

Anionic Polymerization of *n*-Butyraldehyde Azine to Crystalline *trans*-1,4-Poly(*n*-Butyraldehyde Azine)

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ABSTRACT: Anionic polymerizability of *n*-butyraldehyde azine ($C_3H_7CH=N-N=CHC_3H_7$)(BuAz) was investigated by anionic initiators in various solvents. Highly crystalline polymers along with oligomers were obtained by the polymerization of BuAz with CH_3MgI in toluene, diethyl ether, benzene, and 1,4-dioxane. The formation of oligomers was explained by the occurrence of a proton transfer from the monomer to propagating anion. The structures of the polymers obtained were investigated by IR, Raman, 1H NMR, and ^{13}C NMR spectroscopies, which indicated that these azine polymers are composed of *trans*-1,4-addition units. The X-ray diffraction patterns of the polymers showed two distinct diffractions which are ascribable to fiber period of the polymer chain and intermolecular regular structure, respectively, indicating that the polymer is highly crystalline. The polymer was thermally stable up to 100°C, in spite of existence of azo group in the main chain.

KEY WORDS *n*-Butyraldehyde Azine / Poly(*n*-Butyraldehyde Azine) / Anionic Polymerization / 1,4-Addition / Crystalline Polymer / Chain Transfer /

Numerous studies on the polymerization of butadiene, isoprene, and their derivatives have been reported so far. However, only a few papers had been published on the polymerization of the nitrogen homologues of diene compounds before we found that azine derivatives were polymerized by anionic initiators.¹⁻⁴⁾

Although Neureiter succeeded in preparing formaldehyde azine ($CH_2=N-N=CH_2$, 2,3-azabutadiene) which is isostructural to butadiene, he did not mention any polymerizabilities of formaldehyde azine except that thermal spontaneous polymerization took place at higher temperature than its melting point.⁵ One of the authors (M.K.) has succeeded in the isolation of formaldehyde azine as a dilute tetrahydrofuran (THF) solution, and investigated its anionic polymerizability.

^{3,4} The monomer showed higher anionic polymerizability than butadiene. However, α,ω -disubstituted 2,3-azabutadienes such as acetaldehyde azine ($CH_3CH=N-N=CHCH_3$, AcAz) and propionaldehyde azine ($C_2H_5CH=N-N=CHC_2H_5$, PrAz) were difficult to be polymerized and only methanol soluble oligomers were obtained by anionic polymerization.³

Recently, we reported that PrAz could be polymerized by anionic initiators, especially by Grignard reagents, to form polymers of molecular weights higher than 20000.⁴ The polyPrAz obtained was stereoregular and highly crystalline.

We extended our studies to the anionic polymerization of other azine compounds, and investigated an optimum condition for preparation of high polymers. In this paper,

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anionic polymerizability of BuAz was investigated by anionic initiators in various solvents and BuAz yielded polymers with molecular weights higher than 10000 in the polymerization with CH_3MgI in toluene and 1,4-dioxane. Some differences between BuAz and PrAz were observed in the solvent effect on high polymer formation. The structure of poly-BuAz was investigated by IR, Raman, ^1H and ^{13}C NMR spectroscopies, indicating that polyBuAz was composed of *trans*-1,4-addition units similarly to polyPrAz.⁴ Powder X-ray diffraction of the polyBuAz showed pattern which is assigned to a fiber period of 4.28 Å due to *trans*-1,4-addition. Moreover, a comparison of X-ray diffraction pattern of poly-BuAz with that of polyPrAz suggested the presence of the intermolecular regular structure.

EXPERIMENTAL

Preparation of n-Butyraldehyde Azine

n-Butyraldehyde azine was prepared according to the method reported by Crutius *et al.*⁶ Hydrazine monohydrate (150 g, 1.5 mol) in H_2O (150 ml) was added dropwise to a diethyl ether (300 ml) solution of *n*-butyraldehyde (210 g, 3.0 mol) with vigorous stirring at 30°C. After stirring for 1 h, ether layer was separated from aqueous layer by a separatory funnel. Furthermore, ether soluble fraction was extracted from the aqueous layer by ether for 3 times and added into the ether layer. The ether solution was washed with water and dried over anhydrous Na_2SO_4 . After ether was removed by a rotary evaporator, *n*-butyraldehyde azine was isolated by distillation and purified by successive distillations (bp 182°C/760 mmHg).³

Solvents

Hexane, diethyl ether, THF, toluene, and 1,4-dioxane were distilled under argon atmosphere and purified by the same method as described in ref 7.

