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Polymerization of Trifluoroacetaldehyde Azine (1,1,1,6,6,6-Hexafluoro-3,4-diaza-2,4-hexadiene)

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ABSTRACT: Trifluoroacetaldehyde azine (TFAcAz) was prepared as a new monomer and its polymerizabilities were studied. Poly(TFAcAz) was obtained by bulk polymerization with triethylamine at −20 °C, although only oligomers were obtained by typical anionic initiators. The structure and properties of the polymer were investigated by IR, Raman, and solid-state ^{13}C NMR spectroscopies, powder X-ray diffraction, and thermogravimetric analysis. The polymer is crystalline, composed of 1,2-addition units with pendant C=N double bonds, and decomposed to the monomer at about 200 °C.

Introduction

Although a number of compounds with C=C or C=O double bonds have been polymerized to high polymers by radical or ionic initiators, there are no papers on the polymerization of compounds with C=N double bonds, to our knowledge, except for carbodiimide,[1] isocyanates,[2,3] imines,[4] 1-azabutadiene,[4] and azine compounds.[5−12] Formaldehyde azine (CH_2=N−N=CH_2), which is the simplest azine, was prepared in 1959,[5] but there had been no systematic studies on the polymerizations of azine compounds before our research. We have systematically investigated the polymerizabilities of azine compounds to understand the polymerizabilities of the C=N double bond and obtain new polymers.[6−10] Recently, we reported formation of a crystalline *trans*-1,4 polymer by anionic polymerization of alkyl azine compounds (RCH=N−N=CHR, R = CH_3, C_2H_5, *n*-C_3H_7) with Grignard reagents.[11−13]

In the extension of our research, we have chosen and synthesized trifluoroacetaldehyde azine (R = CF_3, TFAcAz), because TFAcAz does not have any hydrogen atoms on its α-carbon, which might cause chain transfer. We studied its polymerizabilities with various initiators at various temperatures and found that TFAcAz was polymerized to a new type of crystalline polymer with trialkylamine at −20 °C. In this paper, the polymerizability of TFAcAz and the structure of the obtained polymer are described.

Experimental Section

Preparation of Trifluoroacetaldehyde Azine (TFAcAz). A solution of trifluoroacetaldehyde hydrate[14] (114.3 g, 0.761 mol) in diethyl ether (100 mL) was placed in a 500 mL flask fitted with a dropping funnel, a magnetic stirrer, and a condenser. A solution of hydrazine monohydrate (19.2 mL, 0.381 mol) in water (40 mL) was added slowly with continuous stirring during 30 min. Stirring was continued under reflux for 2 h. An organic layer was separated from an aqueous layer, and the aqueous layer was extracted with diethyl ether (50 mL) four times. A combined organic layer was washed with saturated aqueous sodium chloride (50 mL) and dried with anhydrous sodium sulfate. After successive distillations over calcium hydride, TFAcAz was obtained as a pale yellow liquid (*Warning!* TFAcAz has a pungent smell and irritates the mucous membrane): yield 20.5 g, 28.0%; mp −6 to −4 °C; bp 54−56 °C; IR (KBr) 1160 (CF), 1280 (CF), 1328 (CF) cm^{-1}; Raman 975 (NN), 1640 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.56 (q, J = 3.74 Hz); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 119 (q, J = 273.4 Hz), 147 (q, J = 39.1 Hz); ^{19}F NMR ($CDCl_3$, 470.5 MHz) δ −71 (d, J = 3.76 Hz). Anal. Calcd for $C_4F_6H_2N_2$: C, 25.01; H, 1.05; N, 14.59; F, 59.35. Found: C, 24.53; H, 1.07; N, 14.39. EI-MS [MH^+] Calcd 193. Found 193.

Initiators. Commercially available *n*-butyllithium (*n*-BuLi) (1.5 M *n*-hexane solution) and methylmagnesium iodide (CH_3MgI) (2.0 M diethyl ether solution) were transferred to ampules, respectively, by means of syringes under an argon atmosphere. The concentration was determined by double titration. Potassium methoxide/18-crown-6 complex (CH_3OK/18-crown-6) was prepared according to the method of Kurcok et al.[15] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was dried with calcium hydride and stored under an argon atmosphere. Triethylamine (Et_3N), tri-*n*-butylamine (*n*-Bu_3N), and pyridine were distilled over calcium hydride under reduced pressure and stored under an argon atmosphere.

