

Polymer Communication

Polymer formation utilizing ‘crisscross’ addition (crisscross addition polymerization) of acetaldehyde azine and 1,4-phenylene diisocyanate

Akihito Hashidzume^a, Junya Shiota^a, Yusuke Ueno^a, Tetsuya Noda^a,
Yoshinori Takashima^a, Akira Harada^a, Mikiharu Kamachi^{b,*}

^a Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

^b Department of Applied Physics and Chemistry, Faculty of Engineering, Fukui University of Technology, 6-3-1 Gakuen, Fukui 910-8505, Japan

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Abstract

Acetaldehyde azine (AcAz) underwent ‘crisscross’ addition with two equivalents of phenyl isocyanate to form a one-to-two adduct in a moderate yield (63.0%). Using crisscross addition of AcAz, polymeric products were obtained from AcAz and 1,4-phenylene diisocyanate in a high yield (>80%). The polymer obtained was soluble in 1,1,1,3,3,3-hexafluoro-2-propanol, and insoluble in many organic solvents, including *n*-hexane, benzene, toluene, chloroform, diethyl ether, tetrahydrofuran, acetone, ethanol, methanol, dimethyl sulfoxide, and *N,N*-dimethylformamide. The structure of the polymer obtained was characterized by IR and ¹H NMR spectroscopies. The thermal behavior of the polymer was also investigated by thermogravimetric analysis.

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1. Introduction

Compounds carrying C=N bond undergo various types of reactions, including addition, cycloaddition, substitution, and cleavage, similar to compounds carrying C=C or C=O bond [1]. However, polymer formation from C=N compounds has been an underexamined subject [2], comparing with polymer formation from C=C or C=O compounds. Since polymers formed from C=N compounds possess nitrogen atoms in their main chain, they are promising materials with various functions [3]. Therefore, we have been studying on the polymer formation from C=N compounds, especially aldehyde azines [4,5] and azastylene derivatives [6,7].

‘Crisscross’ addition is a useful synthetic method yielding heterocyclic compounds from azines. After the first report on crisscross addition by Bailey et al. [8], a number of examples of crisscross addition have been reported [9]. Furthermore, crisscross addition has been also used for synthesis of polymers containing bicyclic moieties in their main chain [10]. However,

the type of azines which undergo crisscross addition is rather limited to aromatic aldehyde azines [11], perfluoroacetone azine [12,13], and acetone azine [14].

In the course of our work on the reactivity and polymerizability of alkyl aldehyde azines, we came across the fact that acetaldehyde azine (AcAz), a simple alkyl aldehyde azine, underwent crisscross addition with phenyl isocyanate (PhIC) under mild conditions. To our best knowledge, this is the first example of crisscross addition of alkyl aldehyde azines. Thus, in the present communication, we report on the crisscross addition of AcAz and PhIC and its utilization to polymer formation from AcAz and 1,4-phenylene diisocyanate (Ph(IC)₂).

2. Results and discussion

AcAz reacted with two equivalents of PhIC in tetrahydrofuran THF at 25 °C to yield a colorless crystalline product in a moderate yield (63.0%). The structure of the product was examined by several techniques, including elemental analysis, EI-mass spectroscopy, and X-ray crystallography. The C, H, and N contents of the product (C, 67.03; H, 5.79; N, 17.36%) agree with those of a one-to-two adduct of AcAz and PhIC (C, 67.07; H, 5.63; N, 17.38%). The EI-mass

* Corresponding author. Tel.: +81 776 22 8111; fax: +81 776 29 7891.

E-mail address: zxd04767@nifty.com (M. Kamachi).

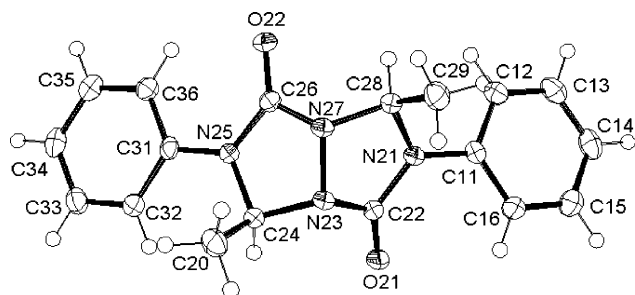
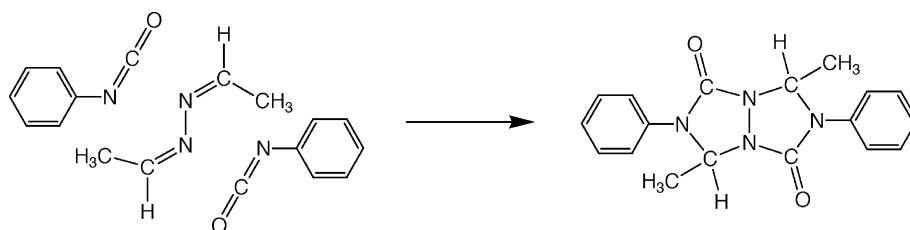