Initiators

Commercially available *n*-Butyllithium (*n*-BuLi) (1.5 M hexane solution) was diluted with polymerization solvent for a concentration to be adjusted. The solution was put into an ampoule with a stopcock by a hypodermic syringe under an argon atmosphere. The concentration was determined by double titration.⁸ Commercially available ethylmagnesium chloride ($\text{C}_2\text{H}_5\text{MgCl}$), methylmagnesium bromide (CH_3MgBr), and methylmagnesium iodide (CH_3MgI), whose concentrations were determined by the double titration method,⁸⁾ were put into ampoules, using hypodermic syringes under argon atmosphere.

Anionic Polymerization

n-Butyraldehyde azine (5.0 g, 36 mmol) was dissolved in solvent under argon atmosphere. The solution was cooled below -15°C over ice-salt-water bath and an initiator (3 mol%) was added slowly with stirring. The polymerization system immediately turned deep red with *n*-BuLi as an initiator, and it gradually turned yellow with the Grignard reagents as initiators. The polymerization system was allowed to stand at constant temperature for a given time and formed gel. After a given time, the gel was put into excess methanol and insoluble polymer was separated from methanol soluble products, and collected by filtration.

Methanol-insoluble polymer was purified by successive reprecipitation from toluene-methanol and obtained as pale yellow powder. The molecular weights of the polymers were estimated by GPC using THF as an eluent. A calibration curve formed by standard polystyrenes was used for the estimation of the molecular weight. Elemental analysis, Found: C, 68.45%; H, 11.55%; N, 19.48%, Calcd for $(\text{C}_8\text{H}_{16}\text{N}_2)_n$: C, 68.52%; H, 11.50%; N, 19.98%.

The residual pale yellow oil obtained from methanol-soluble fraction by an evaporator was dissolved in diethyl ether, and washed

with water to remove some water soluble salts formed from the initiator. After the ether layer was dried over anhydrous Na_2SO_4 , diethyl ether was removed to give oily products, whose structures were determined by spectroscopic methods, and whose molecular weights were determined by GPC. Elemental analysis data of the residual yellow oil were also consistent with that of the monomer.

Physicochemical Measurements

Absorption spectra were measured in chloroform with a Shimadzu UV-2100 spectrometer. IR spectra were recorded on a JASCO DC-402G spectrometer. Raman spectra were taken using Ar-laser 5145 Å excitation line by a JASCO R-800 spectrometer equipped with a HTV-R649 photomultiplier. Frequency calibration of the spectra was carried out with natural emission of a neon lamp from 0 cm^{-1} to 2000 cm^{-1} as standards. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL FX-90Q and a JEOL GSX-400 spectrometers as a CDCl_3 solution at 30°C . ^{13}C NMR spectra were recorded under complete decoupled condition. GPC analysis was carried out with a TOSOH high-speed liquid chromatograph system, CCP&-8010 series equipped with RI and UV detectors using THF as an eluent. Mass spectra were recorded by EI method on a JEOL JMS SX-2 spectrometer. Mass number was calibrated by using cesium iodide (CsI) or toluene. Powder X-ray diffraction

patterns were taken by a Rigaku RAD-ROC diffractometer using nickel-filtered $\text{Cu-K}\alpha$ radiation. Thermogravimetric analysis was performed using a Rigaku program temperature controller PTC-10 at a heating rate of about $10^\circ\text{C min}^{-1}$ under a nitrogen stream (20 ml min^{-1}).

RESULTS AND DISCUSSION

Anionic Polymerization

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

The results of the bulk and toluene-solution polymerization of BuAz by six kinds of anionic initiators are shown in **Table I**. BuAz was polymerized in quantitative yields by anionic initiators such as alkyl-lithium and Grignard reagents. Most of polymerized products were methanol soluble oligomers whose molecular weights were less than 1000. Methanol insoluble polymers were obtained along with the formation of oligomers. The highest molecular weight of the methanol insoluble polymers, over 10000, was obtained by the polymerization of BuAz with CH_3MgI . However, molecular weights of methanol insoluble polymers obtained by CH_3MgBr and $\text{C}_2\text{H}_5\text{MgCl}$ were less than 10000, and decreased in the following order: $\text{CH}_3\text{MgI} > \text{CH}_3\text{MgBr} > \text{C}_2\text{H}_5\text{MgCl}$. This suggests that molecular weight can be controlled by the type of the