Polymerizations of TFAcAz with Trialkylamines. A typical polymerization of TFAcAz with triethylamine is described below.

TFAcAz (0.5 mL, 2.6 mmol) in an ampule was cooled with an ice−salt−water bath to −20 °C. Triethylamine (0.010 mL, 0.065 mmol) was added to the TFAcAz under an argon atmosphere and the ampule was sealed. After about 30 min, the reaction mixture solidified. After 72 h, the ampule was opened. The solidified products were washed with acetone and dried. Poly(TFAcAz) was obtained as a pale yellow powder. The polymer was insoluble in toluene, *p*-xylene, benzene, chloroform, dichloromethane, DMF, DMSO, 1,4-dioxane, *N*-methylpyrrolidone, quinoline, hexafluoro-2-propanol, ethyl acetate, methanol, ethanol, acetone, *n*-hexane, 1,1,2-trichloro-1,2,2-trifluoroethane, THF, trifluoroacetic acid, diethyl ether, and TFAcAz: Yield 58.6%; mp 250−270 °C (dec); IR (KBr) 1140 (CF), 1270 (CF), 1638 (C=N) cm^{-1}; Raman 1045 (CF), 1265 (CF), 1648 (C=N) cm^{-1}; solid-state ^{13}C NMR (100.5 MHz) δ 65.9, 120.8. Anal. Calcd for $(C_4F_6H_2N_2)_n$: C, 25.01; H, 1.05; N, 14.59; F, 59.35. Found: C, 24.99; H, 1.11; N, 14.60.

Polymerizations of TFAcAz with *n*-BuLi, CH_3MgI, CH_3OK/18-Crown-6, DBU, or Pyridine. A given amount of an initiator was added to TFAcAz (1 mL, 5.2 mmol) in an ampule under an argon atmosphere at −20 °C and the ampule was sealed. After 30, 48, or 72 h, the ampule was opened. The resulting products, soluble oligomer, were investigated by GPC and ^1H NMR spectroscopy.

Oligomerization of TFAcAz. TFAcAz (1 mL, 5.3 mmol) in an ampule was cooled with an ice−salt−water bath to −20 °C. Et_3N (0.3 mL, 2.2 mmol) was added to TFAcAz under an argon atmosphere. After 4.5 h, the polymerization was terminated with methanol (3 mL). A solution was separated from the obtained polymer by centrifugation. After evaporation of volatile fractions, adducts of monomer and of dimer with methanol were obtained as a red-orange viscous oil. Their

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Table 1. Bulk Polymerizations of TFAcAz[a]

initiator (mol %)	time, h	conv, %	polymer yield, %	$\bar{M}_w$[b]
n-BuLi (0.57)	30	42[b]	0	1800
CH_3MgI (0.57)	30	23[b]	0	1300
CH_3OK/18-crown-6 (1.0)	30	49[b]	0	1800
DBU (9.1)	48	81[b]	0	1200
Et_3N (2.4)	72		59[d]	–[e]
pyridine (9.1)	72	0[c]	0	

[a] At −20 °C. [b] By GPC. [c] By ^1H NMR. [d] Acetone-insoluble fraction. [e] Insoluble in THF.

structures were investigated by ^1H NMR and EI-mass spectroscopies: Adduct of monomer with methanol: ^1H NMR ($CDCl_3$, 270 MHz) δ 3.50 (s), 4.89 (m), 7.04 (q, J = 4.7 Hz), 7.45 (bs); EI-MS [M^+] Calcd 224. Found 224. Adduct of dimer with methanol: ^1H NMR ($CDCl_3$, 270 MHz) δ 3.42 (s), 3.65–3.80 (m), 5.06 (q, J = 5.3 Hz), 5.94 (bs), 6.38 (q, J = 4.2 Hz); EI-MS [M^+] Calcd 416. Found 416.

Thermal Depolymerization of Poly(TFAcAz). Poly(TFAcAz) (15 mg) in an ampule was heated at about 200 °C under vacuum (~ 10^{-2} mmHg) for 10 h. TFAcAz was obtained as a volatile product: Yield 9 mg, 60%; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.56 (q, J = 3.74 Hz); EI-MS [M^+] Calcd 192. Found 192.