Fig. 1. Molecular structure (ORTEP [15]) for the one-to-two adduct of AcAz and PhIC.

spectrum of the product showed a peak at $m/z=322$ as a molecular ion peak, indicative of the formation of a one-to-two adduct of AcAz (MW = 84) and PhIC (MW = 119). Since we successfully obtained single crystals of the product, the chemical structure of the product was determined by X-ray crystallographic analysis (see Supporting Information). The ORTEP [15] structure in Fig. 1 indicates that the one-to-two adduct is 4,8-dimethyl-2,6-dioxo-3,7-diphenyl-1,3,5,7-tetraazabicyclo[3.3.0]octane formed by crisscross addition of AcAz and PhIC, as shown in Scheme 1. IR, Raman, and NMR spectra for the product are consistent with the structure.

Since crisscross addition of AcAz and PhIC readily proceeds in a moderate yield, we examined crisscross addition of AcAz and Ph(IC)₂ to obtain polymer. Table 1 lists the conditions and results of crisscross addition of AcAz and Ph(IC)₂ under bulk conditions. While AcAz (3.0 mol) and Ph(IC)₂ (3.0 mol) were mixed at 60 °C, the reaction mixture turned gradually from colorless to pale yellow and finally

solidified. After 6.0 h (run 6), the solid reaction mixture was crushed with a micro spatula washing with methanol and then with THF to yield a pale yellow powder in a high yield (78.4%). The powder was soluble in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), but insoluble in many organic solvents, including *n*-hexane, benzene, toluene, chloroform, diethyl ether, THF, acetone, ethanol, methanol, dimethyl sulfoxide, and *N,N*-dimethylformamide. Values of M_w for the methanol-insoluble and THF-soluble fractions were determined to be $(0.9–1.5) \times 10^3$ by GPC, indicative of polymer formation. Data in Table 1 indicate that the yield of the THF-insoluble polymer increased in the first 6.0 h (runs 1–6) and then leveled off at ca. 75% (run 7). Fig. 2(a) demonstrates how the polymer yield depends on the mole fraction of AcAz in the feed (x_{AcAz}). This figure seems to exhibit a maximum of the polymer yield around $x_{AcAz}=0.50$. It should be noted that the polymer yields at $x_{AcAz}<0.5$ are lower than the dotted line, which represents the polymer yield calculated for alternating copolymerization, while those at $x_{AcAz}>0.5$ are higher. Since, in crisscross addition, an azine reacts with two equivalents of dienophile, the polymer formed from AcAz and Ph(IC)₂ may be composed of n molecules of AcAz and $(n+1)$ molecules of Ph(IC)₂, where n denotes a natural number (Scheme 2). Thus, in the case where the mole number of Ph(IC)₂ is larger than that of AcAz in the feed (i.e. $x_{AcAz}<0.5$), low molecular weight oligomers may be formed dominantly, resulting in lower polymer yields. Fig. 2(b) shows the mole fraction of AcAz in copolymer (X_{AcAz}) as a function of x_{AcAz} . As x_{AcAz} is increased, X_{AcAz} gradually increases from ca. 0.36 to ca. 0.51 in the region $0.10 \leq x_{AcAz} \leq 0.70$, and then only slightly decreases to ca. 0.47 in the region $0.70 \leq x_{AcAz} \leq 0.90$. This dependency of



Scheme 1. 'Crisscross' addition of AcAz with PhIC.

Table 1
Conditions and results of 'crisscross' addition of AcAz and Ph(IC)₂ under bulk conditions

Run	AcAz (mmol)	Ph(IC) ₂ (mmol)	Time (h)	Yield ^a (%)	Yield ^b (%)	$M_w \times 10^{-3c}$	M_w/M_n^c
1	3.0	3.0	0.5	2.6	2.6	0.9	1.3
2	3.0	3.0	1.0	6.7	14.0	0.9	1.3
3	3.0	3.0	1.5	12.3	16.0	1.1	1.4
4	3.0	3.0	2.0	23.0	15.0	1.2	1.3
5	3.0	3.0	3.0	55.4	36.4	1.1	1.4
6	3.0	3.0	6.0	78.4	10.9	1.5	1.4
7	3.0	3.0	24	74.8	19.0	1.2	1.7

At 60 °C.

^a For the THF-insoluble fraction based on the total amount of AcAz and Ph(IC)₂.

