Polymer 50 (2009) 2246–2251

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Crisscross addition polymerization of alkyl aldazines and 1,4-phenylene diisocyanate

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ARTICLE INFO

Article history:
Received 7 January 2009
Received in revised form
12 March 2009
Accepted 15 March 2009
Available online 25 March 2009

Keywords:
Crisscross addition polymerization
Alkyl aldazines
1,4-Phenylene diisocyanate

ABSTRACT

Crisscross addition polymerization of alkyl aldazines (i.e., acetaldehyde azine, propionaldehyde azine, and butyraldehyde azine (BuAz)) and 1,4-phenylene diisocyanate ($Ph(IC)_2$) was investigated under various conditions. The crisscross addition polymerizations in pyridine yielded polymers in higher yields. The polymers obtained in the present study exhibited very limited solubilities and contained fractions insoluble in conventional organic solvents. However, since the BuAz/$Ph(IC)_2$ polymers obtained at 24 and 48 h were soluble in pyridine, the M_w values for these polymers were determined to be 2.2×10^3 and 4.4×10^3, respectively, by small angle X-ray scattering. These data indicated that molecular weights of the pyridine-insoluble polymers were as high as or close to 10^4. IR, ^1H NMR, and MALDI-TOF-MS data confirmed the formation of linear polymers by crisscross addition polymerization. Thermogravimetric analyses indicated that the polymers were considerably decomposed in the region of 300–400 °C, but the polymers exhibited residual weights of 15–25% even at 500 °C. Differential scanning calorimetry data indicated that glass transition temperatures for the polymers were higher than the onset of decomposition presumably because of the rigid backbone.

1. Introduction

Crisscross addition, which has been first reported by Bailey et al. [1,2], is a reaction yielding bicyclic compounds from azines and 2 equiv of dipolarophile. There have been a number of publications on crisscross addition so far [3,4]. Some of them have dealt with the synthesis of polymers containing bicyclic moieties in their main chain [5–9]. Although crisscross addition efficiently forms unique bicyclic structures, the type of azines which undergo crisscross addition is rather limited: There have been only a few types of azines (e.g., perfluoroacetone azine [10–22] and acetone azine [23]) other than aromatic aldazines [24–30]. This may somehow restrict the application of crisscross addition.

We have been working on the reactivity and polymerizability of azines [31–37]. In our preceding paper [38], we have reported that acetaldehyde azine (AcAz), the simplest alkyl aldazine, undergoes crisscross addition with phenyl isocyanate (PhIC) to form a one-to-two adduct of AcAz and PhIC. To the best of our knowledge, this is the first example of crisscross addition of alkyl aldazine. Furthermore, we have also obtained polymeric products from mixtures of AcAz and 1,4-phenylene diisocyanate ($Ph(IC)_2$) without any initiators or catalysts under bulk conditions [38]. Although it was not possible to determine the molecular weights of the products because of their low solubility, the structure of the products was well characterized by comparing their spectroscopic data with those of the one-to-two adduct of AcAz and PhIC, indicating that the products were formed by crisscross addition polymerization of AcAz and $Ph(IC)_2$. On the basis of the preceding study, this study deals with crisscross addition polymerization of alkyl aldazines (i.e., AcAz, propionaldehyde azine (PrAz), and butyraldehyde azine (BuAz)) and $Ph(IC)_2$ under various conditions.

2. Experimental

2.1. Materials

Acetaldehyde azine (AcAz), propionaldehyde azine (PrAz), and butyraldehyde azine (BuAz) were prepared from the corresponding aldehydes and hydrazine monohydrate, respectively, according to the procedure of Curtius and Zinkeisen [39]. These alkyl aldazines were purified by successive distillations over calcium hydride under an argon atmosphere. 1,4-Phenylene diisocyanate ($Ph(IC)_2$) was purchased from Sigma–Aldrich and used without further purification. Toluene and tetrahydrofuran (THF) used for the crisscross addition polymerization were distilled over sodium in

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doi:10.1016/j.polymer.2009.03.025

the presence of benzophenone and stored under an argon atmosphere. Pyridine used for the crisscross addition polymerization was distilled over calcium hydride under vacuum prior to use. Other reagents were used without further purification.

2.2. *Crisscross addition polymerization of alkyl aldazines and Ph(IC)$_2$*

A typical procedure for crisscross addition polymerization of alkyl aldazines and Ph(IC)$_2$ is described below.

