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Hisaya Sato[a]; Teiji Tsuruta[a]
[a] Department of Synthetic Chemistry, Faculty of Engineering University of Tokyo, Tokyo, Japan

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Polymerization of α,β -Unsaturated Aldimines

HISAYA SATO and TEIJI TSURUTA

Department of Synthetic Chemistry
Faculty of Engineering
University of Tokyo
Bunkyo-ku, Tokyo, Japan

SUMMARY

N-Alkylmethacrylaldimines were prepared directly from methacrolein and primary amines. Polymerization of some kinds of α,β-unsaturated aldimines were examined using various kinds of initiators. Methacryl- and acrylaldimines were polymerized by anionic catalysts. Polymerization of these imines proceeded exclusively through vinyl-opening. From the results of homo- and copolymerizations of cyclohexylmethacrylaldimine (HMI) and/or other conjugated vinyl monomers, anionic polymerizabilities of these monomers was found to decrease in the order:

$$\underset{(C{=}C{-}C{=}O)}{\text{methyl methacrylate}} \quad > \quad \underset{(C{=}C{-}C{=}N)}{\text{HMI}} \quad > \quad \underset{(C{=}C{-}C{=}C)}{\text{isoprene}}$$

From the NMR spectra of poly(HMI) the tacticity of this polymer was studied, and the relation between tacticity and polymerization conditions is briefly discussed. Croton- and cinnamaldimines were not polymerized under any of the conditions examined.

In the last two decades many investigations have been made on the polymerization of α,β-unsaturated carbonyl compounds, such as acrylates, methacrylates, and acrylonitrile. Only a few reports [1, 2], however, have been published on the polymerization of α,β-unsaturated imines. Since the electronic character of imine group lies between those of vinyl and carbonyl groups, α, β -unsaturated imines (C=C–C=N) may be anticipated to possess medium polymerizability between α, β -unsaturated carbonyl compounds (C=C–C=O) and diolefins (C=C–C=C). We examined the polymerization behavior of the unsaturated imines by the use of various types of initiator. Cationic or radical initiators failed to induce polymerization of the α,β-unsaturated imines. On the other hand, some anionic initiators such as organoalkali and organoalkaline earth compounds, were found to initiate polymerization.

Nuclear magnetic resonance (NMR) spectra of poly(methacrylaldimines) provide us with information on the tacticity of the polymers. Relations between tacticity and polymerization conditions are discussed.

EXPERIMENTAL

a. **Materials.** *Methacrylaldimines.* Two moles (140 g) of methacrolein was placed in a four-necked round-bottom flask fitted with mechanical stirrer, dropping funnel, thermometer, and condenser. The flask was cooled below 0°C in an ice-salt bath. Primary alkyl amine (1.5-1.8 moles) was added through the dropping funnel while the reaction mixture was kept below 0°C. After all the amine was added, the solution was stirred for 30 min below 0°C. In the case of lower alkyl amines, such as methyl-, propyl-, and butylamine, about 50 g of potassium hydroxide pellets was added. The organic layer which separated from the water layer was dried and distilled two or three times. In the case of higher alkyl amines, such as cyclohexyl- or benzylamine, the reactants become too viscous to be separated from the water layer. The product was distilled under reduced pressure without removing the water. After the first distillation the organic layer was separated from water layer. It was dried and purified by distillation under reduced pressure.

Acrylaldimine. Acrylaldimines have been reported to synthesized by two different ways [2, 3]. In this experiment the monomers were synthesized by the pyrolysis of anthracene adducts.

Crotonaldimines and Cinnamaldimines. Crotonaldimines and cinnamaldimines were synthesized by the same method as methacrylaldimine. The aldimines obtained were N-isopropylcrotonaldimine (bp 128°C), N-cyclohexylcrotonaldimine (bp 64-5°C/4 mm Hg), and N-methylcinnamaldimine (bp 103-5°C/4 mm Hg).

Cinnamaldehyde anile was synthesized according to Zalkaev [4] and purified by recrystallization from ethanol, mp 106-7°C.

Solvent. Toluene and tetrahydrofuran were dried and purified by the usual method.

Catalysts. n-Butyllithium was prepared from n-butylchloride and metallic lithium in petroleum ether and the solvent was displaced by toluene.