Measurements. Infrared spectra were recorded on a Jasco FT/IR-3 spectrometer. Raman spectra were obtained on a Jasco R-800 spectrometer by using an Ar-laser 5145 Å excitation line. Frequency calibration of the spectra was carried out with the natural emission of a neon lamp from 0 to 2000 cm^{-1}. ^1H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270. ^{19}F NMR spectra were measured on a JEOL JNM-GX500 as a $CDCl_3$ solution. GPC analyasis was performed in THF with a TOSOH CO-8011 system by using TSK gel. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron impact (EI) method. Mass number was calibrated by using cesium iodide (CsI). Powder X-ray diffraction patterns were taken by using nickel-filtered Cu K_α radiation with a Rigaku RAD-ROC diffractometer. Thermogravimetric analysis was carried out under a slow stream of nitrogen (20 mL/min) by using a Rigaku PTC-10 program temperature controller at a heating rate of about 10 °C/min.

Results and Discussion

Synthesis and Identification of TFAcAz. TFAcAz was synthesized from trifluoroacetaldehyde hydrate and hydrazine monohydrate according to the procedure of Curtius et al.[16] Successive distillations over calcium hydride were required for purification of TFAcAz, because TFAcAz has a low boiling point (54–56 °C) and easily reacts with moisture. TFAcAz was identified by ^1H, ^{13}C, ^{19}F NMR, IR, Raman, and EI-mass spectroscopies and elemental analysis (Experimental Section).

Seeking Initiators for Polymer Formation. TFAcAz, similarly to alkyl azines, could not be polymerized with 2,2′-azobis(isobutyronitrile) (AIBN) or with aluminum chloride.[11,12]

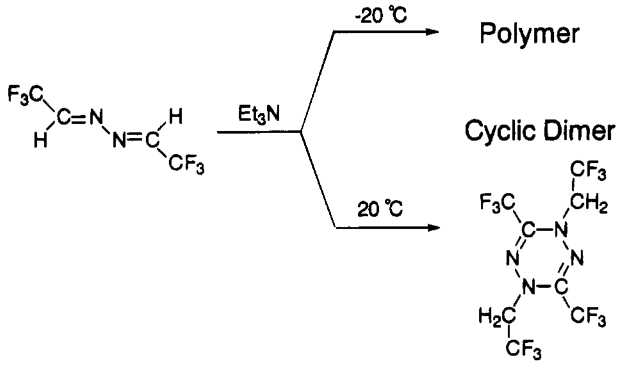
Anionic polymerizabilities were investigated with six kinds of initiators. The results on bulk polymerizations at −20 °C are shown in Table 1. Oligomers ($\bar{M}_w$ = 1800) were formed with n-BuLi, a typical anionic initiator. When the polymerization was performed with CH_3MgI that gave polymers in the case of alkyl azine compounds,[11,12] only soluble oligomers ($\bar{M}_w$ = 1300) were obtained. CH_3OK/18-crown-6 also gave only soluble oligomers ($\bar{M}_w$ = 1800) and did not give polymers. Furthermore, organic bases were used as initiators to investigate the polymerizability with initiators that have weaker nucleophilicity than the above three initiators. When DBU, one of the strongest organic bases, was used, oily oligomers ($\bar{M}_w$ = 1200) were generated. However, a solid polymer was obtained in the frozen state (below −10 °C) by the polymerization with Et_3N. Moreover, no reaction occurred with pyridine, which is a weaker base than Et_3N.[17] Thus, we found that Et_3N is an appropriate initiator for the polymerization of TFAcAz.

Table 2. Bulk Polymerization of TFAcAz[a]

TFAcAz, mL (mmol)	cat. (mol %)	time, h	yield,[d] %
1.0 (5.2)[b]	Et_3N (2.0)	24	31.0
0.50 (2.6)[c]	Et_3N (2.4)	72	58.6
0.50 (2.6)[c]	Et_3N (9.1)	24	39.3
0.50 (2.6)[c]	Et_3N (9.1)	72	48.6
0.50 (2.6)[c]	Et_3N (23.1)	72	28.2
0.50 (2.6)[c]	n-Bu_3N (1.7)	72	19.9
0.50 (2.6)[c]	n-Bu_3N (9.1)	72	30.6

[a] At −20 °C. [b] In air. [c] Under an argon atmosphere. [d] Acetone-insoluble fraction.