Ph(IC)$_2$ (480 mg, 3.0 mmol) was placed in an ampule equipped with a three-way stop-cock and dried under vacuum overnight. BuAz (421 mg, 3.0 mmol) and pyridine (10 mL) were added using a syringe into the ampule under an argon atmosphere. The mixture was sonicated for 5 min to be homogenized. The ampule was immersed in an oil bath thermostated at 60 °C. The reaction mixture gradually became viscous. After 48 h, the viscous reaction mixture was cooled down to room temperature and then became a gel-like mixture. Washing the gel-like mixture with methanol several times, the polymer formed was obtained as a methanol-insoluble fraction. After drying in vacuo, the polymer was obtained as a colorless powder: yield 85.2%; mp 300–350 °C dec; IR (ATR) $\nu_{\max}$ 2965 (aliphatic C–H), 2940 (aliphatic C–H), 2880 (aliphatic C–H), 1725 (C=O), 1515 (aromatic C=C), 1365 (CH$_3$), 1200 (C–N), 835 (1,4-disubstituted benzene); ^{1}H NMR (pyridine-d_5, 270 MHz) δ 0.7–1.0 (methyl), 1.5–1.7 (methylene), 1.7–2.0 (methylene), 3.7 (methyl), 6.2–6.4 (methine), 7.6–8.0 (phenyl). Anal. Calcd for $(C_8H_{16}N_2)_{12}(C_8H_4N_2O_2)_{13}(CH_4O)_2(H_2O)_3$: C, 62.49; H, 6.70; N, 18.04. Found: C, 62.41; H, 6.53; N, 18.02%.

2.3. *Measurements*

IR spectra were recorded using powder samples on a JASCO FT/IR-8300 spectrometer equipped with a JASCO ATR PRO410-S cell. ^{1}H NMR spectra for the polymers obtained were measured on a JEOL JNM-EX270 or GSX400 spectrometer using pyridine-d_5 as a solvent. Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) experiments were performed on a Shimadzu/KRATOS Axima CFR Ver.2.2.3 mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix. Mass number was calibrated by using α-cyano-4-hydroxycinnamic acid and insulin. Small angle X-ray scattering (SAXS) measurements were carried out on a Rigaku R-AXIS VII imaging plate at the BL40B2 beamline in SPring-8. The wavelength and camera length were set at 0.10 nm and 1500 mm, respectively. The details of SAXS experiments were described elsewhere [40–42]. Thermogravimetric analysis (TGA) data were collected with an SII Nanotechnology TG/DTA6200 under a steam of nitrogen (200 mL/min) at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) data were obtained on an SII Nanotechnology DSC6220 under air at a heating rate of 10 °C/min. To minimize the effect of thermal history of the samples, the DSC data were recorded after heating and cooling scans at 10 °C/min in the temperature range of room temperature to ca. 195 °C.

3. Results and discussion

3.1. *Crisscross addition polymerization of AcAz and Ph(IC)$_2$*

Table 1 lists typical examples of conditions and results of crisscross addition polymerization of AcAz and Ph(IC)$_2$. Under bulk conditions, polymer was obtained in a relatively high yield (ca. 75%) at 6 h, but the polymer yield leveled off at ca. 75% (runs 1 and 2 in Table 1) because the reaction mixture became solid in 6 h [38]. To optimize the conditions, crisscross addition polymerizations were examined in solution, in which the concentrations of AcAz and Ph(IC)$_2$ were fixed at 0.30 M. In toluene or THF, polymer was obtained at 24 h only in a low yield (25.1 or 13.4%) presumably because of the low solubilities of Ph(IC)$_2$ and the polymer in the solvent (runs 3 and 4 in Table 1). In pyridine, on the other hand, polymer was obtained at 48 h in a yield (84.3%) higher than those under the bulk conditions although the polymerization proceeded in pyridine more slowly than did the bulk polymerization (runs 5–7 in Table 1). The noteworthy is that the polymerization solution became viscous during the polymerization time and it turned into a gel-like mixture after cooling down to room temperature, indicative of the formation of higher molecular weight polymers.

Table 1
Examples of conditions and results of crisscross addition polymerization of AcAz and Ph(IC)$_2$.

Run	Solvent	Time/h	Yield/%[a]
1	–	6	78.4
2	–	24	74.8
3	Toluene	24	25.1
4	THF	24	13.4
5	Pyridine	6	26.6
6	Pyridine	24	76.9
7	Pyridine	48	84.3

Polymerizations were carried out at 60 °C. For solution polymerizations (runs 3–7), the concentrations of AcAz and Ph(IC)$_2$ were fixed at 0.30 M.

[a] For the methanol-insoluble fraction based on the total amount of AcAz and Ph(IC)$_2$.

3.2. *Crisscross addition polymerization of alkyl aldazines and Ph(IC)$_2$ in pyridine*

As described above, pyridine is a useful solvent for crisscross addition polymerization of AcAz and Ph(IC)$_2$. Thus, crisscross addition polymerizations were examined for mixtures of an alkyl aldazine (i.e., AcAz, PrAz, or BuAz) and Ph(IC)$_2$ using pyridine as a solvent under various conditions to understand details of the crisscross addition polymerization.

