Macromolecules **1991,** *24,* 5504-5507

Polymerization of Azabutadiene (Azine) Derivatives. Preparation of a Stereoregular Polymer from Propionaldehyde Azine

Akira Harada, Hirofumi Fujii, and Mikiharu Kamachi*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Received January 18, 1991; Revised Manuscript Received May 15, 1991

ABSTRACT: Polymerizations of azine compounds (RCH=NN=CHR, R = C_2H_5 or CH_3) were carried out by various anionic initiators. Oligomers of these monomers were obtained with *n*-BuLi or C_2H_5ZnCl as initiators. Highly crystalline and stereoregular polymers were obtained when the polymerizations of propionaldehyde azine (PrAz) were carried out with some of the Grignard reagents: High polymers were prepared by CH_3MgI. The structure of polymers obtained was investigated by IR, Raman, ^1H NMR, and ^{13}C NMR spectroscopy, indicating that these azine polymers are composed of a trans-1,4-addition unit. The X-ray diffraction patterns of the polymers show that these polymers are highly crystalline. The thermogravimetric analysis of these polymers shows that a gradual weight loss starts at about 120 °C.

Introduction

Although a number of compounds with a C=C or C=O bond have been polymerized to high polymers by radical or ionic initiators, no paper has been reported, to our knowledge, on the polymerization of compounds with C=N bonds except for carbodiimide,[1] isocyanates,[2,3] 1-azabutadiene, and 2-azabutadiene.[4,5] Formaldehyde azine (azabutadiene) was prepared for the first time by Neureiter[4] in 1959, who noticed that it spontaneously polymerized at a temperature higher than its melting point. However, he had not mentioned what type of polymerization took place and what structural units the polymer had. One of the authors (M.K.) reinvestigated the polymerizability of azine compounds and found that formaldehyde azine could be stored without polymerization as a dilute THF solution and was easily polymerized by anionic initiators or water to form the polymer with 1,4 and 1,2 units.[7,8] In further studies concerning the polymerizability of azine compounds, α,ω-disubstituted azine compounds were polymerized to oligomers by *n*-butyllithium (*n*-BuLi).[9-11] Recently, we studied again the polymerization of azine compounds, acetaldehyde azine (AcAz) and propionaldehyde azine (PrAz), and found that PrAz was polymerized to highly crystalline and stereoregular polymers by Grignard reagents. To our knowledge, this is the first example of an azine polymerization in which high polymers were obtained from α,ω-disubstituted azabutadienes. In this paper, the preparation of high polymers from α,ω-disubstituted azine compounds and the characterization of the polymers obtained are mentioned.

Experimental Section

Reagents. Acetaldehyde azine (bp 90 °C) and propionaldehyde azine [bp 63 °C (43 mmHg)][12] were prepared from hydrazine hydrate and the corresponding aldehyde according to the procedure of Curtius et al.[12] These azine compounds were dried with calcium hydride just before their polymerization.

Solvents. Tetrahydrofuran, hexane, and toluene were purified as described in references.[13]

Initiator. Ethylzinc chloride (C_2H_5ZnCl) was prepared according to the same method mentioned by Noltes.[14] The crystalline compound was isolated and recrystallized from dried hexane under a nitrogen atmosphere. *n*-BuLi (1.5 M *n*-hexane solution) commercially available was transferred to an ampule with a stopcock by means of a hypodermic syringe under a nitrogen atmosphere, and a solution with a given concentration of *n*-BuLi was prepared by adding solvents. The concentration was determined by double titration.[15] Commercially available ethylmagnesium chloride (C_2H_5MgCl), methylmagnesium bromide (CH_3MgBr), and methylmagnesium iodide (CH_3MgI) were transferred into ampules, respectively, by using hypodermic syringes under a nitrogen atmosphere. The concentration was determined by double titration.[15]

Polymerizations. (a) Polymerization with *n*-BuLi. A polymerization ampule equipped with a nitrogen inlet and with a stopcock was connected to a high-vacuum system, evacuated, and flushed with dried nitrogen by opening the stopcock. The ampule was removed from the high-vacuum system under nitrogen flushing, and then a solution of *n*-BuLi in hexane was injected into the ampule by means of a hypodermic syringe under nitrogen. The ampule was again connected to a high-vacuum system, hexane was evaporated, and then the polymerization solvent and monomer, which was previously dried and degassed, were distilled into the ampule. After being sealed under high vacuum ($>10^{-4}$ mmHg), the ampule was placed in a thermostat at a given temperature. The polymerizations proceeded homogeneously during the process.