Calcium zinc tetraethyl was prepared from calcium metal and diethylzinc in benzene.

n-Butyl- and phenylmagnesium bromide were prepared from metallic magnesium and n-butyl bromide and bromobenzene, respectively, in diethyl ether by the usual method.

Di-n-butylmagnesium was prepared by adding a small portion of dioxane to n-butylmagnesium bromide ether solution. The solvent was displaced by toluene.

Lithium aluminum hydride was obtained commercially and diethyl ether solution was used.

Commercial triethylaluminum and diethylzinc were used after purification by distillation under reduced pressure.

Benzophenone monosodium, benzophenone anile monosodium, and naphthalene sodium were prepared by stirring metallic sodium with equimoles of benzophenone, benzophenone anile, and naphthalene, respectively, in THF for 24 hr under nitrogen.

b. **Polymerization.** Polymerizations were carried out under nitrogen in sealed tubes. After a definite time, small amount of methanol was added to decompose catalysts. The reaction mixture was poured into a large volume of methanol to precipitate polymers. Polymers obtained were purified by reprecipitation with a benzene-methanol system.

c. **Polymer Properties.** Intrinsic viscosities were measured in chloroform at 30°C using Ubbelohde's viscometer.

Infrared spectra were taken in film cast from chloroform or benzene solution of polymers.

NMR spectra were run using 15 wt% solution of polymer in o-dichlorobenzene at 150-160°C by Japan Electron Optics Lab. Co. model C-60 high resolution spectrometer.

RESULTS AND DISCUSSION

1. Synthesis of Monomers

a. **Methacryl- and Acrylaldimines.** Methacrylaldimines have not been synthesized directly by condensation reactions between methacrolein and

Table 1. N-Alkylmethacrylaldimines $CH_2=C(CH_3)-CH=NR$ (I)

R	bp (°C)	Yield %
Methyl	75	15
Isopropyl	105	25
n-Butyl	146	32
sec-Butyl	128	43
Cyclohexyl	61 (7 mm Hg)	35
Benzyl	65 (2 mm Hg)	30
α-Phenylethyl	74 (2 mm Hg)	28

primary amines. Mima and Miya reported the synthesis of methacrylaldimines through the pyrolysis of anthracene adducts [1]. We succeeded in the direct preparation of methacrylaldimines by dropping 1.5-1.8 moles of primary amines into 2.0 moles of methacrolein at -10 to 0°C. The uv spectra of N-n-butyl- and N-cyclohexylmethacrylaldimines were measured in methanol.

n-BMI λ_{max} 220 mμ ϵ 23,000

HMI λ_{max} 221 mμ ϵ 22,000

These values coincide with those of N-n-butylcrotonaldimine (λ_{max} 220 mμ, ϵ 23,000) [5].

Acrylaldimines ($CH_2=CH-CH=NR$; II) prepared were as follows: N-n-butylacrylaldimine (II; R = n-C_4H_9), bp 67°C (95 mm Hg); N-cyclohexylacrylaldimine (II; R = cyclo-C_6H_{11}), bp 67-8°C (20 mm Hg).

b. Infrared and NMR Spectra of Methacryl- and Acrylaldimines. Figures 1 and 2 show ir spectra of methacryl- and acrylaldimines, respectively. Absorptions observed are assigned as follows:

Methacrylaldimines	
1640-1645 cm^{-1} 1620-1625 cm^{-1}	$\nu_{C=C}$ and $\nu_{C=N}$ (conjugated)
850-850 cm^{-1}	$\delta_{CH=N}$ (out-of-plane)
900-910 cm^{-1}	$\delta_{CH_2=C\langle}$ (out-of-plane)
1800-1830 cm^{-1}	$\delta_{CH_2=C\langle}$ (over tone)

N-Cyclohexylacrylaldimine

1645 cm^{-1} 1608 cm^{-1}	$\nu_{C=C}$ and $\nu_{C=N}$	(conjugated)
926 cm^{-1}	$\delta_{CH_2=CH-}$	(out-of-plane)
1865 cm^{-1}	$\delta_{CH_2=CH-}$	(over tone)

