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Anionic cyclopolymerization of methacrylic anhydride with the aid of bulky aluminum Lewis acid

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1. Introduction

Methacrylic anhydride (MAAn) is known to undergo cyclopolymerization by radical polymerization to form soluble polymers with six-membered anhydride units as a major structural unit [1,2], while five-membered unit formation is favored at high temperatures [3]. Since MAAn can be categorized in polar vinyl monomers carrying electron withdrawing carbonyl function, it is potentially polymerizable by anionic mechanism; i.e., NMR chemical shift value of β -methylene carbon of MAAn (128.84 ppm) as a measure of electron density at the carbon atom is in between those of methyl methacrylate (MMA) (125.23 ppm) and methyl acrylate (130.56 ppm) [4], suggesting enough high reactivity in anionic polymerization. However, there have been no reports on the anionic polymerization of MAAn, while its amide analogs, N-substituted diacrylamides and dimethacrylamides, are known to undergo anionic cyclopolymerization; the diacrylamides form polymers with five-membered cyclic units [5,6], and the dimethacrylamides afford polymers with six-membered ring units [7], while the difficulty of anionic polymerization of the latter was noted later by Kodaira et al. [8]. In the anionic polymerization chemistry, MAAn has been used as an acylating agent for endfunctionalization of living polymer anions such as poly(ethylene oxide) anion [9], polystyrene anion [10], and PMMA anion [11].

ABSTRACT

Methacrylic anhydride was anionically polymerized for the first time by a lithium ester enolate with the aid of the bulky aluminum bisphenoxides in dichloromethane at -78 °C to afford polymers consisting of six-membered cyclized units as confirmed by NMR and IR spectroscopy, while a less bulky trialkylaluminum was ineffective. At higher temperatures, no polymeric product formed partly due to the carbonyl addition reaction of the alkyl group in the aluminum compound to the monomer. From the model reactions in the presence and absence of the aluminum compounds, importance of formation of an enolate–aluminate type species is suggested. Tacticity of PMMA derived from poly(MAAn) is rich in syndiotacticity in comparison to radically prepared one.

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These precedent examples of the use of MAAn in the polymer syntheses imply that the reactivity of MAAn against nucleophiles is dominantly as a carbonyl compound but not as a vinyl one.

Herein we report the first successful anionic polymerization of MAAn by using appropriate additives, bulky aluminum Lewis acids in particular. Selectivity in the reaction of MAAn with nucleophilic initiating and propagating species could be controlled in a way favorable to the polymer formation. The soluble polymers with cyclic units were obtained almost exclusively in moderate yields. The role of the additives is discussed in some detail.

2. Experimentals

2.1. Materials

Methacrylic anhydride (Aldrich) was dried over CaH₂ and distilled under reduced nitrogen pressure just before use. Dichloromethane (Wako, super dehydrated grade) was dried over CaH₂ and distilled under high vacuum just before use. Me₃SiOLi (Aldrich) was dried at 100 °C in vacuum for several hours and used as dry toluene solution [12]. Isopropyl α -lithioisobutyrate (Li-*i*PrIB) was prepared and recrystallized in toluene by a procedure slightly modified from the ones reported previously [13–15]. Alkylaluminum bisphenoxides (RAl(ODBP)₂; R = Me, Et) were prepared from 2,6-di-*tert*butylphenol (2 equiv.) (Tokyo Chemical Industry) and the respective trialkylaluminum (1 equiv.) (Kanto Chemical) in heptane at 0 °C, and purified by recrystallization according to References [16,17]. Tributylaluminum (Kishida Chemical) was used as a toluene





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solution. Trimethylsilyldiazomethane (2.0 M in Et₂O (Aldrich)), LiAlH₄ (Aldrich), CaH₂ (Nacalai Tesque), and butyllithium (*n*-BuLi) (Kanto Chemical) were used as received. Toluene, benzene (Aldrich, anhydrous grade), and heptane (Wako, super dehydrated grade) were mixed with a small amount of *n*-BuLi and distilled under high vacuum just before use. Diethyl ether (Aldrich, anhydrous grade) was dried over LiAlH₄ and distilled under high vacuum just before use.