(b) Polymerization with C_2H_5ZnCl or Grignard Reagents. A given amount of C_2H_5ZnCl or the Grignard reagent was placed in a polymerization ampule, which was previously evacuated and flushed with dried nitrogen. The ampule was again connected to a high-vacuum system, and then monomer and solvent were distilled into the ampule. Preparations of samples for the polymerizations and polymerizations were carried out according to the same procedure as described in a. The polymerizations proceeded homogeneously during the process.

The polymerization systems were added to an excess of methanol to separate methanol-insoluble and -soluble polymers. The methanol-insoluble polymer was isolated by filtration, washed with excess methanol, and dried. The crude methanol-soluble polymer was separated from the filtrate by evaporating methanol. It was dissolved in diethyl ether, and inorganic salts were removed by washing the diethyl ether solution with distilled water. After drying the etherial solution with a thermally treated molecular sieve, the methanol-soluble polymer was isolated by evaporating the filtrate. All polymerization reactions and the subsequent isolation of the polymers were carried out by the same procedure as described in the polymerization.

Found for polyAcAz: C, 57.21; H. 9.65; N, 33.12%. Calcd for the monomer unit: C, 57.11; H, 9.59; N, 33.30%. Found for polyPrAz: C, 64.19; H, 10.88; N, 24.91%. Calcd for the monomer unit: C, 64.25; H, 10.78; N, 24.97%.

Measurements. UV-visible spectra were measured in cyclohexane with a Shimadzu UV-2100 spectrometer. IR spectra were recorded on a Jasco DC-402G spectrometer. Raman spectra were measured by using an Ar-laser 5145A excitation line with a Jasco R-800 spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-100-15 spectrometer as a $CDCl_3$ solution. ^{13}C NMR spectra were recorded under a complete decoupled condition. GPC analysis was carried out with a Tosoh high-

0024-9297/91/2224-5504$02.50/0

Table I
Bulk Polymerization of Azine Compounds (0 °C)

monomer	initiator (mol %)	time, h	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	convn
AcAz	n-BuLi (3.5)	20	630	2.38	99
	CH_3MgBr (0.9)	144	2500	1.87	99
	C_2H_5ZnCl (3.3)	185	700		99
PrAz	n-BuLi (4.8)	62	1300	1.60	99
	CH_3MgBr (3.3)	50	7000	1.29	98
	C_2H_5ZnCl (3.4)	83	3800	1.69	99
	CH_3MgI (3.1)	23	7800	1.32	90
	(0.56)	23	18800	1.81	60
	(0.35)	48	24900	1.91	34

[a] GPC (THF), calibrated by standard polystyrene. Radical polymerization with AIBN or BPO: no polymer (60 °C). $CH_3CH{=}NN{=}CHCH_3$ = acetaldazine (AcAz); $CH_3CH_2CH{=}NN{=}CHCH_2CH_3$ = propionaldehyde azine (PrAz).

speed liquid chromatograph HGC-810A. The molecular weights were calibrated by standard polystyrene. The measurement of low-angle light scattering (LALLS) was carried out in THF solution by a Tosoh LS-8000 light scattering photometer. Powder X-ray diffraction patterns were taken by using nickel-filtered Cu Kα radiation with a Rigaku RAD-ROC diffractometer. Thermogravimetric analysis was performed under a slow stream of nitrogen (20 mL/min) by using a Rigaku program temperature-controller PTC-10 at a heating rate of about 10 °C/min.

Results and Discussion

Polymerization. AcAz and PrAz could not be polymerized with radical initiators such as α,α'-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO).

