Polymerization of Acetaldazine

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ABSTRACT: Addition polymerization of the carbon—nitrogen double bond in acetaldazine, the azomethine analog of 2,4-hexadiene, has been studied. No polymer was obtained by radical initiator, while an oligomer with molecular weight of 800–1200 was obtained by *n*-butyllithium in aprotic solvents. The structure of the oligomer thus obtained was investigated by IR, UV and mass spectroscopies and chemical functional tests. The oligomer was composed of 1,2-addition structure ($-\text{CH}-\text{N}-$) and 1,4-addi-

tion structure ($-\text{CH}-\text{N}=\text{N}-\text{CH}-$). It was confirmed that the comparison of the number of oligomers with the number of charged initiator indicated an easy occurrence of a proton transfer from the acetaldazine monomer to the propagating anion. In addition, the anionic polymerizability of acetaldazine is discussed using various initiators for anionic polymerization in comparison of the half-wave potential of acetaldazine with that of various vinyl compounds and butadiene.

KEY WORDS Acetaldazine / Anionic Polymerization / Radical Polymerization / Micro Structure / Half-Wave Potential / 1,2-Addition / 1,4-Addition / Oligomer /

Only a few addition polymerizations of the compounds having carbon—nitrogen double bonds have been reported.¹⁻⁶ In 1959, Shashoua showed that isocyanates were polymerized to 1-nylons of high molecular weight by a variety of anionic catalysts at low temperatures. This was the first unequivocal demonstration of the polymerization of the carbon—nitrogen double bond. Since then, information concerning the anionic polymerization of isocyanates has been reported.²⁻⁵ In addition, the anionic polymerization of carbodiimide was reported by Robinson⁶ in 1964; the carbon—nitrogen double bonds of these compounds have greater π -delocalization than the isolated carbon—nitrogen double bond. If this π -delocalization is an important factor for the polymerization of carbon—nitrogen double bonds, the polymerization of azine compounds could be expected to occur. In this regard, Neureiter⁷ has reported that formaldazine spontaneously polymerized without a catalyst at room temperature, and the type of polymerization which took place was not specified. On the other hand, papers concerning the reaction of azine compounds with organometallics have been presented,^{8,9} while the

occurrence of a polymer in these reactions was not mentioned.

In this paper, the polymerization of acetaldazine by various catalysts and the investigation of the structure of the oligomers obtained are described, where both 1,2-addition and 1,4-addition take place. In addition, the anionic polymerizability of acetaldazine is discussed.

EXPERIMENTAL

Monomer

Acetaldazine was prepared from hydrazine hydrate and acetaldehyde according to the procedure of Curtius,¹⁰ and purified by reduced pressure distillation through a Widmer Column under nitrogen.

Solvents

Benzene, toluene, dioxane and heptane were purified in the usual manner¹¹ and were dried over metallic sodium. Tetrahydrofuran and dimethoxyethane were refluxed over metallic sodium and distilled into an ampoule on a high vacuum system.

Catalysts

According to the method of Ziegler,¹² *n*-butyllithium (BuLi) was prepared in *n*-heptane, and the concentration (6.6 mol%) was determined by double titration.¹³ *n*-Butylmagnesium chloride was prepared by the reaction of magnesium with *n*-butyl chloride and was titrated by the method of Gilman.¹⁴ Monosodium benzophenone was prepared by adding a tetrahydrofuran solution of benzophenone to an ampoule coated with a fresh sodium film through a breakable seal under high vacuum. The concentration was checked by the back titration method.¹⁵ Sodium naphthalene was formed by distilling tetrahydrofuran from a graduated glass into an evacuated flask which contained a known amount of naphthalene and was coated with an excess of sodium film.¹⁶ This filtrate was titrated by the method of Gilman.¹⁴

2,2'-Azobisisobutyronitrile was purified by recrystallization from 95-% ethanol. Benzoyl peroxide was purified by fractional precipitation from a chloroform solution, using ethyl alcohol as precipitant.