Crisscross addition polymerizations were carried out at varying polymerization times fixing the concentrations of comonomers at 0.30 M ([azine] = [Ph(IC)$_2$] = 0.30 M). Fig. 1 compares the polymer yields as a function of time for AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$. The polymer yield increases with time and levels off at ca. 24, 48, and 60 h for AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$, respectively. These plots indicate that the crisscross addition polymerization for AcAz/Ph(IC)$_2$ proceeds faster than do those

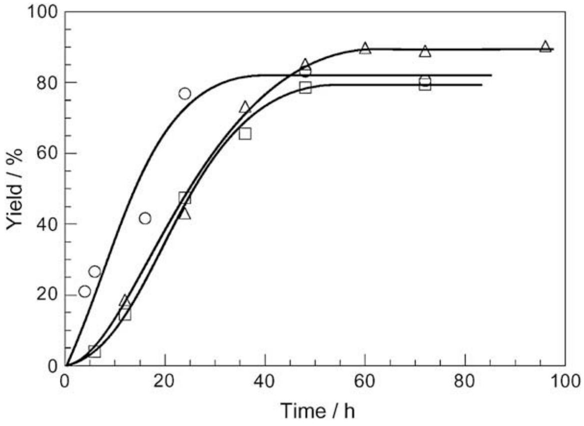


Fig. 1. The polymer yield as a function of time for AcAz/Ph(IC)$_2$ (circle), PrAz/Ph(IC)$_2$ (square), and BuAz/Ph(IC)$_2$ (triangle) at 60 °C. Here the concentrations of the comonomers were fixed at 0.30 M ([azine] = [Ph(IC)$_2$] = 0.30 M).

for PrAz/Ph(IC)$_2$ and BuAz/Ph(IC)$_2$. This may be because the steric hindrance of longer alkyl substituents in azine retards the polymerization. The polymer yields at saturation are ca. 80, 80, and 90% for AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$, respectively. This observation indicates that a longer alkyl substituent in azine provides a higher polymer yield presumably because of increased solubility of the polymer obtained.

Crisscross addition polymerizations were also carried out at varying mole fractions of azine in comonomer feed (x_{Az}) fixing the total concentration of the comonomers at 0.60 M ([azine] + [Ph(IC)$_2$] = 0.60 M). Yields of the polymer (i.e., the methanol-insoluble fraction) at 24 h are plotted in Fig. 2a as a function of x_{Az} for AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$. For all the azines, plots seem to show maxima at $x_{Az} = 0.5$. It should be noted here that the polymer yields are lower than the dotted straight lines at $0 < x_{Az} < 0.5$, while higher at $0.5 < x_{Az} < 1.0$. As can be seen in Scheme 1, linear polymers formed by crisscross addition polymerization are composed of n molecules of azine and $(n + 1)$ molecules of Ph(IC)$_2$. Thus, oligomers (i.e., the methanol-soluble fractions) may be formed preferably at $x_{Az} < 0.5$, resulting in lower polymer yields. The mole fractions of azine in the polymers obtained (X_{Az}) were determined by elemental analysis for AcAz/Ph(IC)$_2$ and PrAz/Ph(IC)$_2$ or by ^{1}H NMR for BuAz/Ph(IC)$_2$, and these X_{Az} values are plotted in Fig. 2b as a function of x_{Az}. For all the azines, X_{Az} gradually increases from ca. 0.4 to ca. 0.5 with increasing x_{Az} from 0.1 to 0.9. The dependencies of X_{Az} on x_{Az} can be also explained by the effect of the polymer terminals. These observations are indicative of the formation of linear polymers not cyclic ones. This will be further discussed in the later subsection.