AcAz and PrAz were quantitatively polymerized in quantitative yields by anionic initiators. Results of the bulk polymerization of aldehyde azines by three kinds of anionic initiators are shown in Table I. Oligomers were obtained in quantitative yields by the treatment of AcAz with n-BuLi. As the initiators were added to AcAz, the mixture immediately turned to a red viscous solution. The red disappeared as soom as small amounts of methanol were added. Higher molecular weight oligomers were obtained by polymerization with the Grignard reagents as initiators.

Similarly, PrAz was also polymerized with the anionic initiators. The polymerization system gradually turned orange-red with n-BuLi and C_2H_5ZnCl as initiators, and it turned yellow with the Grignard reagents as initiators and formed gels. Polymers with a molecular weight higher than 20 000 were obtained from PrAz with the Grignard reagents as initiators, especially CH_3MgI. The molecular weights of the polymers decreased in the following order: $CH_3MgI > CH_3MgBr > C_2H_5MgCl$. This order suggests that the molecular weight can be controlled by the type of the halide of the Grignard reagents. Oligomers were obtained by the polymerization of PrAz as well as AcAz with C_2H_5ZnCl and n-BuLi. Molecular weights of the oligomers obtained by C_2H_5ZnCl were larger than those obtained by n-BuLi. Since n-BuLi has a higher nucleophilicity and forms a higher nucleophilic propagating anion, the decrease in the molecular weight is probably due to the proton abstraction of the propagating anion from the monomer. The presence of the proton abstraction was made clear by NMR and mass spectrometric detection of a deuterated monomer ($CDH_2CH{=}NN{=}CHCH_3$) in the monomer recovered from the bulk polymerization system stopped by C_2D_5OD, as shown later.

Table II
Polymerization of Azine Compounds by Grignard Reagents in Solution[a]

monomer (M)	catalyst (mol %)	solvent	time, h	convn, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
AcAz (5.2)	CH_3MgBr (1.4)	THF	122	97[d]	1300	3.00
(3.4)	CH_3MgI (2.3)	ether	22	99[d]	3800	1.99
(3.4)	(2.0)	hexane	25	99[d]	1700	1.63
PrAz (3.0)	CH_3MgI (2.3)	THF	48	79[d]	900	2.48
(3.3)	(1.3)	ether	40	50[c]	14900	1.74
(3.2)	(0.72)	toluene	48	6[c]	5100	3.42
(3.2)	(0.35)	hexane	49	49[c]	34600	1.88
(1.2)	(0.92)	hexane	60	60[c]	10000	1.42

[a] At 0 °C. [b] By GPC (THF), calibrated by standard polystyrene. [c] Methanol-insoluble fraction. [d] From area ratio of the monomer peak to oligomer peaks in GPC.

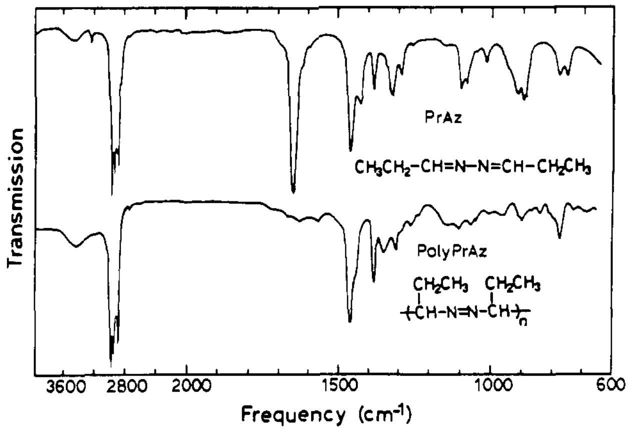

Figure 1. IR spectra of PrAz and polyPrAz (KBr).

Results on the solution polymerization of AcAz and PrAz are shown in Table II. Only oligomers were obtained from the polymerization of AcAz in the solution as well as in bulk. In the case of PrAz, high polymers could be prepared by the solution polymerization with CH_3MgI in hexane or diethyl ether. Especially, polymers with molecular weights higher than 30 000 were obtained with a lower initiator concentration. The molecular weight determined by the GPC method was consistent within 10% with that obtained by the LALLS method: The molecular weight of a polymer was determined to be 24 800 and 22 500, respectively.