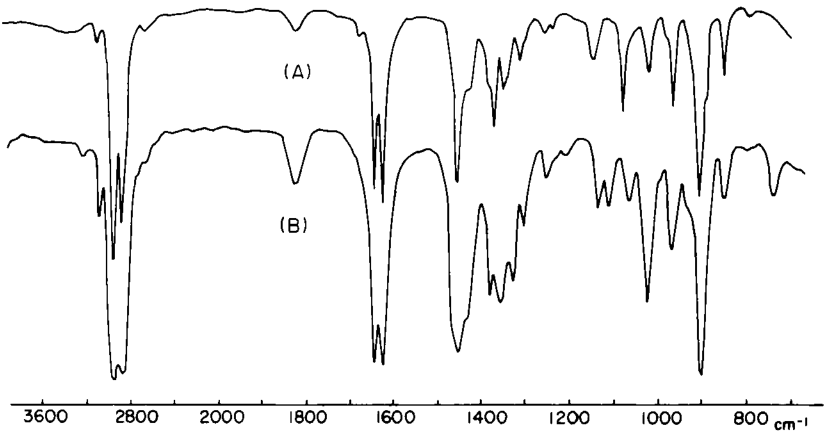


Fig. 1. Ir spectra of methacrylaldimines. (A) N-Cyclohexylmethacrylaldimine (HMI). (B) N-n-Butylmethacrylaldimine (BMI).

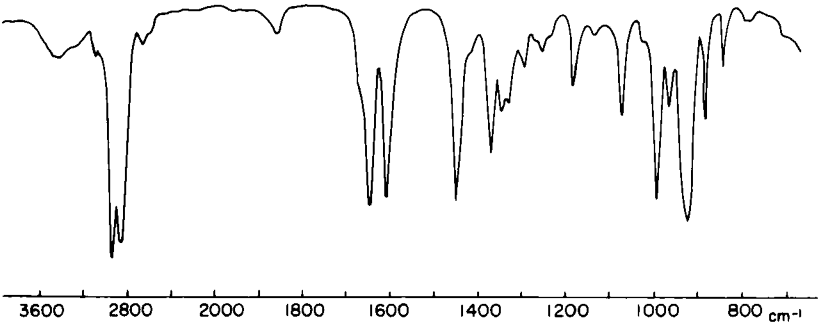
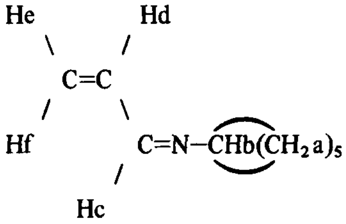
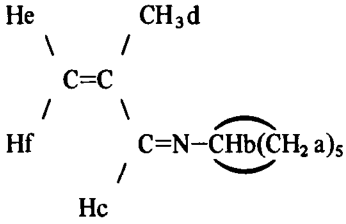


Fig. 2. Ir spectrum of cyclohexylacrylaldimine (HAI).

NMR spectra of N-cyclohexylacrylaldimine (HAI) and methacrylaldimine (HMI) were recorded under 60 Mc at 23°C using tetramethylsilane as inner standard. Figures 3 and 4 show the NMR spectra of HAI and HMI, respectively. Chemical shifts and coupling constants were obtained as follows:



Ha	8.0-9.0 τ		
Hb	7.07	Jcd	8.0 cps
Hc	2.35	Jde	19.4
Hd	3.80	Jdf	16.8
He	4.54	Jef	1.4
Hf	4.64		



Ha	8.0-9.0 τ
Hb	7.14
Hc	2.55
Hd	8.17
He	4.71
Hf	5.02

2. Polymerization of N-Cyclohexylmethacrylaldimine

Polymerization of HMI was carried out using various kinds of catalysts. The results are shown in Table 2. Alkyl metals of the Ia and IIa groups, such as n-BuLi, $CaZnEt_4$, and n-Bu_2Mg, were found to initiate polymerization of HMI. As seen from Table 2, the catalytic activity decreases in the order: n-BuLi > $CaZnEt_4$ > n-Bu_2Mg. This order agrees with that of the electropositive nature of the metallic elements. Grignard reagents (RMgX) and $LiAlH_4$ failed to polymerize HMI, in contrast with the case of methyl methacrylate.