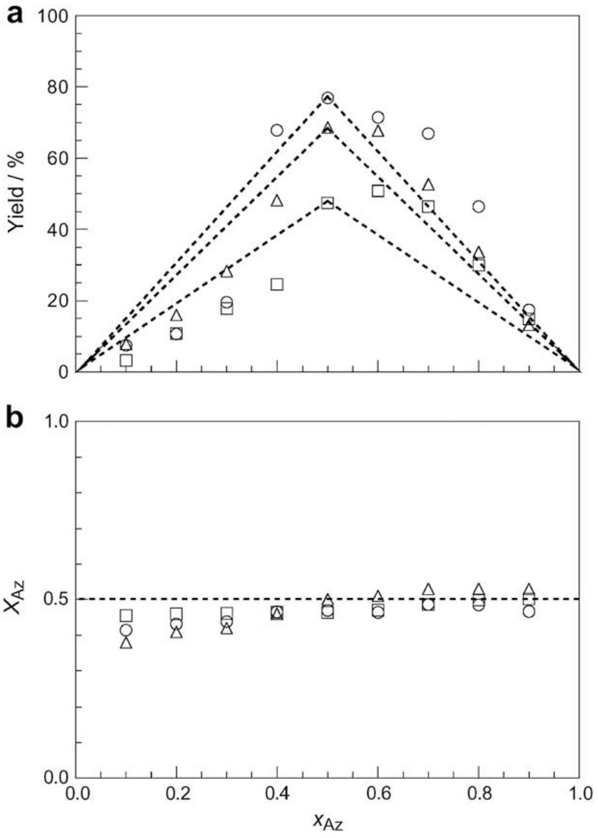
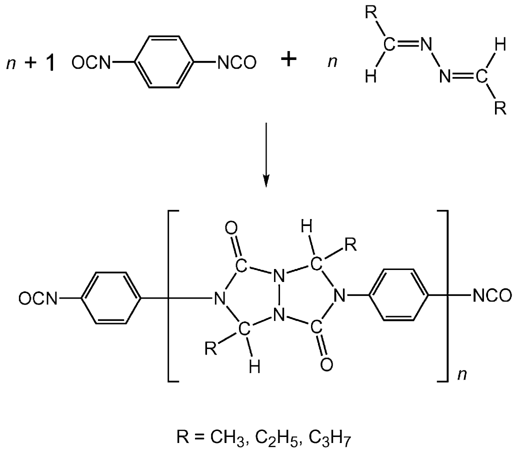


Fig. 2. The copolymer yield (a) and the mole fraction of azine in copolymer (X_{Az}) (b) as a function of the mole fraction of azine in the feed (x_{Az}): AcAz/Ph(IC)$_2$ (circle), PrAz/Ph(IC)$_2$ (square), and BuAz/Ph(IC)$_2$ (triangle). Here the total concentration of the comonomers was fixed at 0.60 M ([azine] + [Ph(IC)$_2$] = 0.60 M).



Scheme 1. Crisscross addition polymerization of alkyl aldazines and Ph(IC)$_2$.

All the polymers obtained in the present study exhibited very limited solubilities and contained fractions insoluble in various organic solvents, including benzene, toluene, chloroform, diethyl ether, THF, acetone, dimethyl sulfoxide, *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone, and 1,1,1,3,3,3-hexafluoro-2-propanol. Pyridine was a relatively good solvent for the polymers, but the polymers obtained at longer polymerization times (≥ca. 24 h for AcAz/Ph(IC)$_2$ and PrAz/Ph(IC)$_2$, and ≥ca. 60 h for BuAz/Ph(IC)$_2$) contained pyridine-insoluble fractions. Since the BuAz/Ph(IC)$_2$ polymers obtained at 24 and 48 h were soluble in pyridine, the M_w values for these BuAz/Ph(IC)$_2$ polymers were determined to be 2.2×10^3 and 4.4×10^3, respectively, by SAXS, as listed in Table 2. The molecular weights of the pyridine-insoluble polymers should be higher than those for the pyridine-soluble ones because IR spectra for the pyridine-soluble and insoluble polymers were almost the same. It is thus likely that M_w values for the pyridine-insoluble polymers are as high as or close to 10^4 [43].

Some of the polymers obtained were fractionated into fractions soluble and insoluble in pyridine (runs 1, 2, and 5 in Table 2). Table 2 also includes inherent viscosities ($(\ln \eta_r)c^{-1}$) determined for the pyridine-soluble fractions at a polymer concentration (c) of 4.9×10^{-3} g/cm^3 with an Ubbelohde viscometer using pyridine as a solvent. The values of $(\ln \eta_r)c^{-1}$ are 12, 25, and 27 cm^3/g for the pyridine-soluble fractions of AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$, respectively, indicating that the solubility of the polymers

Table 2
Examples of conditions and results of crisscross addition polymerization of alkyl aldazines and Ph(IC)$_2$ in pyridine.

Run	Azine	Time/h	Yield[a]/%	w_{sol}[b]	$(\ln \eta_r)c^{-1}$ [c]/cm^3/g	M_w[d]/10^3
1	AcAz	24	76.9	0.66	12	–[e]
2	PrAz	24	47.8	0.79	25	–[e]
3	BuAz	24	43.1	1.0	27	2.2
4	BuAz	48	85.2	1.0	–[f]	4.4
5	BuAz	60	89.7	0.90	26	–[e]

Polymerizations were carried out in pyridine at 60 °C. The concentrations of azine and Ph(IC)$_2$ were fixed at 0.30 M.

[a] For the methanol-insoluble fraction based on the total amount of AcAz and Ph(IC)$_2$.

[b] Weight fraction of the pyridine-soluble polymer.