2.2. Polymerizations

All the anionic polymerizations were carried out in glass ampoules filled with dried nitrogen which was passed through a Molecular Sieves-4A cooled at -78 °C. A typical polymerization procedure is as follows; an initiator solution was prepared by adding CH₂Cl₂ (5 mL), additive (1 mmol) and Li-*i*PrIB (0.2 mmol, 0.4 mL of benzene solution) via hypodermic syringes at an ambient temperature, successively. The polymerization reaction was initiator solution at -78 °C. After 24 h of polymerization period, the reaction was quenched by adding a small amount of acetic acid (AcOH) in toluene (3 M). The reaction mixture was then poured into diethyl ether (300 mL), and the precipitate was collected by filtration and dried under vacuum at an ambient temperature for 4 h.

2.3. Recovery of polymers under anhydrous conditions

The polymers obtained by the procedure described in Section 2.2 were partially hydrolyzed through quenching with the acid and work-up. In order to recover the polymeric product without hydrolysis, the polymerization was carried out at -78 °C using the procedure described above at a molar ratio of $[MAAn]_0/[Li-iPrIB]_0/[MeAl(ODBP)_2]$ to be 100/1/10; $[MAAn]_0 = 1.0$ M, $[Li-iPrIB]_0 = 10$ mM in CH₂Cl₂ (15 mL) solution. After 48 h, the solvent was removed in vacuo at 0 °C, where the polymerization did not proceed. The residue was washed with dried diethyl ether, and then dried in vacuo; yield of poly(MAAn) 1.07 g (45.9%).

2.4. Derivatization of poly(MAAn) to PMMA

The derivatization was performed according to the procedure for that of silyl methacrylate polymers to PMMA [18] with slight modification. The obtained poly(MAAn)s (20 mg) were dispersed in CH₃OH (2 mL) containing a small amount of conc. H₂SO₄ (2 drops), and the solution was kept at 65 °C for 24 h. After concentrating it by evaporation, the product was dispersed in CHCl₃ (1 mL), to which acetylacetone (0.1 mL) and trimethylsilyldiazomethane (2.0 M in Et₂O, about 1 mL) were added. After overnight, the reaction mixture was quenched by adding a small amount of acetic acid, poured into hexane (100 mL), and the precipitate was collected by decantation and then washed with distilled water.

2.5. Equimolar reaction of MAAn and Li-iPrIB

The equimolar reactions were carried out in glass ampoules filled with dried nitrogen at -78 °C with a similar procedure to the polymerization at a molar ratio of MAAn/Li-*i*PrIB/MeAl(ODBP)₂ to be (i) 1/1/0 or (ii) 1/1/5 (MAAn 0.50 mmol (77.1 mg) in CH₂Cl₂ (5.0 mL)). After 1 h of reaction period, the reaction was quenched by adding 1M HCl aq. (1.5 eq.). The solvent was removed in vacuo. The products were analyzed by GC, GC–MS, and ¹H NMR. The yields in case (i) and case (ii) were 32.7 mg and 217 mg, respectively, the latter contained 2,6-di-*tert*-butylphenol derived from MeAl(ODBP)₂.

2.6. NMR spectroscopic coordination experiment of MAAn with MeAl(ODBP)₂

Coordination to MAAn by MeAl(ODBP)₂ was confirmed by ¹³C NMR analysis of a mixture of MAAn and MeAl(ODBP)₂ in toluene- d_8 . Toluene- d_8 was distilled under high vacuum directly to sealable NMR tubes. MeAl(ODBP)₂ was added via hypodermic syringes at an ambient temperature, and after cooled to $-78 \degree$ C, MAAn was added, where [MAAn]/[MeAl(ODBP)₂] ratios of 1/0.5, 1/1, and 1/2, where [MAAn] = 0.34 ([MAAn]/[AI] = 1/0.5, 1/1), 0.17 mmol ([MAAn]/[AI] = 1/2) in 0.6 mL toluene- d_8 solution. The measurements were performed at $-78, -60, -40, -20, 0 \degree$ C, and then at $-78 \degree$ C again.