Polymerizations

A polymerization ampoule with a nitrogen inlet and stopcock was connected to a high-vacuum system, evacuated, and then flushed with nitrogen from the nitrogen inlet. The ampoule was removed and then a solution of the catalyst was injected by a hypodermic syringe into the ampoule under nitrogen. The ampoule was again connected to a high-vacuum system and then weighed amounts of solvent and acetaldazine, which were previously dried and degassed, were distilled into it. After the ampoule was sealed off, it was placed in a thermostat. After a given time, the contents were put into ether containing a few percent of methanol. The ether solution was shaken with distilled water and dried by anhydrous potassium carbonate. A polymer was obtained from the ether solution by evaporation. In the polymerizations by sodium naphthalene or sodium benzophenone, residual naphthalene and benzophenone were separated by the extraction with petroleum benzin.

The elementary analysis of the water-insoluble oligomer (mol wt, 730) obtained from butyllithium at -78°C was as follows

Calcd for $C_{36}H_{74}N_{16}$:

C, 59.14; H, 10.20; N, 30.66.

Found: C, 58.67; H, 9.82; N, 30.48.

The elementary analysis of the oligomer (mol wt, 730) was calculated by assuming a terminal butyl group originated from the initiator.

In the radical polymerization, a polymerization ampoule, in which 2,2'-azobisisobutyronitrile or benzoyl peroxide was previously placed, was connected to a high-vacuum system; acetaldazine and the solvent were distilled into it. After the ampoule was sealed, it was placed in a thermostat. No polymer or oligomer was obtained. The monomer was recovered in 93% by vacuum distillation.

Chemical Functional Tests for the Determination of the Structure of the Oligomer

After the treatment of 0.5 g of oligomer with 20 ml of 0.1 *N* HCl, the volatile product was added to an excess of 2,4-dinitrophenylhydrazine reagent¹⁷ and Tollen's reagent¹⁸ by high-vacuum distillation. The residual oligomer was isolated by evaporating the solvent and the volatile product completely. The oligomer was neutralized by 0.1 *N* NaOH and was put into an excess of Tollen's reagent.¹⁸

Pyrolysis of the Oligomer

A 0.3 g sample of oligomer was put into a 10 ml ampoule equipped with a sample tube for the mass spectrometer, evacuated under high-vacuum system, and heated at 150°C for 2 hr. Gas obtained from its pyrolysis was characterized by mass spectrometry.

Measurements

The IR spectra were measured on a Nippon Bunko IRS infrared spectrometer. The electronic spectra were measured on a Hitachi model EPS-2 spectrometer. The mass spectrum was measured on a Hitachi model HRU-10Z mass spectrometer. Molecular weights were determined from benzene solutions by a vapor pressure osmometer (Mechro Lab., 301A).

The polarographic measurement were conducted on a Yanagimoto model PA-102; as a supporting electrolyte, a 0.05-*N* solution of tetraethyl ammonium iodide in a 3:1 mixture of dioxane and water was used.

RESULTS AND DISCUSSION

Catalyst Screening

Various potential catalysts were screened for

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Table I. Polymerization of acetaldazine by various catalysts; monomer-10.24 mmol

Polymerization catalyst	Solvent	Temp, °C	Reaction time, hr	Yield, %	Mol wt
BuLi ^a	THF	-78	2	52.2 ^d	1180
"	"	0	2	72.2 ^d	803
"	Toluene	0	2	48.4 ^d	884
Na(Naph) ^a	THF	0	2	72.6 ^d	873
BuMgBr ^a	THF	0	2	33.7 ^d	721
Na(Ketyl) ^a	THF	0	2	27.9 ^d	805
LiAlH ₄ ^a	THF	0	20	0	
"	"	30	20	12.0 ^d	334
MeONa ^a	Hexane	0	30	0	
AIBN ^b	THF	60	48	0	
BPO ^b	THF	60	48	0	
BF ₃ OEt ₂ ^c	(CH ₂ Cl) ₂	0	0.5	7.2 ^e	213

^a (1.2~6.0) × 10⁻² mmol.

^b 0.61 × 10⁻³ mol.

^c 0.86 × 10⁻² mol/l.

^d Water insoluble.

^e Water soluble.

their ability to polymerize acetaldazine. The results are shown in Table I.

Acetaldazine failed to be polymerized by radical initiators. The reaction system was colored orange-red by typical anionic catalysts, and oligomers were obtained in good yields. A time-conversion curve in the polymerization catalyzed by butyllithium is shown in Figure 1. The yield of the oligomer was 72.2% although the monomer was completely consumed after 2 hr according to gas chromatographic analysis. Lower water-soluble oligomers may have been lost when the ether solution of the oligomer was shaken with distilled water in order to remove the inorganic

species in it.