[c] Determined at $c = 4.9 \times 10^{-3}$ g/cm^3 in pyridine at 25 °C using an Ubbelohde viscometer.

[d] Determined by SAXS in pyridine.

[e] It was not possible to determine M_w because the polymer contained a pyridine-insoluble fraction.

[f] The polymer was not completely soluble in pyridine at 4.9×10^{-3} g/cm^3.

increases in the order of AcAz/Ph(IC)$_2$ < PrAz/Ph(IC)$_2$ < BuAz/Ph(IC)$_2$ polymers [44]. Comparing the (ln η_r)c^{-1} values with that for the BuAz/Ph(IC)$_2$ obtained at 24 h, it is likely that the molecular weights for the AcAz/Ph(IC)$_2$ and PrAz/Ph(IC)$_2$ polymers are as high as a few thousands.

The crisscross addition polymerizations proceeded much faster under concentrated conditions (i.e., [azine] = [Ph(IC)$_2$] = 1.5 M), consistent qualitatively with the kinetic consideration by Flory [45]. Under the concentrated conditions, the reaction mixtures became very hard solids in 24 h. These solid products were insoluble in all the solvents examined, suggestive of the formation of higher molecular weight polymers. Since it was not possible to purify the polymers obtained under the concentrated conditions, these polymers could not be characterized.

3.3. Structure of the polymers obtained

The structures of the pyridine-soluble polymers of AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$ were characterized by IR, ^{1}H NMR, and MALDI-TOF-MS spectroscopies.

Fig. 3 shows IR spectra for the pyridine-soluble polymers of AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$. All the spectra contain absorption bands ascribable to the C–H, the C=O, the aromatic ring, and the C–N at ca. 2900, 1725, 1515, and 1200 cm^{-1}, respectively. These spectra agree well with the IR spectrum for the one-to-two adduct of AcAz and phenyl isocyanate (PhIC) [38]. It should be noted here that there are no absorption bands ascribable to the –N=C=O at ca. 2200 cm^{-1} although the IR spectrum for the AcAz/Ph(IC)$_2$ polymers obtained under bulk conditions, which were also purified by washing with methanol, contained the bands due to –N=C=O at chain ends [38]. This observation is suggestive of some reactions of the –N=C=O groups at the chain ends.

Fig. 4 compares ^{1}H NMR spectra for the pyridine-soluble polymers of AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz/Ph(IC)$_2$. All the spectra indicate the resonance bands ascribable to phenyl and methine protons in the regions of 7.6–8.0 and 6.2–6.5 ppm, respectively. The resonance bands ascribable to the corresponding alkyl groups (i.e., methyl, ethyl, and propyl groups) are seen in the region of 0.8–2.0 ppm. These spectra correspond well to that for the one-to-two adduct of AcAz and PhIC [38]. The noteworthy is that there are resonance bands ascribable to methyl protons at ca. 3.7 ppm, indicative of addition of methanol molecules to the –N=C=O chain ends during purification. From the spectra, M_n values were calculated to be 1.5×10^3, 2.4×10^3, and 4.1×10^3 for the AcAz/Ph(IC)$_2$, PrAz/Ph(IC)$_2$, and BuAz(IC)$_2$ polymers, respectively. The M_n (4.1×10^3) agrees well with the M_w (4.4×10^3) determined by SAXS for the BuAz/Ph(IC)$_2$. The addition of methanol molecules was confirmed by MALDI-TOF-MS for the BuAz/Ph(IC)$_2$ polymer obtained at 24 h, which indicated a series of peaks ascribable to polymers bearing –NHCOOCH$_3$ at both the chain ends (Fig. S1 in Supporting Information). Furthermore, the C, H, and N contents of the BuAz/Ph(IC)$_2$ polymers obtained at 48 h agreed with the calculated values for the polymer consisting of 12 units of BuAz, 13 units of Ph(IC)$_2$, and 2 units of methanol (see Experimental) [46]. These observations indicate that the content of linear polymer bearing two –NHCOOCH$_3$ groups is almost unity and that a polymer chain carries two reactive –N=C=O groups at both ends before purification (i.e., washing with methanol). Therefore, the polymers obtained by crisscross addition polymerization can be used as telechelic polymers to prepare other telechelics and multiblock copolymers [47].