Scheme 1. Reactions of TFAcAz with Et_3N



Polymerizations of TFAcAz with Trialkylamines. To obtain optimum conditions for the polymerization of TFAcAz, the polymerizations with trialkylamines were performed under various conditions, and the results are shown in Table 2. The polymerization system gradually changed from pale yellow to red-brown upon addition of each of the amines. After about 30 min, the system solidified. After 24 or 72 h, the ampule was opened and the reaction mixture was washed with acetone to remove remaining monomer, oligomer, and the added amine and to obtain polymer as a pale yellow powder. Table 2 shows that the polymerization rate is not high as compared to those of usual radical or ionic polymerizations. The result is mainly due to the formation of a considerable amount of soluble oligomeric species.[18] Triethylamine gave the polymer in higher yield than tri-n-butylamine, as shown in Table 2. The obtained polymer was insoluble in many solvents (Experimental Section). Since no solvent has been found in which the polymer is soluble, the molecular weight of the obtained polymer could not be determined. On the other hand, the oligomer obtained from the same system has a molecular weight higher than 1000; thus it should hold for the polymer as well.

When the reactions of TFAcAz with trialkylamines were performed at +20 °C, a cyclic dimer of TFAcAz was obtained as a pale yellow crystal (mp 26.8–27.1 °C) (Scheme 1).[19] At −20 °C, the polymerization took place in the frozen state rather than the cyclization, indicating that the cyclization reaction may be suppressed in the frozen state. However, at −78 °C, polymerization did not occur. We surveyed the optimum temperature for the polymerization in the frozen state and found that the optimum temperature was about −20 °C. The

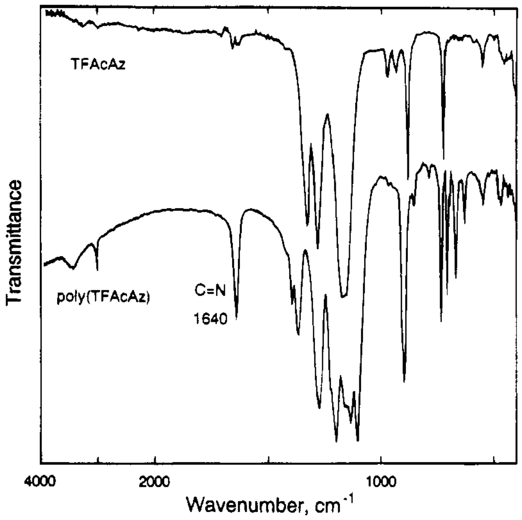


Figure 1. IR spectra of (a) TFAcAz and (b) poly(TFAcAz) (KBr).

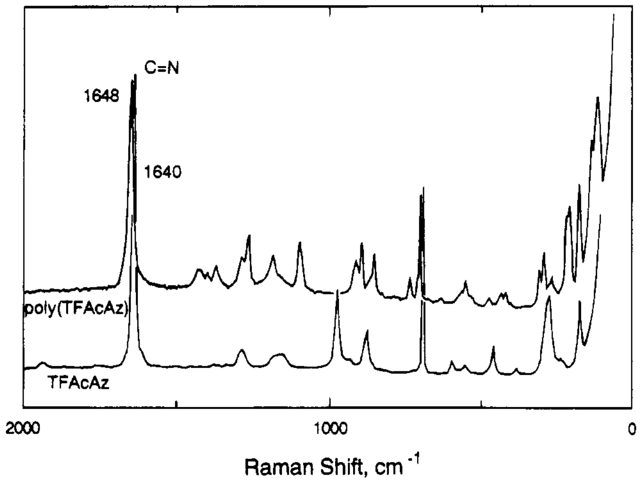


Figure 2. Raman spectra of (a) TFAcAz and (b) poly(TFAcAz) (5145 Å argon laser excitation).

finding is consistent with the case that polymer was obtained in higher yield in the frozen state than in the liquid state in the polymerization of acetaldehyde azine ($R = CH_3$).[13]

Structure of Poly(TFAcAz). The C, H, and N contents of the polymer were consistent with those of TFAcAz (Experimental Section). This result shows that the polymer is formed by the addition polymerization.