2.7. Characterizations

¹H NMR spectra of poly(MAAn)s were recorded in dimethyl sulfoxide- d_6 (DMSO- d_6) at 30 °C on a Jeol JNM-ECS 400 spectrometer. The chemical shifts were referred to the signal due to residual hydrogens in the solvent (at 2.49 ppm). ¹H NMR spectra of PMMAs derived from poly(MAAn)s were recorded in chloroform-d at 55 °C on the same spectrometer. The chemical shifts were referred to the signal due to CHCl₃ in the solvent (at 7.24 ppm).

Molar masses and its distributions of the polymers were determined at 40 °C by size-exclusion chromatography (SEC) using a Jasco model GPC-900 chromatograph equipped with two Polymer Laboratories SEC columns [PL-gel, Mixed C (300 mm × 7.5 mm)], using tetrahydrofuran (THF) as an eluent, and calibrated against standard PMMA samples (Shodex, MW: 1.25×10^6 , 6.59×10^5 , 1.95×10^5 , 4.96×10^4 , 2.06×10^4 , 6.82×10^3 , 2.00×10^3). IR spectra were recorded in KBr disc (for succinic anhydrideand glutaric anhydride) or in liquid paraffin mull (for poly(MAAn) and MAAn) with a Jasco FT/IR-410 Fourier-transform infrared spectrophotometer. Gas chromatography–mass spectrometry (GC–MS) was performed on a Jeol JMS-700 mass spectrometer.

3. Results and discussion

3.1. Anionic polymerization of MAAn

Anionic polymerization of MAAn was attempted in CH₂Cl₂ at -40 or -78 °C with a lithium ester enolate, Li-*i*PrIB, as an initiator in the presence or absence of additives which are known to be effective for stereospecific living polymerizations of methacry-late monomers [12,17]. In the absence of additives, the reaction did not give any polymeric products. Me₃SiOLi has been known to be an effective additive in combination with Li-*i*PrIB for highly isotactic-specific living polymerization of MMA [12]. The polymerization of MAAn in the presence of Me₃SiOLi (five-fold excess to the initiator) gave a soluble polymer in a low yield at -78 °C, while the reaction at elevated temperature (-40 °C) did not afford any polymeric product.

Several organoaluminum compounds are also known effective as additives for controlled anionic polymerizations via stabilization of propagating species [17,19–21] and/or monomer activation through coordination at the carbonyl group of acrylic monomers [17,22–25]. While the addition of *n*-Bu₃Al, an effective additive for syndiotactic-specific living polymerization of methacrylates [26], brought about no positive effect, the polymerization at -78 °C with bulky aluminum bisphenoxides, ethyl- and methylaluminum bis(2,6-di-*tert*-butylphenoxide)s, EtAl(ODBP)₂ and MeAl(ODBP)₂, respectively, afforded soluble polymers in moderate yields. The polymerizations at -40 °C did not proceed as in the case of Me₃SiOLi, suggesting the occurrence of serious side reactions at elevated temperature. Since the polymerization in the presence of MeAl(ODBP)₂ showed highest polymer yield, effects of the reaction conditions were studied in some detail. The ratio of MeAl(ODBP)₂ to Li-*i*PrIB was found critical for the polymerization as seen in Table 1 (runs 10–14), that is, the excess amount of the aluminum additive is necessary for the successful polymerization and the larger amount of the aluminum compound enhances the polymer yield but in a less drastic manner when the ratio exceeds five. The polymerization was also examined at different monomer-to-initiator ratio up to 100. However, the yield was limited at higher monomer-to-initiator ratio, probably due to slow propagation of the system, so that the preparation of higher molar-mass polymer is still difficult.