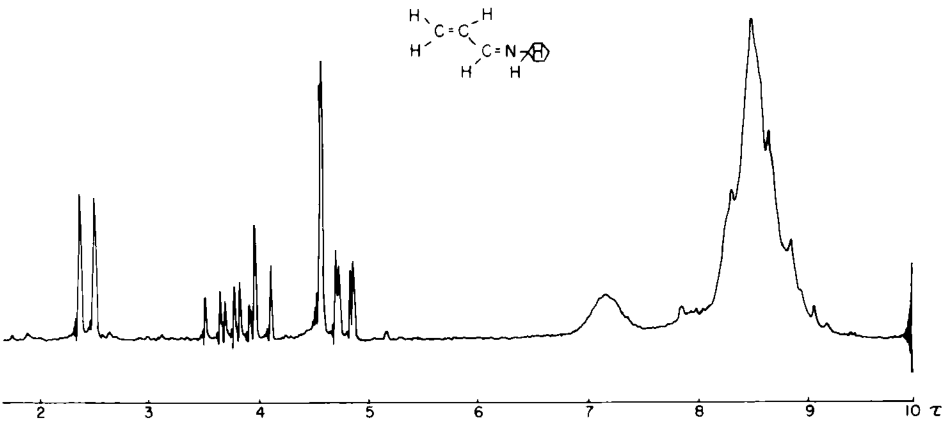


Fig. 3. NMR spectrum of HAI.

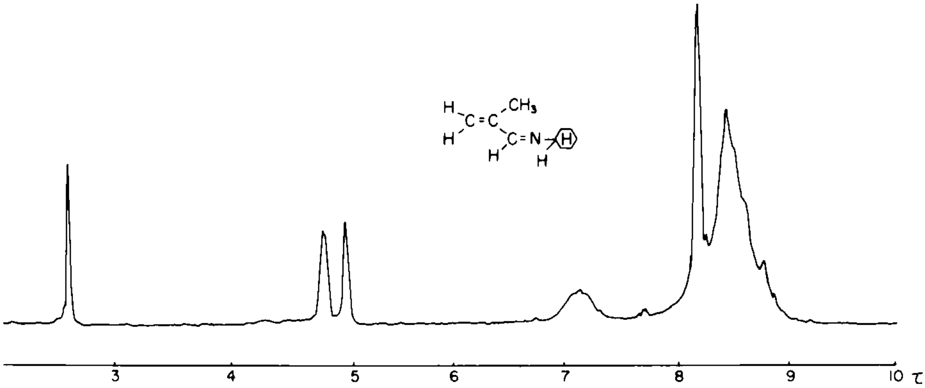


Fig. 4. NMR spectrum of HMI.

The chemical behaviors of benzophenone monosodium, benzophenone anile monosodium, and naphthalene monosodium toward the three types of conjugated monomers are summarized in Table 3. This result indicates that anionic polymerizabilities of these monomers decrease in the order: MMA > HMI > IP.

Figure 5 shows IP spectra of poly(HMI) prepared with $CaZnEt_4$ at -20°C. No absorption bands of $\nu_{C=C}$ (1600-1640 cm^{-1}) and $\delta_{CH_2=C}$ (900-950 cm^{-1}) are observed, a fact which indicates neither 1,2- nor 1,4-opening (Eqs. 2 or 3) takes place.

Table 2. Polymerization of N-Cyclohexylmethacrylaldimine[a]

Catalyst[b]	Temperature (°C)	Time (days)	Yield %	$[\eta]$[c] (dl/g)	Softening point (°C)
n-BuLi	-78	1	1	1.64	150-6
	-60	1/6	13		
	-40	1/6	85		144-8
	-20	1/6	99	1.42	144-8
	0	1/6	83		143-6
$CaZnEt_4$	-78	5	0		
	-50	5	94	1.02	140-5
	-20	1/6	40	0.85	143-8
	30	5	21	0.18	
n-Bu_2Mg	-50	5	0		
	-20	1	8	2.45	160-5
PhMgBr	0	2	0		
BuMgBr	-78	10	0		
$LiAlH_4$	0	2	0		
$AlEt_3$	-78	6	0		
$ZnEt_2$	20	2	Trace		
$NaNH_2$	-20	2	1		
$(Ph_2C{=}O)$ Na	0	1	0		
$(Ph_2C{=}NPh)$ Na	0	1	99	0.41	144-8
(Naph) Na	0	1	99	0.28	140-5

[a] Polymerization was carried out in toluene. 0.15 moles of monomer was solved in 10 ml of solvent with $CaZnEt_4$, BuMgBr, and Et_3Al as catalyst. 0.1 mole of monomer was used with other catalysts.

[b] Catalyst used was 2 mole % for monomer.

[c] Measured in $CHCl_3$ at 30°C.