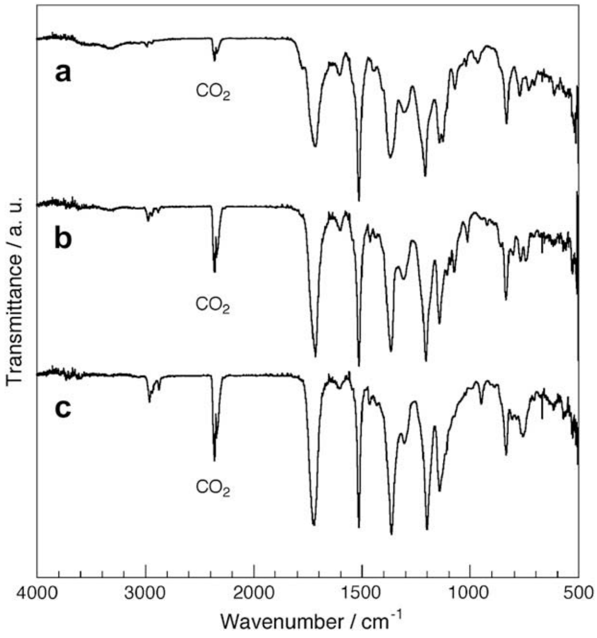


Fig. 3. IR spectra for the pyridine-soluble polymers of AcAz/Ph(IC)$_2$ (a), PrAz/Ph(IC)$_2$ (b), and BuAz/Ph(IC)$_2$ (c) (ATR).

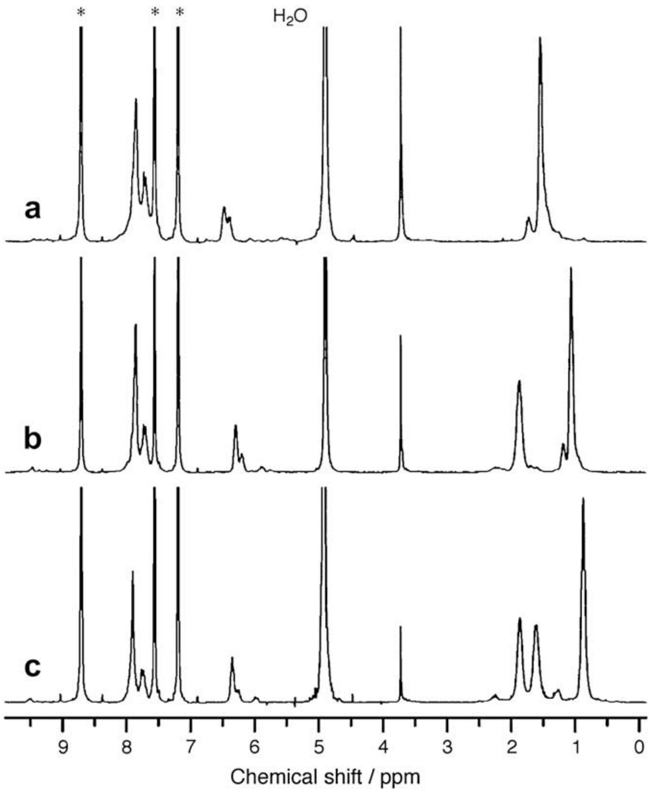


Fig. 4. ^{1}H NMR spectra for the pyridine-soluble polymers of AcAz/Ph(IC)$_2$ (a), PrAz/Ph(IC)$_2$ (b), and BuAz/Ph(IC)$_2$ (c) (pyridine-d_5). Asterisks indicate the signals due to the solvent.

These characterization data led us to conclude the formation of linear polymers by the crisscross addition polymerization of alkyl aldazines and Ph(IC)$_2$.

3.4. Thermal behavior of the polymers obtained

The thermal behavior of pyridine-insoluble polymers was investigated by TGA and DSC (Fig. 5 and Fig. S3 in Supporting Information, respectively). As can be seen in Fig. 5, TGA data show

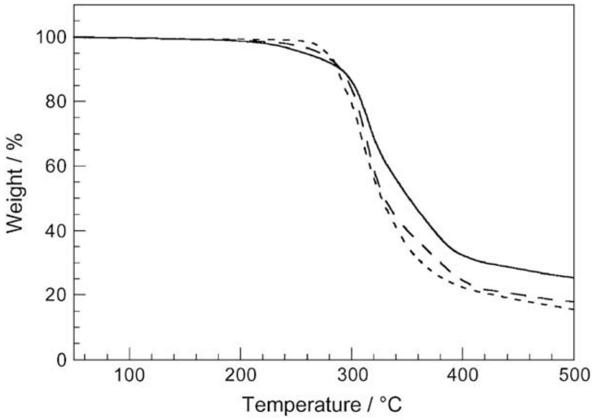


Fig. 5. TGA curves for the pyridine-insoluble polymers of AcAz/Ph(IC)$_2$ (solid line), PrAz/Ph(IC)$_2$ (broken line), and BuAz/Ph(IC)$_2$ (dotted line) under a steam of nitrogen (200 mL/min). The amounts of samples were ca. 2 mg, and the heating rate was set at 10 °C/min.