The degree of polymerization of PrAz was larger than that of AcAz, which was obtained under similar conditions in spite of the increase in the bulkiness of the substituent group. This seemed to be explained by the fact that PrAz has lower active hydrogens in the α,ω-dialkyl groups, which can be transferred to the initiator and the propagating anion. In order to confirm the presence of the proton-transfer reaction, therefore, the bulk polymerization with n-BuLi was stopped by C_2H_5OD and the volatile compounds were taken out of the polymerization system by a high-vacuum system. The NMR and mass spectrometries showed that considerable amounts of deuterated azine (e.g., $CH_2DCH{=}NN{=}CH_3$) were present in the volatile fraction. Since the deuterated azine is considered to be formed by the reaction of C_2H_5OD with carbanion $^-CH_2CH{=}NN{=}CHCH_3$, which was obtained by a proton abstraction of the initiator or the propagating anion from the monomer, the proton-transfer reaction is concluded to be one of the molecular weight limiting reactions.

Structure of the Polymer. The C, H, and N contents of the polymers were consistent with those of the corresponding monomers as shown in the Experimental Section. These results show that the polymers are formed by the addition polymerization.

IR spectra of PrAz and its polymer are shown in Figure 1. An absorption band at 1651 cm^{-1} in the monomer is assigned to the stretching vibration of the C=N bond. This absorption band disappeared in the IR spectrum of the polymer, indicating that polymer does not contain

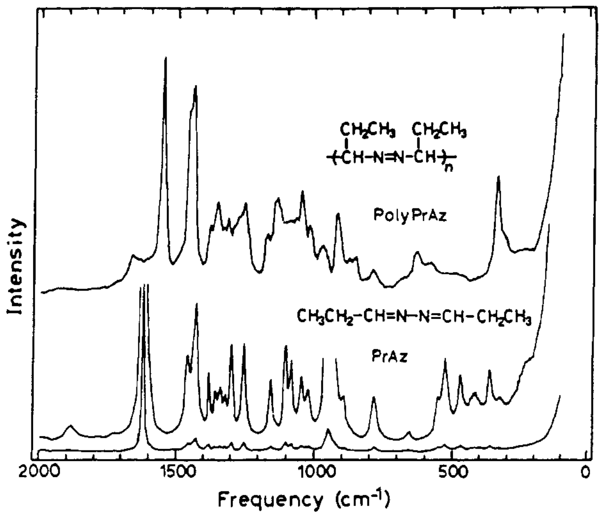

Figure 2. Raman spectra of PrAz and polyPrAz.

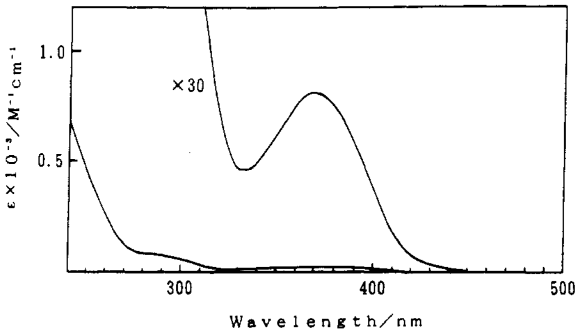

Figure 3. UV-visible spectrum of polyPrAz in cyclohexane. [PrAz unit] = 2.43×10^{-3} M.