Table I. Polymerization of *n*-butyraldehyde azine (BuAz) by various initiators^a

BuAz (M)	Initiator	Solvent	Yield ^b /%	\bar{M}_w	\bar{M}_w/\bar{M}_n
2.0	CH_3MgI	Toluene	23	14000	1.48
2.0	CH_3MgBr	Toluene	18	3800	1.10
2.0	$\text{C}_2\text{H}_5\text{MgCl}$	Toluene	12	2700	1.05
2.0	<i>t</i> -BuMgCl	Toluene	7	1900	1.03
2.0	<i>n</i> -BuLi	Toluene	10	6900	1.24
Bulk	<i>n</i> -BuLi	—	6	2400	1.10
Bulk	<i>n</i> -BuLi-TMEDA	—	4	1900	1.06

^a Initiator, 2 mol%; under argon, 50 h; temp, -20°C ; conv., $>99\%$.

^b Methanol insoluble fraction.

Table II. Solvent effects on polymerization of *n*-butyraldehyde azine (BuAz)^a

BuAz (M)	Solvent	Temp/°C	Yield ^b /%	\bar{M}_w	\bar{M}_w/\bar{M}_n
bulk	—	0	45	4100	1.21
2.0	Hexane	0	25	4900	1.18
2.0	Hexane	-40	40	4200	1.17
2.0	Ether	-20	20	5300	1.20
2.0	Toluene	-20	23	14000	1.48
2.0	THF	-20	20	3400	1.10
2.0	1,4-Dioxane	-20 ^c	28	17000	1.33
2.0	Benzene	-20 ^c	25	6700	1.32

^a Under argon, 50 h; initiated by CH₃MgI (2 mol%); conv., >99%.

^b Methanol insoluble fraction.

^c Frozen state.

halide of the Grignard reagents.

In order to get an optimum condition for high polymer formation, the influence of solvents was investigated on polymer yield and molecular weight in the polymerization with CH₃MgI. The results are shown in Table II. Although monomers completely disappeared during the polymerization, the yields of methanol insoluble polymers were in the region from 20 to 45%, depending on the polymerization solvent. The degree of polymerization of methanol insoluble polyBuAz decreased in the following order in solvents, 1,4-dioxane > toluene > benzene > diethyl ether > hexane.

The solvent effect on the solution polymerization of BuAz was considerably different from that of PrAz.⁴ In BuAz, toluene was solvent suitable for polymer formation while hexane was not a suitable solvent for the polymer formation, because the polymerization of BuAz was homogeneous in the polymerization in toluene, and polyBuAz was precipitated during polymerization in hexane. In 1,4-dioxane, polymerization occurred even in an apparently frozen state at -20°C and polymers whose molecular weights are higher than 10000 were obtained, indicating that chain transfer may be suppressed in the frozen state.

Total amounts of polymers and methanol soluble oligomers correspond to those of charged monomers, indicating that poly-

merization takes place quantitatively. Since the number of polymers and oligomers is larger than that of initiators, the formation of oligomers might be explained by the occurrence of a proton transfer from the monomer to the propagating anion. In order to confirm the presence of the proton transfer reaction, therefore, the bulk polymerization with *n*-BuLi was stopped by the addition of C₂H₅OD and the volatile compounds were taken out from the polymerization system by high vacuum system. The polymerization system initiated by *n*-BuLi instead of CH₃MgI was used for the confirmation of the proton transfer reaction, because the former gave larger amounts of oligomers than the latter in the bulk polymerization. The mass spectroscopies showed that considerable amounts of deuterated azine (C₃H₆DCH=N-N=CHC₃H₇) ([MH]⁺ = 142) were present in the volatile fraction (Figure 1). Since the deuterated azine is considered to be formed by the reaction of C₂H₅OD with carbanion, ⁻C₃H₆CH=N-N=CHC₃H₇, 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 Polymer

The C, H, N contents of the polymers were consistent with those of the corresponding