3.2. Structure of polymer

The structure of the obtained polymers was examined by IR and NMR analyses. Normally, anionic polymerization is terminated by adding protic terminator such as acidified alcohol. In the ordinary polymerization procedure, the reaction was quenched with acetic acid in toluene. Through this procedure, acid anhydride units in either pendant group or cyclized unit might be cleaved so that the structural information of the polymer formed would be lost. To prevent such difficulty, the polymer formed with MeAl(ODBP)₂ was recovered without quenching the reaction with acidic terminator under anhydrous conditions as described in the Experimental Section. IR spectrum of the polymer shows absorptions due to C=O stretching at 1759 and 1801 cm^{-1} , which is close to those for a six-membered cyclic model, glutaric anhydride (1758, 1808 cm⁻¹), rather than those of MAAn (1730, 1789 cm⁻¹) or those of succinic anhydride (1785, 1869 cm⁻¹), a five-membered cyclic model (Fig. 1). ¹H NMR spectrum of the polymer did not show olefinic proton signals due to pendant methacryloyl group, though the signals of unreacted MAAn remained (Fig. 2a). Absence of C=C stretching vibration (1637 cm⁻¹) observed in the IR spectrum of the monomer also confirms the absence of methacryloyl side group.

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ł h.

Tacticity of the polymer was estimated by ¹H NMR analysis for PMMA samples derived from the products through complete cleavage of anhydride group to carboxylic group followed by methylation with trimethylsilyldiazomethane. While the PMMA derived from radically prepared poly(MAAn) is rich in heterotactic (*mr*) and syndiotactic (*rr*) triads as reported previously [27], those from poly(MAAn)'s obtained with the aluminum bisphenoxides are rich in syndiotacticity (rr) (Table 1, supplementary Fig. S1). The mr sequence formation in the radical cyclopolymerization is rationalized by different stereospecificity in the intramolecular (cyclization) and intermolecular addition processes; the former prefers meso addition while the latter favors racemo addition. The stereochemical difference in the radical and anionic processes may be most evident in the intramolecular, cyclization process, that is, the anionic process favors racemo additions both in the intramolecular (cyclization) and intermolecular additions. The detailed study on the stereochemical aspect of this anionic cyclopolymerization is now under way.

3.3. Role of the aluminum bisphenoxide

Nucleophilic species may react with MAAn at C=O and C=C double bonds. If all the nucleophiles (initiator) are consumed by the C=O attack, the initiation reaction should not proceed. Thus the suppression of the C=O attack is inevitable for the success of the anionic polymerization of MAAn. To investigate the effect of the added aluminum bisphenoxide in this regard, an equimolar reaction of MAAn and Li-*i*PrIB was examined in CH₂Cl₂ at -78 °C in the presence or absence of MeAl(ODBP)₂. The product without the aluminum compound consisted of two major components [A] and [B] in the ratio of 60:36 (GC peak area), the structures of which were estimated from GC-MS and ¹H NMR analyses (supplementary Fig S2 and S3) as shown in Scheme 1. The compound [A] consists of one methacrylic acid unit and one initiator fragment, isopropyl isobutyrate unit, and should be derived from a one-to-one adduct

Run	Additive	Temp., °C	MAAn/additive/Li-iPrIB	Yield%	$M_{\rm n}/10^{3}$		$M_{ m w}{}^{ m b, c}$	Tacticity	//% ^{b, d}	
					SEC ^{b, c}	¹ H NMR ^{b, d}	M _n	mm	mr	rr
1	None	-40	25/0/1	Trace	_	-	_	_	-	_
2		-78	25/0/1	Trace	_	-	_	_	_	-
3	Me ₃ SiOLi	-40	25/5/1	Trace	_	_	_	_	_	_
4		-78	25/5/1	8.9	3.8	-	144	23.5	42.5	34.0
5	n-Bu₃Al	-40	25/5/1	Trace	-	-	_	_	_	-
6		-78	25/5/1	Trace	_	_	_	_	_	_
7	EtAl(ODBP) ₂	-40	25/5/1	Trace	_	_	_	_	_	_
8		-78	25/5/1	44.3	2.3	3.9	1.06	3.2	27.2	69.6
9	MeAl(ODBP)2	-40	25/5/1	Trace	_	_	_	_	_	_
10		-78	25/5/1	61.5	3.1	5.4	1.18	2.4	23.8	73.8
11			25/0.5/1	Trace	_	_	_	_	_	_
12			25/1/1	Trace	_	_	_	_	_	_
13			25/2/1	31.7	2.4	3.3	1.08	2.2	24.0	73.8
14			25/10/1	68.1	3.6	5.8	1.12	1.1	27.7	71.1
15 ^e			50/5/1	42.9	4.9	9.6	1.28	1.1	24.7	74.2
16 ^e			50/10/1	53.5	5.0	9.8	1.27	1.3	26.1	72.7
17 ^e			100/5/1	6.4	4.4	9.4	1.13	0.8	22.6	76.6
18 ^e			100/10/1	23.2	5.6	15.4	1.36	0.8	24.7	74.5
19 ^f			25/5/1	55.6	3.1	5.0	1.22	1.0	26.1	72.9
20 ^g	<radical></radical>	60	1000/0/1	100	77.8	_	1.91	12.5	44.1	43.4

^a MAAn 5.0 mmol, CH₂Cl₂ 5.0 mL.