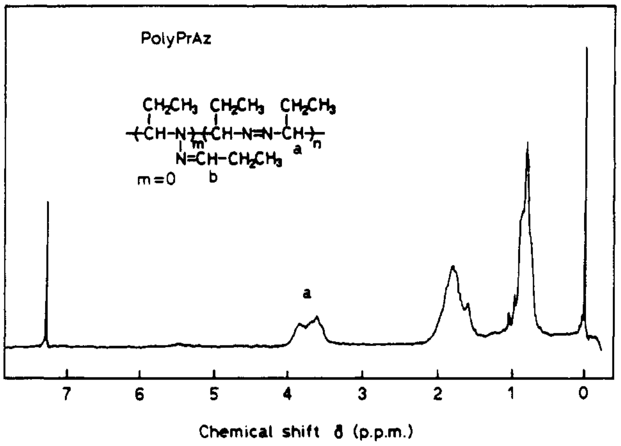

Figure 4. ^1H NMR spectrum of polyPrAz in $CDCl_3$. Internal standard: tetramethylsilane.

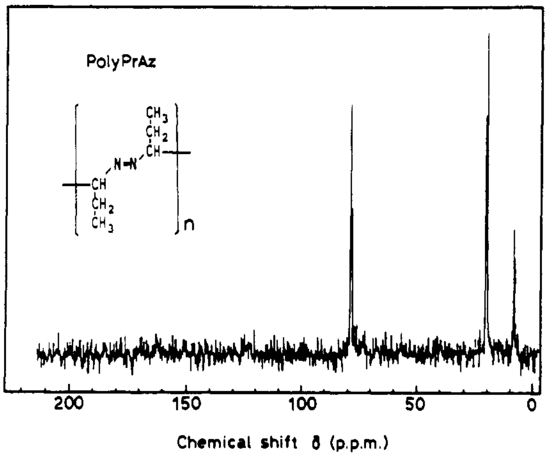

Figure 5. ^{13}C NMR spectrum of polyPrAz in $CDCl_3$. Internal standard: tetramethylsilane.

1,2-addition units. Therefore, the polymer seems to be composed exclusively of a 1,4-addition unit, which has the azo group. However, no absorption band due to the stretching vibration of the azo group expected in the 1,4-addition unit could be observed at about 1550 cm^{-1}, which should usually be observed in azo compounds.[16] This result suggests that an azo group exists in the trans form, which has a symmetrical center and is inactive in IR spectroscopy. Therefore, we measured the Raman spectrum, which is active for the symmetrical N=N group. Raman spectra of PrAz and its polymer are shown in Figure 2. A strong resonance line due to the N=N bond was observed at 1555 cm^{-1}, which could not be found in the monomer. A resonance line due to the C=N bond was observed at 1620 cm^{-1} in the monomer. Therefore, we can conclude that polymer was composed of 1,4-trans units.

The UV-visible spectrum of polyPrAz in the range of 250–500 nm is shown in Figure 3. The spectrum is composed of a strong absorption at a lower wavelength than 250 nm, a shoulder at 296 nm, and a weak absorption at 378 nm, which was discernible by a 30-fold increased sensitivity. The weak absorption at 378 nm is assigned to the $n-\pi^*$ transition of the N=N bond by comparison with the spectrum of diazomethane. The extinction coefficient of this band (ϵ = 23) is larger than that of diazomethane (ϵ = 3–5[17]).

NMR spectroscopy supports the above conclusion. The ^1H NMR spectrum of polyPrAz is shown in Figure 4. Resonance lines are composed of three parts, which have maximum peaks at 0.85 (3 H), 1.83 (2 H), and 3.72 (1 H) ppm assignable to CH_3, CH_2, and CH groups, respectively. If 1,2-addition units are formed in this polymer, a resonance line due to the olefinic proton of RCH=N– should be found in the region between 6.0 and 7.0 ppm. No resonance line could be found in this region, except for a signal due to $CHCl_3$ included in $CDCl_3$. The ^{13}C NMR spectrum of polyPrAz is shown in Figure 5. The ^{13}C NMR spectrum of polyPrAz was composed of three lines at 10.94, 22.90, and 80.80 ppm, respectively, which were split into two lines with a spacing of less than 0.7 ppm. These lines are reasonably assigned to CH_3, CH_2, and CH from a higher field. The splitting of each resonance line into two lines is ascribable to the presence of two kinds of stereoisomer units due to the difference in the stereochemistry of methine carbons (threo and erythro) or an azo group (trans and cis). Since Raman, IR, and UV-visible spectra show that the polymer is composed of a trans azo group, the splitting is probably due to be of the threo and erythro form of the methine carbons.