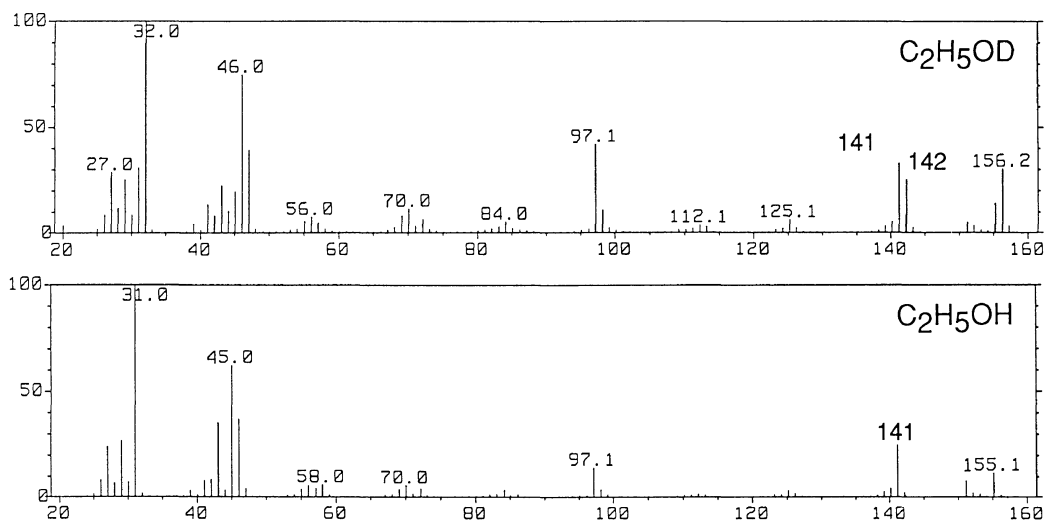


Figure 1. Mass spectra of polymerization system of BuAz trapped by C_2H_5OD (upper) and by C_2H_5OH (lower).

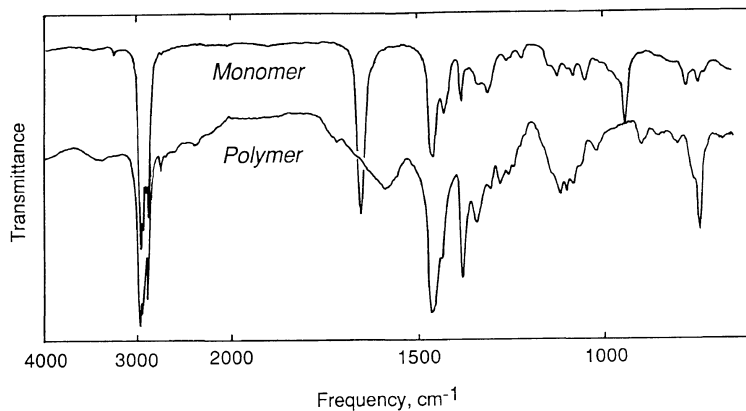


Figure 2. IR spectra of polyBuAz and BuAz (KBr).

monomer as shown in experimental section. This shows that the polymers are formed by an addition polymerization through $C=N-N=C$ bond.

IR spectra of BuAz and polyBuAz are shown in Figure 2. An absorption band at 1650 cm^{-1} of the monomer is assignable to the stretching vibration mode of $C=N$ bond.⁹ The band disappeared in the IR spectrum of the polymer, suggesting that the polymer does not contain 1,2-addition units which gave an absorption band due to $C=N$ bond. There-

fore, the polymer seems to be composed exclusively of 1,4-addition units composed of azo groups. 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 be usually observed in azo compounds.¹⁰ This suggests that 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.

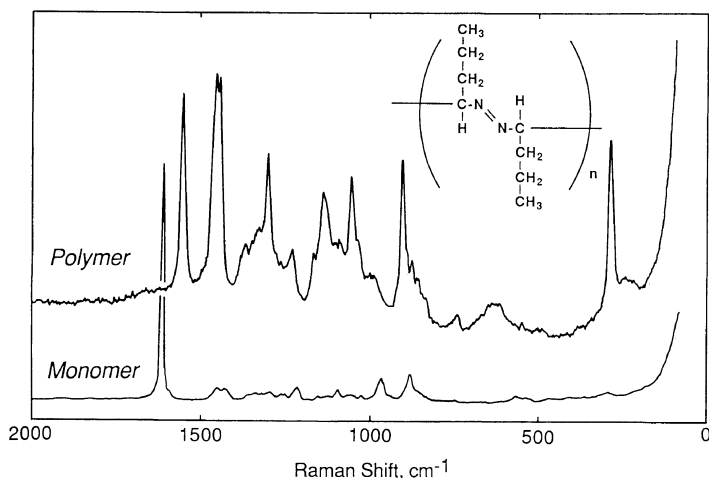


Figure 3. Raman spectra of polyBuAz and BuAz (5145 Å excitation).