The IR and Raman spectra of the monomer and the polymer are shown in Figures 1 and 2. The absorption band assignable to the stretching vibration of the C=N double bond cannot be observed in the IR spectrum of the monomer and it is clearly observed at 1640 cm^{-1} in the Raman spectrum. These results suggest that the TFAcAz molecule has exclusively *s-trans* structure, so that the stretching vibration of the C=N double bond is IR-inactive and Raman-active. On the other hand, in the IR and Raman spectra of the polymer, the signals of the C=N double bonds were observed at 1640 and 1648 cm^{-1}, respectively. These results show that the polymer has a C=N double bond. In the Raman spectra, the peak due to the C=N double bond shifted to higher wavenumber in the polymer, suggesting that the C=N double bonds in the polymer are no longer conjugated. Furthermore, no stretching vibration mode due to the N=N double bond, which was found at about 1550 cm^{-1} in the Raman spectra of poly(alkyl azine)s,[11,12] could be observed in poly(TFAcAz). Therefore, we can conclude that the obtained polymer is composed of exclusively 1,2-units.

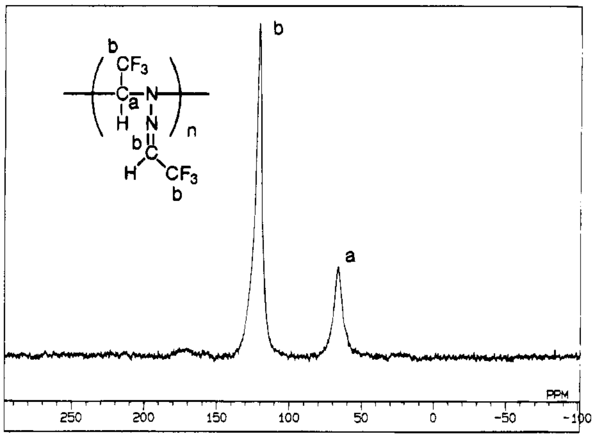
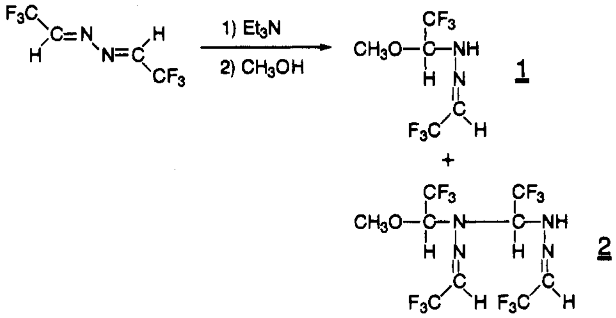


Figure 3. 100.5 MHz solid-state ^{13}C NMR spectrum of poly(TFAcAz) (powder).

Scheme 2. Oligomerization of TFAcAz



Since the polymer was insoluble in organic solvents, the ^{13}C NMR spectrum of poly(TFAcAz) was measured in the solid state. Two resonance bands are observed as shown in Figure 3. On the basis of reference data[20] and relative intensities, the signal at higher field is assignable to the methine carbon in the main chain of the obtained polymer and that at lower field is assignable to the methine carbon in the pendant group and to the carbons of the trifluoromethyl groups. In the case of poly(TFAcAz), no peak could be found in the region due to methine carbon binding to the N=N group at about 80 ppm.[11,12] These results also support that the polymer is composed of 1,2-units.

Since the polymer was insoluble in organic solvents, soluble oligomers were prepared by the termination of polymerization in the early stage with methanol to confirm the structure of the polymer. After evaporation of volatile fractions, the red-orange viscous oil was obtained. The structures of the products were investigated by EI-mass and ^{1}H NMR spectroscopies. The mass spectrum shows that there are peaks at $m/z = 224$ and 416 and is reasonably assigned to **1** and **2** on the basis of their fragmentation (Scheme 2). In the ^{1}H NMR spectrum, there were two peaks assignable to N−H at 5.94 and 7.45 ppm, which bound to $CHCF_3$ in addition to the signals due to OCH_3, $CHCF_3$, and CH=N. These spectra show that **1** and **2** were obtained. These results show the termination of polymerization of TFAcAz with methanol gave a head-to-tail 1,2-dimer, suggesting that polymerization proceeds through head-to-tail 1,2-addition so that the obtained polymer is composed of head-to-tail 1,2-units.