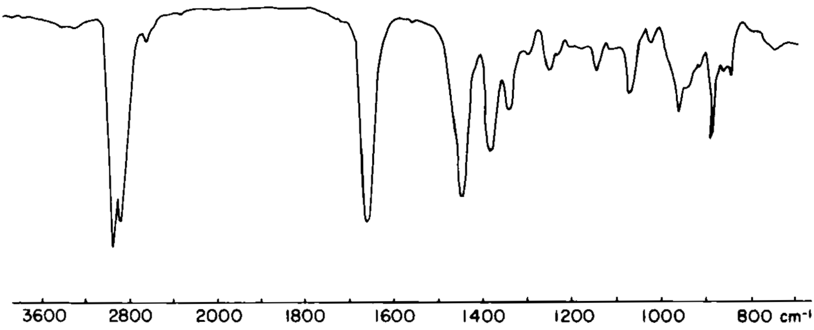


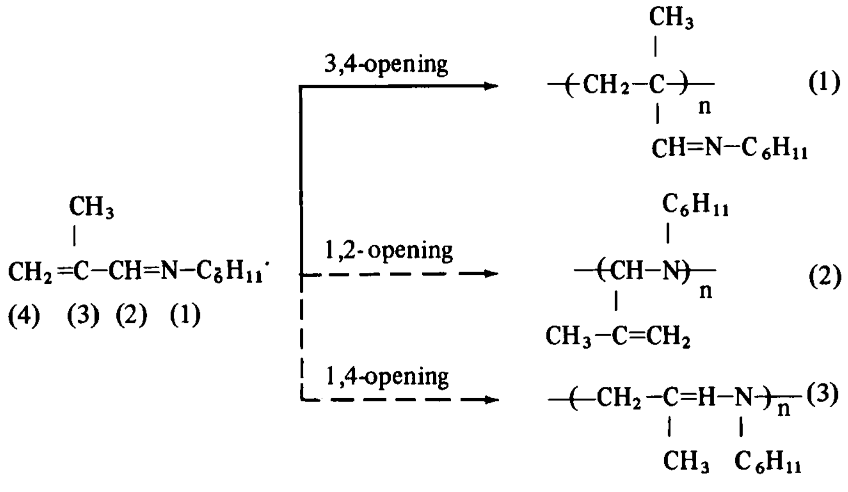
Fig. 5. Ir spectrum of poly(HMI) prepared by $CaZnEt_4$.

Table 3. Polymerization of Conjugated Vinyl Compounds[a]

Conjugate system of monomers	Catalyst[b]		
	$(Ph_2C{=}O)Na$	$(Ph_2C{=}NPh)Na$	(Naph)Na
MMA (C=C–C=O)	+	+	+
HMI (C=C–C=N)	-	+	+
IP (C=C–C=C)	-	-	+

[a]Polymerization was carried out in toluene at 0°C. + Polymer yield was almost quantitative in a few hours. - No polymer formation after 7 days.

[b]The sodium compounds were prepared in THF and 2 mole % for monomer was used.



The strong absorption band of $\nu_{C=N}$ (nonconjugated) is observed at 1665 cm^{-1} and the weak one of $\delta_{CH=N-}$ at 845 cm^{-1}, which suggests that polymerization proceeded exclusively under 3,4-opening (Eq. 1).

A polymer obtained by $CaZnEt_4$ at -20°C was treated with methanolic hydrochloric acid [conc. $HCl{:}CH_3OH{:}H_2O$ = 2:20:1 (by volume)] at 40°C for 48 hr. The nitrogen content of the treated polymer was found to decrease to 3.54%, which means about 60% of cyclohexylamine was removed by hydrolysis. The ir spectrum of the treated polymer (Fig. 6) evidently exhibits the formation of carbonyl groups at the expense of imine group, a new absorption of C=O vibration emerging at 1730 cm^{-1} with considerable decrease of C=N vibration at 1665 cm^{-1}.

Fig. 6. Ir spectrum of MeOH-HCl treated poly(HMI).

Polymers prepared with other initiators exhibited the same ir spectra as that of the polymer with $CaZnEt_4$.

Poly(N-cyclohexylmethacrylaldimine)s prepared with these anionic catalysts were insoluble in methanol, acetone, dimethylformamide, dioxane, and petroleum ether, and soluble in benzene, toluene, tetrahydrofuran, and chloroform.

