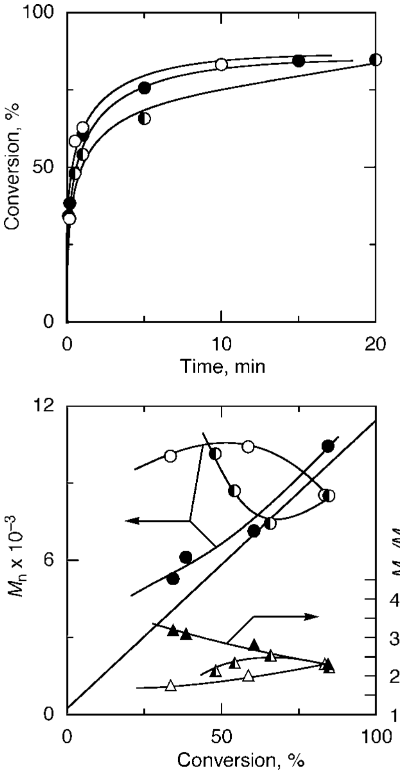


Figure 7. Ru-catalyzed radical polymerization of vinyl methacrylate (VMA) in the presence of EtAl(ODBP)$_2$ (ODBP = 2,6-di-*tert*-butylphenoxy) in R−X/RuCl$_2$(PPh$_3$)$_3$ in toluene at 20 °C the presence of EtAl(ODBP)$_2$; $[VMA]_0/[R{-}X]_0/[RuCl_2(PPh_3)_3]_0/[EtAl(ODBP)_2]_0 =$ 1000/10/5.0/200 mM. R−X: (MMA)$_2$−Cl (◐,◭); EMA−Br (○, △), EMA−I (●, ▲).

due to the extremely fast polymerizations induced by the aluminum compound in comparison to the slow or moderate interconversion between the radical and dormant species catalyzed by the ruthenium complex. However, the molecular weight control at the moderate level was possible with the iodide initiator due to the relatively weak C−I terminal and/or due to some contribution of the iodine-transfer process.[24]

Conclusions

A highly regiospecific radical polymerization of VMA proceeded in the presence of the monoalkylaluminum bulky diphenoxides [$RAl(ODBP)_2$] up to a high conversion (>85%) to give soluble polymers with quantitatively remaining vinyl ester pendants and a relatively high molecular weight ($M_n \geq 10^4$). This method proved effective for the direct synthesis of pendant-functionalized homo- and copolymers with the vinyl ester moieties derived from VMA. The high selectivity is most probably due to the strong interaction of the aluminum Lewis acid with the carbonyl group of VMA. The regiospecificity is also compatible with the ruthenium-catalyzed living radical polymerization of VMA to give the linear soluble polymers with the remaining vinyl ester pendants and controlled molecular weights.

Experimental Section

Materials. VMA (Tokyo Kasei; >98%), MMA (Tokyo Kasei; >99%), and EMA (Tokyo Kasei; >99%) were washed with aqueous NaOH (5%) and water, dried over magnesium sulfate, and distilled from calcium hydride under reduced pressure before use. α,α-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako, >95%) was used as received. $MeAl(ODBP)_2$, $EtAl(ODBP)_2$, *i*-$BuAl(ODBP)_2$, $Et_2Al(ODBP)$, and ATPH were prepared from the corresponding trialkylaluminum and phenol according to the literature.[15,18] $RuCl_2(PPh_3)_3$ (Wako, >97%) was used as received. All metal compounds were handled in a glovebox (VAC Nexus) under a moisture- and oxygen-free argon atmosphere (O_2, <1 ppm). Toluene and toluene-d_8 (Acros, 99.5 atom % D) were distilled over sodium benzophenone ketyl and bubbled with dry nitrogen over 15 min just before use. *n*-Hexane (as an internal standards for gas chromatographic analysis of the monomers) was distilled from calcium hydride before use. $(MMA)_2$−Cl [$Me_2C(CO_2Me)CH_2C-(CO_2Me)(Me)Cl$] was prepared according to the litereture.[25] EMA−Br (ethyl 2-bromoisobutyrate) (Aldrich; >98%) was distilled under reduced pressure before use. EMA−I (ethyl 2-iodoisobutyrate) was prepared according to the literature.[26]

Polymerization of VMA in the Presence of Lewis Acid. The polymerizations with AIBN were carried out by the syringe technique under dry argon in glass tubes equipped with a three-way stopcock. A typical example for the polymerization of VMA with AIBN/$EtAl(ODBP)_2$ is given below. In a 50 mL round-bottomed flask was placed $EtAl(ODBP)_2$ (560 mg, 1.20 mmol), toluene (4.52 mL), *n*-hexane (0.2 mL), VMA (0.72 mL, 6.0 mmol), and AIBN (2.46 mg, 0.015 mmol) at room temperature, and then the solution was evenly charged in five glass tubes and the tubes were sealed by flame. The tubes were immersed in thermostatic oil bath at 60 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C and then with methanol (0.2 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-hexane as an internal standard (5 h, 83% conversion). The quenched reaction mixture was diluted with toluene (10 mL), washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers (0.13 g; $M_n = 45\,600$, $M_w/M_n = 3.33$), including a small amount of remaining catalyst residues.

Ruthenium-Catalyzed Radical Polymerization of VMA in the Presence of Lewis Acid. Ruthenium-catalyzed radical polymerizations of VMA were also carried out by the syringe technique under dry nitrogen in glass tubes equipped with a three-way stopcock. A typical example for the polymerization of VMA with EMA−I/$RuCl_2(PPh_3)_3$/$EtAl(ODBP)_2$ is given below. The reaction was initiated by sequential addition of prechilled solutions of EMA−I (0.016 mmol; 0.02 mL of 0.80 M in toluene) and $EtAl(ODBP)_2$ (0.32 mmol; 0.80 mL of 0.40 M in toluene) via dry syringes into a monomer solution (in toluene; 0.8 mL) containing VMA (1.6 mmol), $RuCl_2(PPh_3)_3$ (0.0080 mmol), and *n*-hexane (0.064 mL) at 20 °C. The total volume of the reaction mixture was 1.6 mL. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C and then with methanol (0.2 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-hexane as an internal standard (15 min, 84% conversion). The quenched reaction mixture was diluted with toluene (10 mL) and rigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration, the filtrate was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers (0.21 g; $M_n = 10\,200$, $M_w/M_n = 2.15$), including a small amount of remaining catalyst residues.

Measurements. The ^1H NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz). The number-average molecular weights (M_n) and molecular weight distributions (MWDs: M_w/M_n) of the polymers were measured by size exclusion chromatography (SEC) using THF at a flow rate 1.0 mL/min at 40 °C on two polystyrene gel columns—both Shodex KF-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm)—that were connected to a JASCO PU-980 precision pump and a JASCO RI-930 detector. The molecular weight was calibrated against seven standard poly(methyl methacrylate) samples ($M_n = 1990-6\,590\,000$). The monomer conversions were determined from the concentration of the residual monomer measured by gas chromatography using *n*-hexane as the internal standard.

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