that a gradual weight loss starts at ca. 200 °C for all the polymers examined, followed by two-step decomposition in the region of 300–400 °C. As the temperature is further increased up to 500 °C, the residual weight gradually decreases to 15–25%. Comparing the TGA data for the three polymers, the residual weight at ca. 320 °C decreases in the order of AcAz/Ph(IC)$_2$ > PrAz/Ph(IC)$_2$ > BuAz/Ph(IC)$_2$, and the weight losses from 320 to 500 °C are almost the same for the three polymers. These observations imply that the weight loss at <320 °C is caused mainly by decomposition of the side chains. TGA data for the pyridine-insoluble and pyridine-soluble fractions of BuAz/Ph(IC)$_2$ were almost the same (Fig. S2 in Supporting Information), indicating that the degradation behavior of the polymer is practically independent on the molecular weight in the region of molecular weight of several thousands. As can be seen in Fig. S3 of Supporting Information, DSC data did not exhibit any signals ascribable to glass transition in the whole temperature range examined (30–193 °C), indicating that the glass transition temperatures for the polymers are higher than the onset of decomposition presumably because of the rigid backbone.

4. Conclusions

On the basis of our previous study, crisscross addition polymerization of alkyl aldazines (i.e., AcAz, PrAz, and BuAz) and Ph(IC)$_2$ was further investigated. Since the crisscross addition polymerizations of AcAz and Ph(IC)$_2$ under several conditions indicated that pyridine was a useful solvent, the crisscross addition polymerizations of alkyl aldazines were investigated in pyridine under various conditions. The crisscross addition polymerization for AcAz/Ph(IC)$_2$ proceeded faster than did those for PrAz/Ph(IC)$_2$ and BuAz/Ph(IC)$_2$ presumably because the steric hindrance of longer alkyl substituents in azine retarded the polymerization. The polymer yield and X_{Az} for the crisscross addition polymerizations carried out at varying x_{Az} were indicative of the formation of linear polymers. All the polymers obtained in the present study exhibited very limited solubilities and contained fractions insoluble in various organic solvents. Among these series of polymers, however, BuAz/Ph(IC)$_2$ polymers were relatively soluble in pyridine presumably because of the longer alkyl substituents. Since the BuAz/Ph(IC)$_2$ polymers obtained at 24 and 48 h were soluble in pyridine, the M_w values for these BuAz/Ph(IC)$_2$ polymers were determined to be 2.2×10^3 and 4.4×10^3, respectively, by SAXS. On the basis of these M_w values, it was likely that M_w values for the pyridine-insoluble polymers were as high as or close to 10^4. The crisscross addition polymerization under concentrated conditions (i.e., [azine] = [Ph(IC)$_2$] = 1.5 M) yielded the reaction mixtures as very hard solids, suggestive of the formation of higher molecular weight polymers. IR, ^{1}H NMR, and MALDI-TOF-MS data confirmed the formation of linear polymers by crisscross addition polymerization. TGA data indicated that a gradual weight loss started at ca. 200 °C for all the polymers examined, followed by considerable decomposition in the region of 300–400 °C. But the polymers exhibited residual weights of 15–25% even at 500 °C. DSC data indicated that glass transition temperatures for the polymers were higher than the onset of decomposition.

Acknowledgments

The synchrotron radiation experiments were performed at the BL40B2 in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal #2007B1296). The authors would like to express their acknowledgment to Assistant Professor Ken Terao, Department of Macromolecular Science, Graduate School of Science, Osaka University, for his technical support on the SAXS measurements and analyses. The authors also thank Associate Professor Fumitoshi Kaneko and Assistant Professor Osamu Urakawa, Department of Macromolecular Science, Graduate School of Science, Osaka University, for allowing us to use the TGA and DSC instruments, respectively, and for their valuable suggestions. The authors are grateful to Emeritus Professor Mikiharu Kamachi, Department of Macromolecular Science, Graduate School of Science, Osaka University and Dr. Tetsuya Noda, Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd. for fruitful discussion and valuable comments.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.03.025.