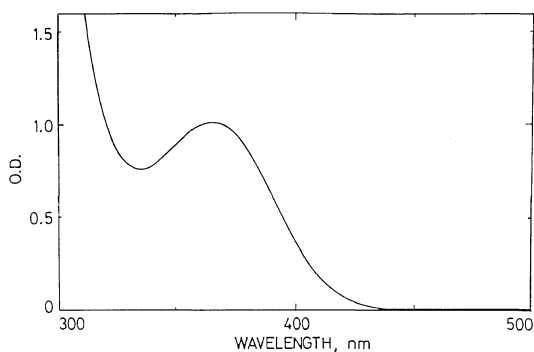


Figure 4. Absorption spectrum of polyBuAz in CDCl_3 .

Raman spectra of BuAz and its polymer are shown in Figure 3. A strong resonance line due to $\text{N}=\text{N}$ bond was observed at 1555 cm^{-1} , which could not be found in the monomer. A resonance line due to the $\text{C}=\text{N}$ 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 absorption spectrum of polyBuAz in the range of 300 to 500 nm is shown in Figure 4. The spectrum is composed of a strong absorption at a lower wavelength than 300 nm and a weak absorption at 365 nm. The weak absorption at 365 nm is assigned to the $n-\pi^*$ transition of $\text{N}=\text{N}$ bond by comparison with the spectrum of diazo-

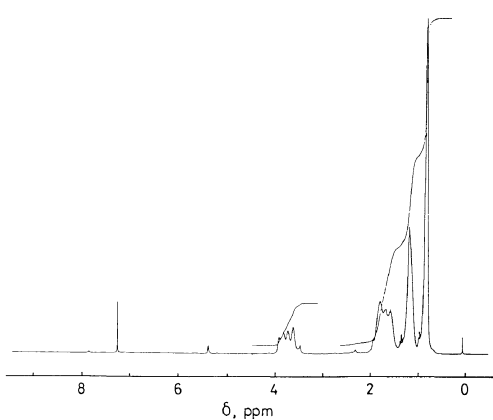


Figure 5. ^1H NMR spectrum of polyBuAz in CDCl_3 .

methane, because the extinction coefficient of this band ($\epsilon=36$) is the same order of magnitude as that of *trans*-diazomethane ($\epsilon=25$, $\lambda=343\text{ nm}$).¹¹

NMR spectroscopy supports the above conclusion. ^1H NMR spectrum of polyBuAz in CDCl_3 is shown in Figure 5. Resonance lines of polyBuAz are composed of four parts which have maximum peaks at 0.8 (3H), 1.2 (2H), 1.6–1.8 (2H), and 3.6–3.9 ppm (1H) assignable to protons of CH_3 , CH_2 , CH_2 , and CH groups, respectively. If 1,2-addition units are formed in this polymer, resonance line due

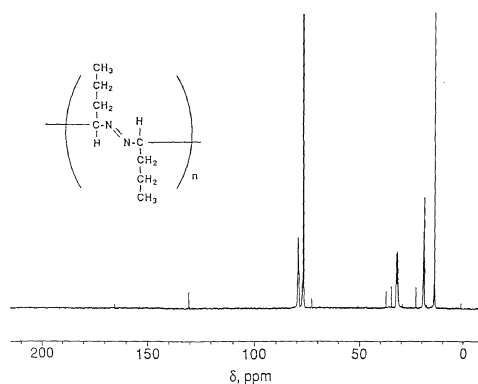


Figure 6. ^{13}C NMR spectrum of polyBuAz in CDCl_3 .