Some kinds of cationic catalyst, Ziegler-Natta catalysts, and radical initiators were examined for the polymerization of HMI, but high polymers were not obtained.

3. Attempted Copolymerization of HMI with Conjugated Vinyl Monomers

Copolymerizations of HMI with methyl methacrylate (MMA), isopropyl crotonate (iPCr), styrene (St), and isoprene (IP) were attempted using several kinds of initiators. When anionic initiators (e.g., n-BuLi, $CaZnEt_4$) were used for copolymerizations of HMI with MMA or IPCr, only poly(MMA) or poly(iPCr) was formed. Anionic copolymerization of HMI with St or IP produced only the homopolymer of HMI. This result shows the anionic polymerizabilities of these monomers to decrease in the order: MMA, iPCr > HMI > St, IP. This order agrees with the results obtained from the homopolymerization study described previously.

Copolymerizations attempted with several radical-type initiators were not successful, neither homopolymer nor copolymer having formed. HMI presumably plays an inhibitor's role in these radical polymerizations.

4. Tacticity of Poly(HMI)

Figure 7 shows a typical NMR spectrum for 15% o-dichloro-benzene solution of poly(HMI) at 150-160°C. A large signal of cyclohexyl methylene protons appears in the range of 8.0-8.8 τ. A smaller signal of methin proton was observed at 7.43. α-Methyl absorption splits into three peaks, at 8.66, 8.72, and 8.78 τ, whose relative heights vary significantly with polymerization conditions. On the analogy of α-methyl signals of poly(MMA), peaks at 8.66, 8.72, and 8.78 τ were attributed to α-methyl protons of monomeric units in isotactic, heterotactic, and syndiotactic triads, respectively. Owing to the overlapping with the strong signals of cyclohexyl methylene, quantitative analysis for isotactic, heterotactic, and syndiotactic triads was very difficult. Table 4 shows the results of an approximate analysis of the NMR spectra of poly(HMI) prepared with some anionic catalysts.

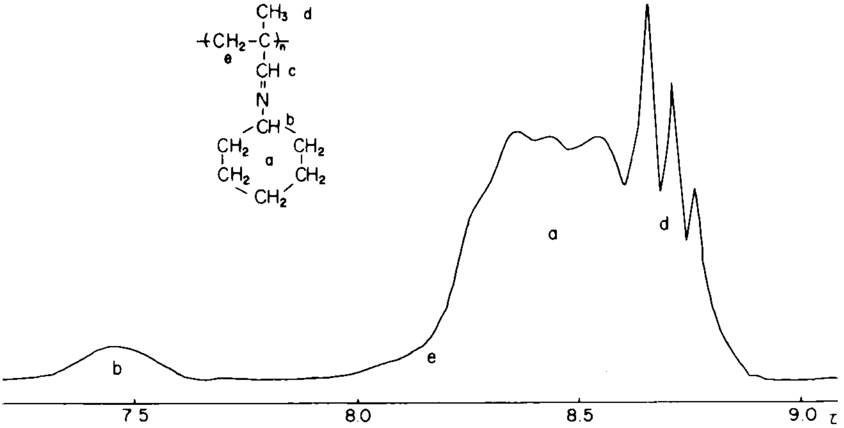


Fig. 7. NMR spectra of poly(HMI). Polymer (No. 2): n-BuLi cat. -60°C.

Polymers prepared with n-butyllithium (polymer No. 1-5) appear to possess large values of I-percentage which decrease as the polymerization temperature increases. The effect of temperature on the tacticity of poly(HMI) prepared with n-butyllithium is rather large, in contrast with the case of poly(MNA).

Isotactic and syndiotactic (diad) propagation steps can be expressed in terms of absolute reaction rate theory:

$$ki = (kT/h) \exp\left\{(\Delta S^{\ddagger}{}_{i}/R) - (\Delta H^{\ddagger}{}_{i}/RT)\right\} \quad (4)$$

$$= (kT/h) \exp\left\{(\Delta S^{\ddagger}{}_{s}/R) - (\Delta H^{\ddagger}{}_{s}/RT)\right\} \quad (5)$$

Table 4. Tacticity of Poly(HMI)

			Tacticity of Poly(HMI)[b]				
No.	Polymerization catalyst[a]	Condition temperature (°C)	I (%)	H (%)	S (%)	i (%)	s (%)
1	n-BuLi	-78	52	27	21	66	34
2		-60	45	31	24	61	39
3		-40	41	34	25	58	42
4		-20	36	36	28	54	46
5		0	33	37	30	52	48
6	$CaZnEt_4$	-20	35	37	28		
7	$n\text{-}Bu_2Mg$	-20	20	39	41		

[a] Catalyst used was 2 mole % of monomer. Polymerization was carried out in toluene.