The powder X-ray diffraction of poly(TFAcAz) is shown in Figure 4. Clear diffraction patterns were

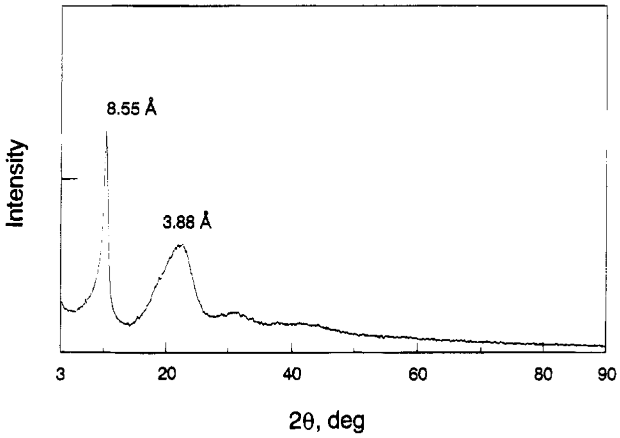


Figure 4. Powder X-ray diffraction pattern of poly(TFAcAz).

observed at 2θ = 22.9 and 10.3°, indicating that the polymer is crystalline. These 2θ angles correspond to distances of 3.88 and 8.55 Å, respectively. Similar X-ray diffraction patterns have been observed in poly(alkyl azine)s.[11,12] On the basis of the substituent effect on the distances, the longer distance was reasonably assigned to the interchain regular structure and the shorter distance to the fiber period of the main chain. If the obtained polymer takes a planar zigzag structure, the estimated distance (3.88 Å) corresponds to two C−N units. Since the obtained polymer is suggested to be composed of head-to-tail 1,2-units, the estimation that the fiber period is composed of two C−N units suggests that the polymer has a syndiotactic regular structure. Poly(TFAcAz) is not soluble in organic solvents, suggesting that the polymer is cross-linked through pendant C=N double bonds. However, the formation of crystalline polymer suggests that the nonsolubility may be ascribed to the interchain regular structure rather than the cross-linking. Furthermore, no swelling of the obtained polymer was observed in any solvent. The result also suggests that cross-linking does not occur during the polymerization.

Thermal Properties of Poly(TFAcAz). The thermal behavior of poly(TFAcAz) was investigated by thermogravimetric analysis (TGA). The result is shown in Figure 5. A gradual weight loss started at around 150 °C, with full decomposition at about 280 °C. This result shows that poly(TFAcAz) is a thermally degradable polymer.

To obtain information on the pyrolysis of poly(TFAcAz), the products obtained by pyrolysis were collected and their structures were analyzed by ^{1}H NMR and EI-mass spectroscopies. These spectra showed that about 60% of the collected products was the monomer, indicating that depolymerization of poly(TFAcAz) occurred at about 200 °C.

Conclusions

TFAcAz was synthesized and isolated as a new monomer and its polymerizabilities were studied. Only oligomers were formed by polymerization with *n*-BuLi, CH_3MgI, CH_3OK/18-crown-6, or DBU. However, poly(TFAcAz) was obtained by bulk polymerization either with triethylamine or with tri-*n*-butylamine at −20 °C. We found that the obtained polymer was crystalline, composed of 1,2-units, and depolymerized at about 200 °C. The TFAcAz was found to have considerably different polymerizability from those of alkyl azine compounds.

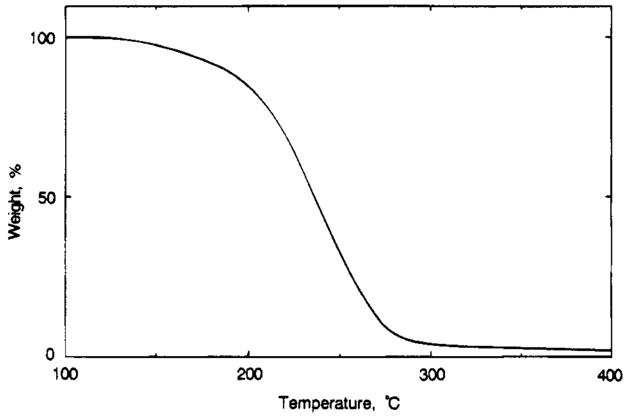


Figure 5. Thermogravimetric analysis (TGA) curve of poly(TFAcAz) in a nitrogen atmosphere. Sample, 1.88 mg; heating rate, 10 °C/min.

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(19) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M.; Kusunoki, M., to be published.
(20) In the ^{13}C NMR spectrum of the cyclic dimer of TFAcAz, the signals of the carbons of the trifluoromethyl groups were observed at 117 and 123 ppm, that of C−N at 53 ppm, and that of C=N at 139 ppm.[19]

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