to olefinic proton of $\text{R}-\text{CH}=\text{N}-$ should be found in the region between 6.0 and 7.0 ppm of the ^1H NMR spectrum. No resonance line could be found in this region except for a signal due to CHCl_3 present in CDCl_3 . ^{13}C NMR spectrum of polyBuAz is shown in Figure 6. The ^{13}C NMR spectrum of polyBuAz is composed of four signals at 13.9, 18.8–19.3, 31.5–32.4, and 79.0–79.5 ppm which were split into two lines with splitting constants less than 1 ppm except for the signal at 13.9 ppm. These lines are reasonably assigned to the carbon atoms of CH_3 , CH_2 , CH_2 , and CH groups, respectively, from high field. The splitting of each resonance line into two lines is ascribable to the presence of some kinds of stereoisomer units due to the difference in the stereochemistry of methine carbons (threo and erythro) or azo groups (*trans* and *cis*). Since Raman, IR, and UV-visible spectra showed that the polymer is composed of *trans* azo group, the splitting is probably due to the threo and erythro form of methine carbons.

Powder X-ray diffractions of polyBuAz and polyPrAz are shown in Figure 7. Clear diffraction patterns were observed at $2\theta = 7.7^\circ$ and 20.8° in the signals of polyBuAz, indicating that this polymer is a highly crystalline polymer. These angles correspond to the distances of 11.44 Å and 4.28 Å, respectively. In the previous work, polyPrAz showed regular

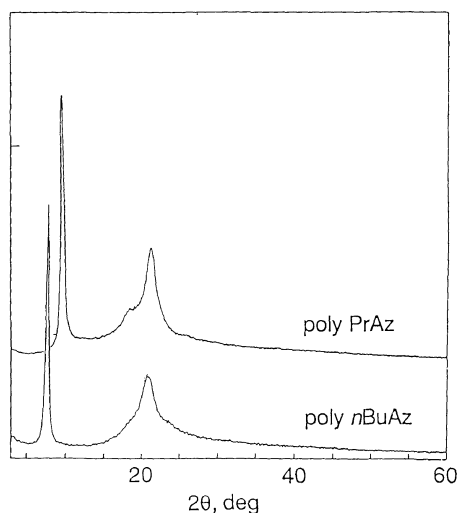


Figure 7. Powder X-ray diffraction patterns of polyBuAz and polyPrAz.

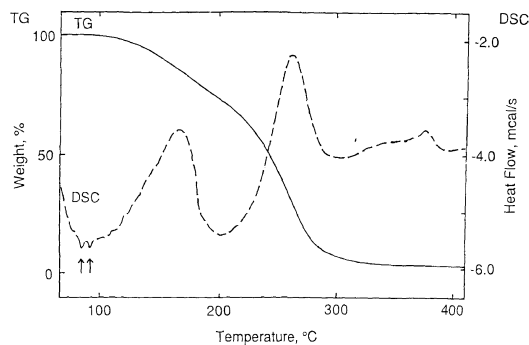


Figure 8. Thermal properties of polyBuAz: TG (—) and DSC (---).

structures at distances of 9.08 Å ($2\theta = 9.1^\circ$) and 4.22 Å (21.0°).⁴ In comparison with both results, 4.28 Å in polyBuAz is consistent with 4.22 Å, being assigned to a fiber period of *trans*-1,4-structure, and 11.44 Å in polyBuAz is larger than 9.08 Å in polyPrAz, which has smaller side group. Therefore, the diffraction pattern at $2\theta = 7.7^\circ$ seems due to intermolecular regular structure.

Thermal Properties of PolyBuAz

The thermal behavior of polyBuAz was investigated by thermogravimetric analysis

(TG) and differential scanning calorimetry (DSC). The results for polyBuAz are shown in Figure 8. A gradual weight loss started at around 100°C in the TG curve, indicating that the polyBuAz was thermally stable up to 100°C, although azo compounds are generally unstable on light irradiation and/or heat, just like as AIBN. Polymeric azo compounds may be stabilized by a thermal relaxation through long main chain.

Endothermic peaks at 86.2°C and 92.3°C, probably due to glass transition and two exothermic peaks at 166.9°C and 261.2°C were observed in the DSC analysis. The weight loss in the range of 120–180°C was about 20% being consistent with the content of nitrogen in the polymer. The evolution of nitrogen gas ($M^+ = 28$) was confirmed by mass spectroscopy. Therefore, the weight loss from 180 to 300°C is ascribed to thermal decomposition of the polymer chain. Colorless oily compounds remained in the polymer system. *trans*-4-Octene and some carbon chain oligomeric species were detected from the oil by ^1H NMR, gas-chromatography, and mass spectroscopy.

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