[b] Tacticity was obtained from NMR spectra.

where subscripts i and s mean isotactic and syndiotactic, respectively. The ratio of isotactic diad probability to syndiotactic, Pi/Ps, is written as:

$$Pi/Ps = k_i/k_s = \exp \left\{ (\Delta S^{\ddagger}_i - \Delta S^{\ddagger}_s)/R - (\Delta H^{\ddagger}_i - \Delta H^{\ddagger}_s)/RT \right\} \quad (6)$$

Therefore, we have the difference in activation enthalpies for propagation:

$$\Delta(\Delta H^{\ddagger}_p) = \Delta H^{\ddagger}_i - \Delta H^{\ddagger}_s = -R\,\delta \ln (P_i/P_s)/(1/T) \quad (7)$$

and for the difference in activation entropies:

$$\begin{aligned} \Delta(\Delta S^{\ddagger}_p) &= \Delta S^{\ddagger}_i - \Delta S^{\ddagger}_s \\ &= R \ln (P_i/P_s) + \Delta(\Delta H^{\ddagger}_p)/T \end{aligned} \quad (8)$$

In Fig. 8, log P_i/P_s is plotted against 1/T. From the slope of the line

$$\Delta(\Delta H^{\ddagger}_p) = -1.7 \text{ kcal/mole}$$

and from Eq. (8).

$$\Delta(\Delta S^{\ddagger}_p) = -2.4 \text{ e.u.}$$

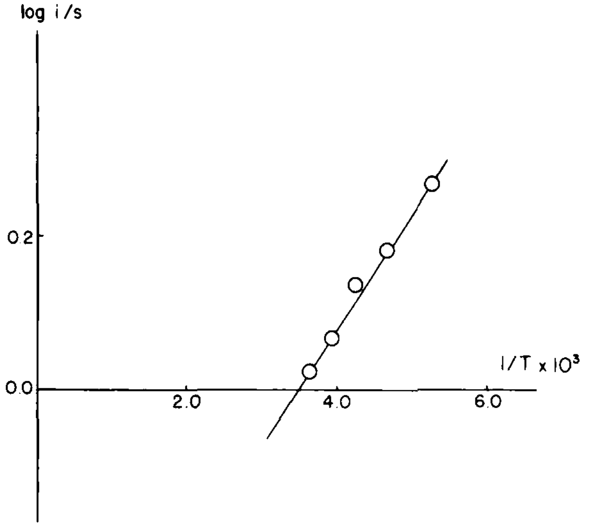
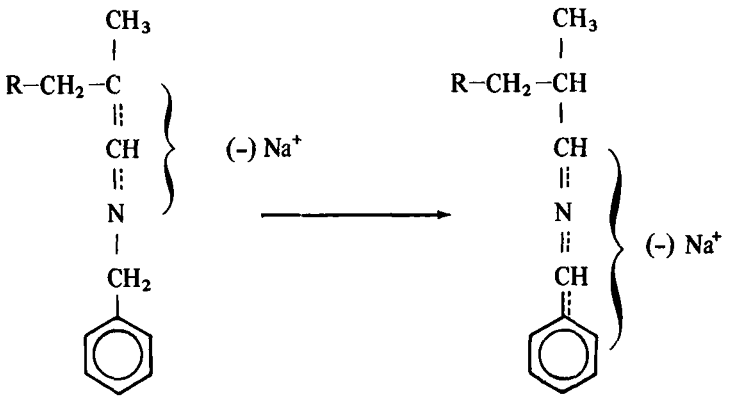


Fig. 8. Effect of temperature on tacticity of poly(HMI) n-BuLi catalyst.

Thus, the differences in both entropy and enthalpy terms are found to be responsible for the differences in the rates of formation of isotactic and syndiotactic structures. In the conditions examined, the smaller entropy for isotactic propagation is overcompensated for by the gain in enthalpy.