^b For the methanol-insoluble and THF-soluble fraction based on the total amount of AcAz and Ph(IC)₂.

^c Determined by GPC for the methanol-insoluble and THF-soluble fraction. Molecular weights were calibrated with polystyrene standards.

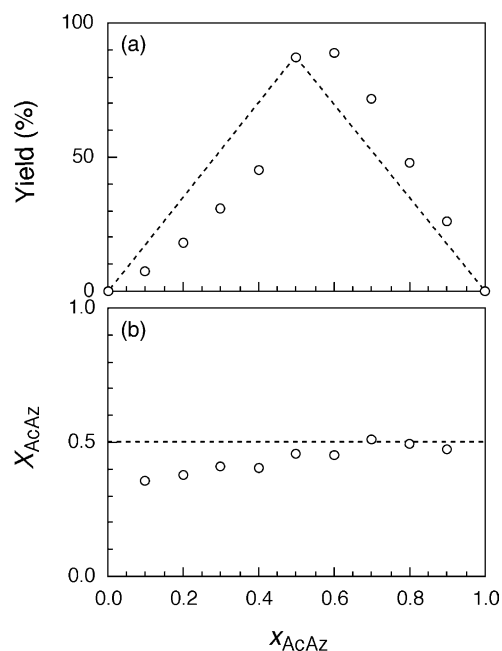


Fig. 2. The copolymer yield (a) and the mole fraction of AcAz in copolymer (X_{AcAz}) (b) as a function of the mole fraction of AcAz in the feed (x_{AcAz}).

X_{AcAz} on x_{AcAz} is also explained by the effect of the chain end. These observations indicate that the polymers were formed through crisscross addition of AcAz and $Ph(IC)_2$.

The structure of the polymer obtained was investigated by IR and 1H NMR spectroscopies, in comparison with the spectra for the one-to-two adduct. Fig. 3 shows the IR spectra for the one-to-two adduct and the polymer obtained. In both the spectra, there are absorption bands due to the stretching vibration of the C=O bond around 1720 cm^{-1} [16]. Absorption bands in the region $1500\text{--}1520\text{ cm}^{-1}$ are assignable to the stretching vibration of the phenyl or phenylene ring [16]. It is noteworthy that the IR spectrum of the polymer

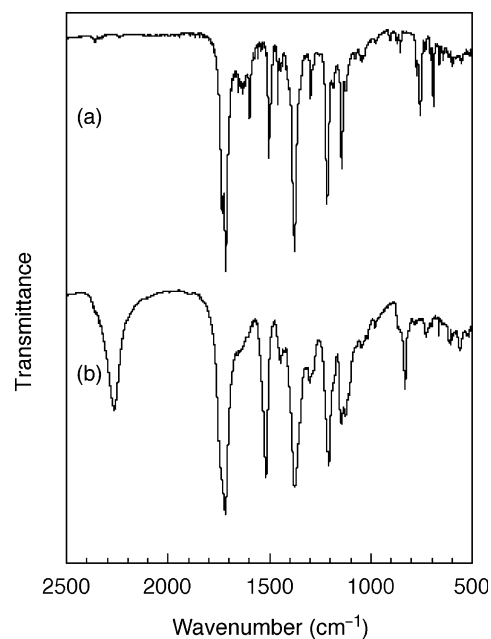
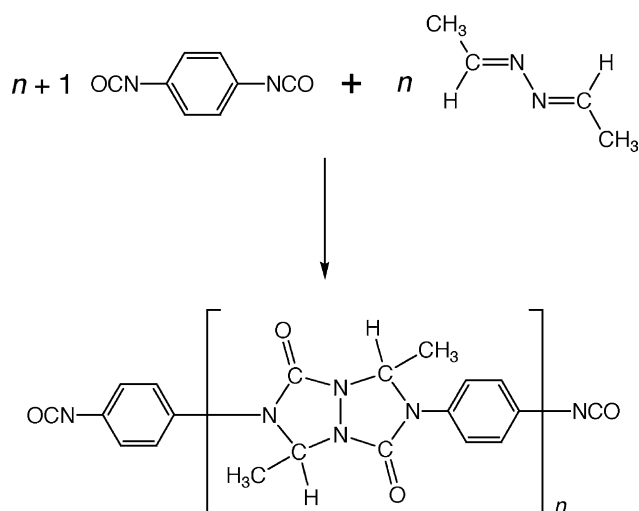


Fig. 3. IR spectra for the one-to-two adduct of AcAz and $PhIC$ (a) and the polymer obtained (b) (KBr disk).



Scheme 2. Polymer formation through 'crisscross' addition of AcAz and $Ph(IC)_2$.