Polymerization was also initiated by a Grignard reagent, by a metal ketyl, and gradually even by lithium aluminum hydride, in which case the color was orange-red. These results show that acetaldazine can be easily polymerized by an anionic mechanism.

When Lewis acid catalysts were also tested, oligomers were obtained in low yield. The catalyst was completely consumed after a short time. The residual acetaldazine was polymerized further when fresh catalyst was added. These results suggest that a termination reaction was very rapid, and it presumably was caused by the oligomer.¹⁹

The Structure of the Oligomer Obtained from Anionic Initiator

The IR spectra of the oligomers obtained by various anionic catalysts were identical, with the exception of the intensities of the absorption bands. The oligomers were pale yellow to yellow viscous liquids, soluble in methanol, acetone, ether, benzene, and dimethylformamide but insoluble in aliphatic hydrocarbons. However, the low-molecular-weight oligomer below 200 was soluble in water. The number-average molecular weight of the water-insoluble oligomer was above 300. The higher-molecular-weight oligomer (above 1000) was slightly soluble in benzene and

Figure 1. Time-conversion curve of water-insoluble fraction: monomer, 1.024 mol/l; catalyst, 6.0 × 10⁻² mol/l; solvent, THF; reaction temp, 0°C.

Figure 2. IR spectra of polyacetaldehyde and its derivatives: (a) —, polyacetaldehyde; (b) ---, after reduction; (c) —·—, after hydrolysis.

toluene. When the oligomer was subject to oxidation and hydrolysis, it became yellow or yellow-brown, as was shown by the increase in its oxygen content with time on contact with the air. The oligomer must be stored, therefore, with extreme care. From the elementary analysis, and by assuming that the oligomer of molecular weight 730 contained a terminal butyl group from the initiator, its structure, $C_4H_9(C_4H_8N_2)_8H$ can be assigned. The IR spectrum of the oligomer is shown in Figure 2a. The absorption bands at 1645, 1555, and 865 cm^{-1} were assigned to $\nu(C=N)$, $\nu(N=N)$, and $\delta(N=C-H)$, respectively, by taking into account the change of the IR spectra before and after the chemical reactions of the oligomer. The validity of such assignments was justified by a linear correlation between the ratio of the optical densities of the $C=N$ and $N=N$ absorption bands and the ratio estimated chemically.²⁰

The IR spectrum, after the reduction of the oligomer by aluminum amalgam, is shown in Figure 2b. The absorption bands at 1645, 1555, and 865 cm^{-1} decreased remarkably and the new

absorption bands characteristic of the NH group appeared at 3200, 1680, 1520, and 760 cm^{-1} . The IR spectrum after the hydrolysis by dilute aqueous hydrochloric acid is shown in Figure 2c. The new broad absorption bands characteristic of N—H appeared, and the modified oligomer became soluble in water. These results indicate

Figure 3. The correlation between the ratio of the 1,2-structure to the 1,4-structure and D_{865}/D_{1555} .

Figure 4. UV spectrum of polyacetaldehyde: solvent, ethanol; polymer concentration, 0.59 g/l.

that the oligomer may have both the 1,2- and the 1,4-structures.

The electronic spectrum of the oligomer was measured in the range from 200 to 700 nm. The absorption band at 238 nm is assigned to the $n-\pi^*$ transition in the $-\text{C}=\text{N}$ group and the band at 375 nm is characteristic of the $n-\pi^*$ transition in the $-\text{N}=\text{N}$ group.^{21,22} A shoulder at 291 nm is similar to the band at 285 nm in acetaldazine. In the course of anionic polymerization a proton transfer may occur from the acetaldazine monomer to the anion on the growing chain. The assumption that the anion obtained by this transfer can polymerize the monomer was confirmed by a larger number of oligomers than butyllithium catalyst, as shown in next section. (Table III). Therefore the shoulder at 291 nm is reasonably assigned to the $n-\pi^*$ transition at the terminal $\text{CH}_3\text{CH}=\text{CH}=\text{N}-\text{N}=\text{CH}-\text{CH}_2$ group obtained from proton transfer.