References

[1] Bailey JR, Moore NH. J Am Chem Soc 1917;39:279–91.
[2] Bailey JR, McPherson AT. J Am Chem Soc 1917;39:1322–38.
[3] Wagner-Jauregg T. Synthesis 1976:349–73.
[4] Rádl S. Aldrichimica Acta 1997;30:97–100.
[5] Stille JK, Anyos T. J Polym Sci 1964;A2:1487–91.
[6] Stille JK, Morgan RA. J Polym Sci 1965;A3:2397–9.
[7] Barlow MG, Suliman NN, Tipping AE. J Chem Soc Chem Commun 1993:9–11.
[8] Maier G. Macromol Chem Phys 1996;197:3067–90.
[9] Maier G, Fenchl A. Macromol Symp 1997;122:297–302.
[10] Forshaw TP, Tipping AE. J Chem Soc D 1969:816–7.
[11] Forshaw TP, Tipping AE. J Chem Soc C 1971:2404–8.
[12] Forshaw TP, Tipping AE. J Chem Soc Perkin Trans 1 1972:1059–62.
[13] Armstrong SE, Tipping AE. J Fluorine Chem 1973;3:119–21.
[14] Armstrong SE, Tipping AE. J Chem Soc Perkin Trans 1 1974:2716–20.
[15] Armstrong SE, Tipping AE. J Chem Soc Perkin Trans 1 1975:1411–7.
[16] Armstrong SE, Forshaw TP, Tipping AE. J Chem Soc Perkin Trans 1 1975:1902–7.
[17] Armstrong SE, Tipping AE. J Chem Soc Perkin Trans 1 1975:538–42.
[18] Burger K, Thenn W, Gieren A. Angew Chem Int Ed Engl 1974;13:474–5.
[19] Gieren A, Narayanan P, Burger K, Thenn W. Angew Chem Int Ed Engl 1974;13:475–6.
[20] Burger K, Thenn W, Rauh R, Schickaneder H. Angew Chem Int Ed Engl 1974; 13:477–8.
[21] Burger K, Thenn W, Rauh R, Schickaneder H, Gieren A. Chem Ber 1975;108:1460–7.
[22] Burger K, Thenn W, Schickaneder H. Chem Ber 1975;108:1468–74.
[23] Satsumabayashi S, Nakano H, Motoki S. Nippon Shika Daigaku Kiyo Ippan Kyoiku-kei 1979;8:87–96.
[24] Häring M, Wagner-Jauregg T. Helv Chim Acta 1957;40:852–71.
[25] Tsuge O, Kanemasa S. Bull Chem Soc Jpn 1972;45:3591–5.
[26] Furukawa M, Sugita M, Kojima Y, Hayashi S. Chem Pharm Bull 1973;21: 2088–90.
[27] Furukawa M, Sugita M, Kojima Y, Hayashi S. Chem Pharm Bull 1974;22:1468–76.
[28] Mathur SS, Suschitzky H. J Chem Soc Perkin Trans 1 1975:2479–83.
[29] Shimizu T, Hayashi Y, Miki M, Teramura K. J Org Chem 1987;52:2277–85.
[30] Kelley C, Mercando LA, Lugan N, Geoffroy GL, Xu Z, Rheingold AL. Angew Chem Int Ed Engl 1992;31:1053–5.

[31] Hashidzume A, Kajiwara A, Harada A, Kamachi M. Macromolecules 1995;28:417–20.
[32] Hashidzume A, Kajiwara A, Harada A, Kamachi M. Bull Chem Soc Jpn 1995;68:2025–31.
[33] Hashidzume A, Kajiwara A, Fujii H, Harada A, Kamachi M. Kobunshi Ronbunshu 1997;54:738–45.
[34] Hashidzume A, Tsuchiya A, Morishima Y, Kamachi M. Macromolecules 2000;33:2397–402.
[35] Hashidzume A, Noda T, Morishima Y, Kajiwara A, Kamachi M. Macromolecules 2000;33:6295–302.
[36] Tsuchiya A, Hashidzume A, Harada A, Kamachi M. Des Monomers Polym 2004;7:277–90.
[37] Kamachi M, Kajiwara A, Hashidzume A, Matsuda K, Harada A. Des Monomers Polym 2004;7:701–10.
[38] Hashidzume A, Shiota J, Ueno Y, Noda T, Takashima Y, Harada A, et al. Polymer 2006;47:501–5.
[39] Curtius T, Zinkeisen E. J Prakt Chem 1898;58:310–32.
[40] Glatter O, Kratky O, editors. Small angle X-ray scattering. London: Academic Press; 1982.
[41] Terao K, Mizuno K, Murashima M, Kita Y, Hongo C, Okuyama K, et al. Macromolecules 2008;41:7203–10.
[42] Kanemaru E, Terao K, Nakamura Y, Norisuye T. Polymer 2008;49:4174–9.
[43] According to the Flory–Huggins theory [48], the solubility limit (the polymer volume fraction) (ϕ_{limit}) is inversely proportional to the polymer molecular weight at $\phi_{\text{limit}} \ll 1$.
[44] Strictly speaking, values of $M_0(\ln \eta_r)c^{-1}$, where M_0 is the molar mass of the monomer unit, should be compared.
[45] Flory PJ. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; 1953 [chapter 3].
[46] The calculated molecular weight (3828.5) of the polymer agrees well with the M_n value (4.1×10^3) determined by ^{1}H NMR.
[47] Maier G, Knopfova V, Voit B, Ly PH, Dung BT, Thanh DB. Macromol Mater Eng 2004;289:927–32.
[48] Flory PJ. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; 1953 [chapter 13].