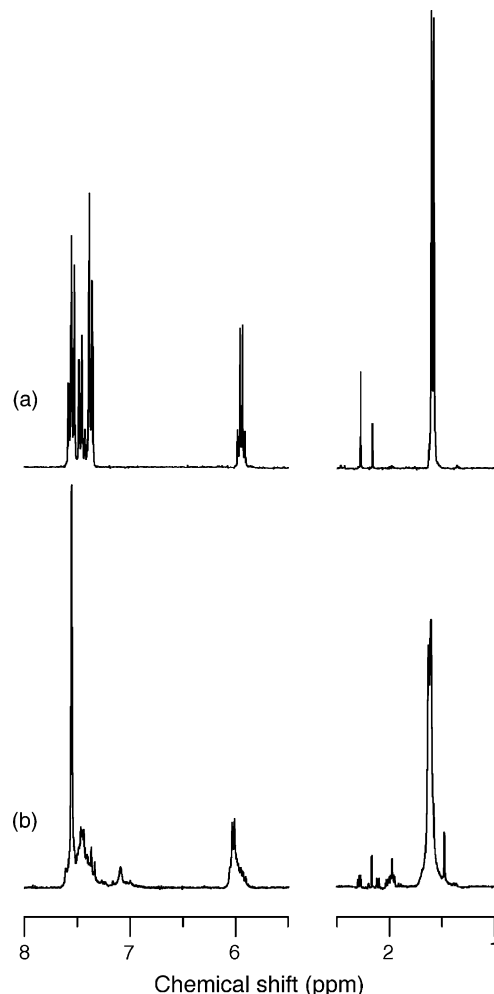


Fig. 4. 1H NMR spectra for the one-to-two adduct of AcAz and $PhIC$ (a) and the polymer obtained (b) in HFIP.

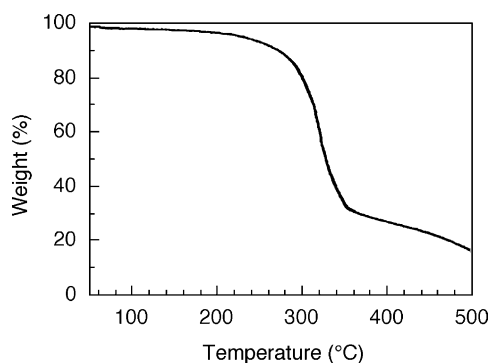


Fig. 5. TGA curve for the polymer obtained under a slow steam of nitrogen (10 mL/min). The amount of sample was 2.16 mg, and the heating rate was set at 10 °C/min.

exhibits an absorption band due to the asymmetric stretching vibration of the -N=C=O bond around 2270 cm^{-1} [16], indicating that the polymer carries unreacted -N=C=O groups at the chain ends. Fig. 4 shows the ^1H NMR spectra for the one-to-two adduct and the polymer obtained. In both the spectra, resonance bands around 1.6 and 6.0 ppm are ascribable to the methyl and methine protons, respectively [17]. There are resonance bands due to the phenyl protons in the region 7.3–7.7 ppm [17]. These spectroscopic data confirms that the polymer obtained was formed through crisscross addition of AcAz and Ph(IC)_2 , as shown in Scheme 2.

Since the polymer obtained contains bicyclic moieties and phenylene rings in the main chain, the polymer may exhibit unique thermal properties. Thus, the thermal behavior of the polymer was investigated by thermogravimetric analysis (TGA) (Fig. 5). As the temperature was increased, a gradual weight loss started at ca. 220 °C, followed by a rapid decomposition in the temperature region 280–350 °C. As the temperature was further increased up to 500 °C, the residual weight decreased gradually to ca. 15%. This observation implies that the polymer obtained is promising as a thermally stable material.

Considering the structure of the polymer obtained (i.e. bicyclic and phenylene groups), the polymer may act as a semi-flexible polymer in solution and exhibit liquid crystallinity [18]. Furthermore, since the polymer bears reactive isocyanate groups at the chain ends, it can be used as precursor for functional block copolymers. Now, we are investigating to optimize the polymerization condition for preparation of higher molecular weight polymers.

3. Conclusions

AcAz underwent crisscross addition with two equivalents of PhIC to yield a one-to-two adduct in a moderate yield (63.0%). To our best knowledge, this is the first example of crisscross addition of alkyl aldehyde azines. Utilizing crisscross addition of AcAz, polymeric products were obtained from AcAz and Ph(IC)_2 as THF-insoluble pale yellow powder in a high yield (>80%). The structure of the polymer obtained was

characterized by IR and ^1H NMR spectroscopies. The thermal behavior of the polymer was also investigated by TGA.

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Supplementary data

Supplementary data associated with this article can be found at doi:10.1016/j.polymer.2005.11.056

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