The structure of the oligomer was further established by qualitative chemical tests for functional groups. The introduction of the volatile product obtained from the treatment of the oligomer with dilute aqueous hydrochloric acid solution into an alcoholic solution of 2,4-dinitrophenylhydrazine gave acetaldehyde hydrazone, indicating the existence of the pendant $-\text{N}=\text{CH}-\text{CH}_3$ groups. On hydrolysis the residual solution also gave a positive Tollen's test.

When the oligomer was stored for 3 hr at 60°C under nitrogen, the optical density at 3190 cm^{-1} increased and that at 1555 cm^{-1} concomitantly decreased. This result suggests that some of the

$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ -\text{CH}-\text{N}=\text{N}-\text{CH}- \end{array}$ units have rearranged to the more stable $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ -\text{CH}-\text{NH}-\text{N}=\text{C}- \end{array}$ units.^{23,24} This rearrangement was very slow below room temperature and the change of the IR spectrum was not appreciable in 1 hr, but was apparent after 1 week.

The predominant gaseous product obtained from the pyrolysis of the oligomer at 150°C under high vacuum was determined by high resolution mass spectrometry to be the nitrogen molecule ($m/e=28.02$). This also supports the presence of the

$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ -\text{CH}-\text{N}=\text{N}-\text{CH}- \end{array}$ units.

From these results, the following structure of the oligomer is proposed.

Anionic Polymerizability of Acetaldazine

Although acetaldazine is an azomethine analogue of hexadiene which is difficult to polymerize anionically, it was polymerized to the oligomer in good yields by various anionic catalysts. The rate of the anionic polymerization of acetaldazine is remarkably larger than that of hexadiene;²⁵ thus, the anionic polymerizability of acetaldazine was qualitatively compared with that of various vinyl and diene compounds.

The polymerization of acetaldazine was realized by a Grignard reagent and a metal ketyl which did not initiate the polymerization of styrene and butadiene.²⁶ Acetaldazine was gradually polymerized to an oligomer even by lithium aluminum hydride, a catalyst which can polymerize methyl methacrylate. However, the polymerization of acetaldazine was not initiated by sodium methoxide, which caused the oligomerization of acrylonitrile and methyl methacrylate.

These results suggest that acetaldazine has a more anionic polymerizability than styrene and butadiene but a less anionic polymerizability than acrylonitrile and methyl methacrylate. Fueno, *et al.*,²⁷ suggested that the half-wave potentials of various vinyl compounds were correlated with the order of the ionic polymerizability. Therefore, the half-wave potential of acetaldazine was determined under the same conditions as Fueno, *et al.* These results are shown in Table II along with Fueno's data.²⁷ The order of the anionic polymerizability predicted by the comparison of the half-wave potential of acetaldazine with those

Table II. Half-wave potential

Substance	$-E_{1/2}$
Acetaldazine	2.04
AN ²⁷	2.01
MMA ²⁷	2.01
St ²⁷	2.35
Isop ²⁷	2.70

Solvent, water-dioxane (1:3).

Supporting electrolyte, tetraethyl ammonium iodide.

Table III. The comparison of oligomer molecular weight with catalyst concentration

Catalyst concn, mmol	Yield, % (water insoluble)	$M_n(DP)$	Concn of the obtained polymer, mmol
24×10^{-2}	53.3	947(11)	50×10^{-2}
36×10^{-2}	52.5	903(11)	49×10^{-2}
60×10^{-2}	69.8	843(10)	70×10^{-2}
120×10^{-2}	80.8	730(9)	108×10^{-2}
230×10^{-2}	86.4	386(4)	221×10^{-2}

Monomer, 10.24 mmol; solvent, THF.

Reaction temp, -78°C .

Reaction time, 60 min.

of various vinyl compounds and dienes was consistent with that observed from polymerization catalysts. This shows that the half-wave potential can be also used as a qualitative measure of the polymerizability of azine compounds.

In spite of such a high anionic polymerizability for acetaldazine, a high-molecular-weight polymer was not obtained. The proton transfer of an α -hydrogen of the monomer is probably an important factor in limiting the increase in the molecular weight, as shown in Table III.

In conclusion, acetaldazine was polymerized to oligomers by various ionic catalysts. The polymerization was the addition polymerization through the carbon—nitrogen double bond and the obtained oligomer has 1,2- and 1,4-units. The anionic polymerizability is high and is comparable to that of methyl methacrylate. The proton transfer of the monomer is an important factor in limiting the molecular weight.

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