^b Measured for PMMAs derived from poly(MAAn)s.

^c Determined by SEC in THF (against PMMA standards).

^d Determined by 400 MHz ¹H NMR (CDCl₃, 55 °C).

^e For 48 h.

^f For 72 h.

^g MAAn 15 mmol, AIBN 2.3 mg, benzene 18.5 mL, 24 h.



Fig. 1. IR spectra of MAAn (a), poly(MAAn) obtained with Li-iPrIB/MeAl(ODBP)₂ (b), glutaric anhydride (c), and succinic anhydride (d).

of Li-*i*PrIB and MAAn formed through the addition of Li-*i*PrIB to C= C bond of MAAn followed by cleavage of methacryloyl group upon acidic work-up. The compound [B] consists of two initiator fragments attached to one methacrylate unit, which formed through the addition of Li-*i*PrIB to C=C and C=O bonds of MAAn. No higher molar-mass products were detected. The results suggest that the carbonyl addition takes place in the initiation process of MAAn polymerization as a side reaction but the normal initiation through C=C attack is also a major process. Nevertheless, only the monomeric product [A] formed, indicating the anionic species formed in the latter process ([C] in Scheme 1) is too stable to add MAAn,



Fig. 2. ¹H NMR spectra of poly(MAAn)s obtained with Li-*iPrlB*/MeAl(ODBP)₂ (a), and that of MAAn (b) (DMSO- d_6 , 30 °C, 400 MHz). Asterisked signal (*) is due to 2,6-di-*tert*-butylphenol derived from MeAl(ODBP)₂, and olefinic signals due to remained MAAn and methacrylic acid (MAA).

probably due to stabilization through the intramolecular coordination of methacryloyl carbonyl group to lithium cation.

The equimolar reaction of MAAn and Li-*i*PrIB in the presence of MeAl(ODBP)₂ gave a product mixture consisting of [A] (38%) and higher molar-mass components but not of [B]. The absence of [B] in the product suggests that the addition of the aluminum Lewis acid suppresses the carbonyl addition reaction. Moreover, the formation of higher molar-mass products indicates that the monomer anion [C] should be activated enough to add MAAn possibly by the action of the added aluminum Lewis acid.

Schlaad and Müller proposed structure models of ester enolatealuminum alkyl complexes based on NMR and quantum chemical calculations [28]. They suggested that, in a one-to-one complex model, aluminum alkyl is coordinated to the carbonyl oxygen (anionic oxygen in the enolate form) instead of ether oxygen, while the dimer and tetramer complex are energetically more stable. Chen and his coworker reported an X-ray structure of an esterenolate complex of an aluminum bisphenoxide, in which the aluminum center also locates at the anionic oxygen of the enolate, while Li cation is linked to the two oxygen atoms of the enolate unit [15]. If this type of structure model is adopted to the MAAn anion formed in the presence of MeAl(ODBP)₂, one can postulate the terminal structure [D] in which acyl carbonyl group is free from the coordination to Li cation and a rotation of the acyl group can give rise to a conformation favorable to the intramolecular addition [E] (Scheme 2).