5. Polymerization of Methacrylaldimines Other than HMI

Polymerizations of N-n-butyl- and N-benzylmethacrylaldimine (BMI and BzMI, respectively) were carried out by using several anionic initiators. Tables 5 and 6 show the results. Alkyl metals of Ia and IIa groups are effective in a way similar to HMI polymerization. Naphthalene sodium polymerizes BzMI in toluene, but not in THF. This fact may be explained in terms of the formation of benzyl anion, such as (II), which is too stabilized in THF to continue the propagation reaction.



(I) (II)

Table 5. Polymerization of N-n-Butylmethacrylaldimine (BMI)[a]

Catalyst	Temperature (°C)	Time (days)	Yield (%)	$[\eta]^b$ (dl/g)
n-BuLi	-78	4	45	0.48
	-20	1/6	95	
$CaZnEt_4$	-50	4	36	0.40
	-20	1/4	53	
$n\text{-}Bu_2Mg$	-20	3	28	1.46

[a] Polymerization was carried out in toluene with 2 mole % initiator for monomer (BMI:0.1 mole, toluene:10 ml).

[b] Measured in chloroform at 30°C.

6. Polymerization of Acrylaldimines

Polymerization of N-n-butyl- (BAI) and N-cyclohexylacrylaldimines(HAI) was carried out under nitrogen. Table 7 shows the results.

These imines were also polymerized by only anionic catalysts. Infrared spectra of the polymers obtained (Fig. 9) have no C=C absorption but only C=N absorption at 1665 cm^{-1}. Therefore, it is concluded that the polymerization proceeded only through vinyl opening.

Table 6. Polymerization of N-Benzylmethacrylaldimine (BzMI)[a]

Catalyst[b]	Solvent	Temperature (°C)	Time (days)	Yield (%)
(Naph)Li	THF	-78	5/6	Trace
		0	2	Trace
(Naph)Na		-78	2	Trace
[c]	Toluene	0	1/3	65
[c]		-78	5/6	53
n-BuLi		0	1/2	78
		-78	5/8	50

[a] Polymerization was carried out with 0.1 mole of monomer solved in 10 ml of solvent.

[b] Catalyst used was 2 mole % of monomer.

[c] THF solution (1 mole/l) was added to toluene.

Table 7. Polymerization of N-Alkylacrylaldimines[a]

Monomer	Catalyst[b]	Temperature (°C)	Polymer yield (%)
BAI	n-BuLi	-78	42
	n-Bu_2Mg	-20	15
HAI	n-BuLi	-78	14
	$CaZnEt_4$	-20	45

[a] Polymerization was carried out in toluene for 2 days. 0.1 mole of monomer was solved in 10 ml of toluene.

[b] Catalyst used was 2 mole % for monomer.

7. Attempted Polymerization of Crotonaldimines and Cinnamaldimines

The polymerizations of N-isopropyl- and N-cyclohexylcrotonaldimines and N-methyl- and N-phenylcinnamaldimines were attempted in vain by using several kinds of catalysts, n-BuLi, $CaZnEt_4$, $SnCl_4$, $BF_3 \cdot Et_2O$, and AIBN at -78 to 80°C.

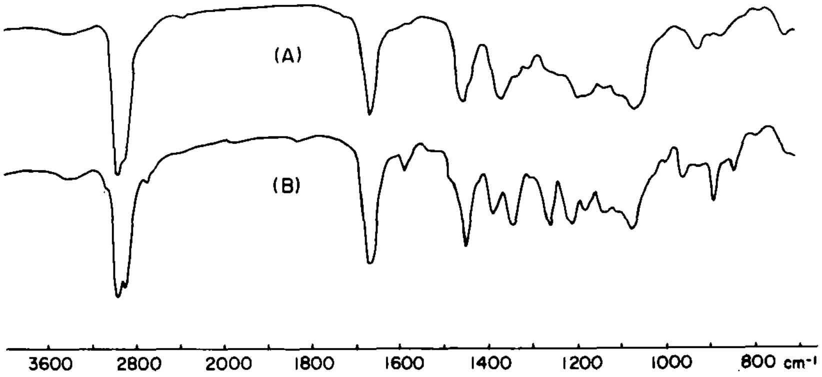


Fig. 9. Ir spectra of poly(acrylaldimines). (A) Poly(BAI) prepared by BuLi (-78°C). (B) Poly(HAI) prepared by BuLi (-78°C).

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