Powder X-ray diffraction of polyPrAz is shown in Figure 6. Clear diffraction patterns were obserbed at 2θ = 9.79° and 21.04°, indicating that this polymer is a highly crystalline polymer. This spectrum shows that a fiber period is 4.72 Å, which corresponds to the structure of a trans-1,4 unit.

The thermal behavior of polyazine was investigated by thermogravimetric analysis and DSC. Results for polyPrAz are shown in Figure 7. A gradual weight loss started at around 120 °C, and 24.6% weight loss was obtained from 120 to 200 °C. The 24.6% was consistent with the content of nitrogen in the polymer. The evolution of the nitrogen gas was confirmed by mass spectrometry. Accordingly, the weight loss at 200 °C is ascribed to thermal decomposition of an azo compound.

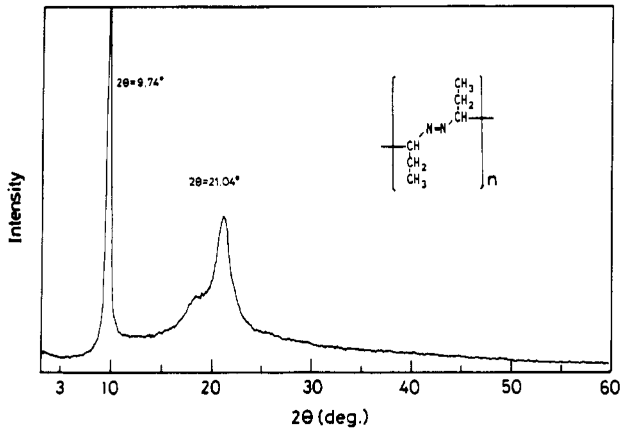

Figure 6. X-ray diffraction of polyPrAz powder.

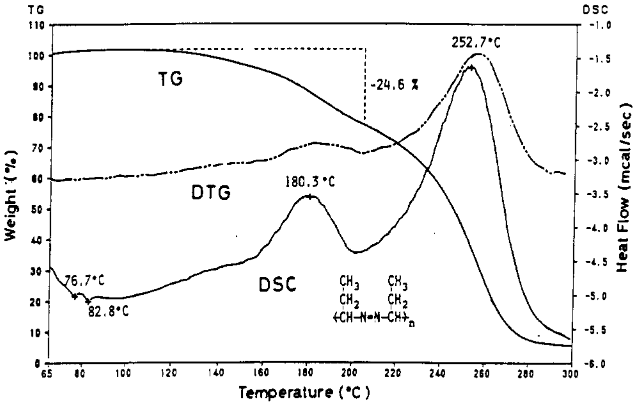

Figure 7. Thermal analysis of polyPrAz in a nitrogen atmosphere. Sample, 14.5 mg; heating rates, 10 °C/min.

Conclusion

Polymerizations of azine compounds were carried out by various anionic initiators. A new type of high crystalline and thermally degradable polymer was obtained by the polymerization of PrAz with some of Grignard reagents: higher polymers were prepared by CH_3MgI. The structure of polymers obtained was characterized by IR, Raman, ^1H NMR, and ^{13}C NMR spectroscopies, indicating that these azine polymers are composed of a trans-1,4-addition unit. X-ray diffraction of the polymer shows that these polymers are highly crystalline. The thermogravimetric analysis of these polymers showed that a gradual weight loss starts at around 120 °C, and nitrogen units were completely removed at 200 °C as nitrogen gas.

Acknowledgment. We thank Dr. A. Kajiwara for his critical reading and helpful discussion of the manuscript. We are also grateful to Dr. A. Miyanaga, Tosoh Co., Ltd., for the measurement of molecular weight by LALLS. X-ray powder diffraction measurement was performed at the X-ray Diffraction Service of the Department of Chemistry, Faculty of Science, Osaka University.

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Registry No. AcAz (homopolymer), 134882-45-4; PrAz (homopolymer), 134882-47-6.