3.4. Coordination of aluminum bisphenoxide with MAAn

Aluminum Lewis acids are known to act as a monomer activator in anionic polymerization of carbonyl-containing monomers including methacrylates [22–25]. In order to examine effects of MeAl(ODBP)₂ in the polymerization of MAAn, ¹³C NMR coordination experiments were conducted in toluene- d_8 at MAAn/MeAl(-ODBP)₂ ratios of 1/0.5, 1/1 and 1/2 (Fig. 3) at -78 °C. At the ratio of 1/0.5, the carbonyl region spectrum showed signal of the free MAAn at 162.83 ppm along with a pair of signals at 160.84 ppm and 178.84 ppm due to a coordinated MAAn carrying MeAl(ODBP)₂ at one of the carbonyl oxygens, resulting in the large lower field shift. At the ratio of 1/1, the free MAAn signal disappeared and the two



Scheme 1. Equimolar reaction of MAAn and Li-*i*PrIB in the presence or absence of MeAl(ODBP)₂.



Scheme 2. Plausible mechanism of the effect of MeAl(ODBP)₂ on the initiation.

peaks due to the coordinated monomer prevailed. When the MeAl(ODBP)₂ was added two-fold of MAAn, the signals observed were almost identical to those of the spectrum at 1/1 ratio, suggesting that the excess aluminum compound did not coordinate to the remaining carbonyl group of the 1/1 coordinated monomer. The β -methylene carbon of the 1/1 coordinated monomer showed also two peaks at 132.0 and 128.9 ppm assignable to the coordinated methacryloyl group and non-coordinated one, respectively. The larger chemical shift value for the former indicates the higher reactivity of the coordinated methacryloyl group toward nucleophilic attack by the initiator.

The temperature-dependent change of the spectrum was also studied for the case of 1/1 ratio (Fig. 4). At -78 °C, the two paired signals were observed as described above. The spectrum at -40 °C did not show the signals responsible to the monomer carbonyls probably due to rapid exchange of the species formed. At 0 °C, a new peak appeared at 202.72 ppm assignable to ketonic carbonyl, which remained when the sample solution was cooled to -78 °C. Alkylaluminums are known to react with acid anhydride as an alkylating agent to form ketonic compounds [29]. Thus the results



Fig. 3. Carbonyl region ¹³C NMR spectra of MAAn (a), mixtures of MAAn and MeAl(-ODBP)₂ with the ratio of 1/0.5 (b), 1/1 (c) and 1/2 (d) measured in toluene- d_8 at $-78 \degree$ C (×: unidentified signals).



Fig. 4. Temperature-dependent changes of carbonyl region ¹³C NMR spectra of a 1/1 mixture of MAAn and MeAl(ODBP)₂ in toluene- d_8 (\times : unidentified signals). The spectrum at the bottom (*) was measured at -78 °C, after the measurement at 0 °C.

suggest that methyl groups of MeAl(ODBP)₂ reacts with MAAn at elevated temperatures to form methyl isopropenyl ketone. In other words, MAAn monomer acts as an acylating agent toward the aluminum compound. This may be one of the reasons why the polymerization at higher temperature was unsuccessful (see Table 1), since the resulting aluminum carboxylate should be ineffective as Lewis acid.

4. Conclusions

Methacrylic anhydride was anionically polymerized for the first time with the aid of the bulky aluminum Lewis acids in dichloromethane at -78 °C. The product polymers consisted of six-membered cyclized units exclusively, as in the reported cases of N-methyldimethacrylamide [7]. Based on the fact that the model reaction of MAAn with the ester enolate initiator did not afford an oligomeric product due to the formation of unimeric anion stabilized by the coordination with the remaining methacryloyl carbonyl group, it is proposed that the formation of the enolate-aluminate type species prevents such coordinative stabilization so that the remaining methacryloyl C=C bond becomes accessible for intramolecular addition to form the cylized unit. Tacticity of PMMA derived from poly(MAAn) is rich in syndiotactic triad in contrast to the cases of radically prepared one, suggesting the different stereochemistry in the intramolecular (cyclization) process between anionic and radical mechanisms. At higher temperatures than -78 °C, no polymeric product formed partly due to the carbonyl addition reaction of MeAl(ODBP)₂ to MAAn. Though the rate of polymerization is so low that the monomer conversion is still moderate and the attained molar mass is limited less than 10⁴, the polymerization system used is known to be effective for living anionic polymerizations of methacrylate and acrylates so that the MAAn can readily be incorporated in the block copolymer syntheses with these monomers as a rigid segment and reactive precursor block for the materials applications of acrylic polymers.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2012.12.078.

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