Chemoselective Synthesis of Diamines with Cationically Polymerizable Groups and Polyimides Synthesis

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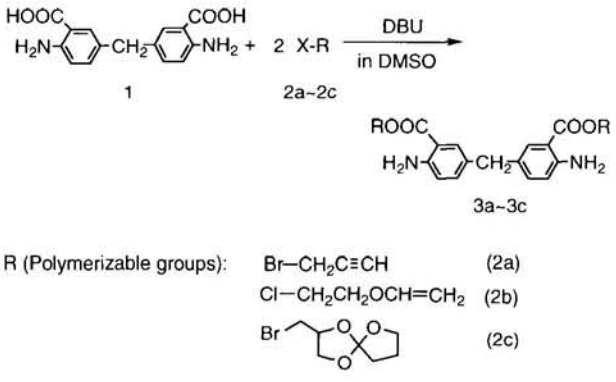
Functional diamines with cationically polymerizable groups were successfully prepared in one-step by the chemoselective reaction of 4,4'-diamino-3,3'-dicarboxydiphenylmethane (**1**) using 1,8-diazabicyclo-[5.4.0]-7-undecene (DBU). The reaction of **1** with propargyl bromide (**2a**), 2-chloroethyl vinyl ether (**2b**), and 2-bromomethyl-1,4,6-trioxa-spiro[4.4]nonane (**2c**) using DBU proceeded chemoselectively under mild conditions without any protection of the amino group to produce the corresponding diamines (**3a-3c**) in high yields.

Photosensitive polyimides containing polymerizable groups have been synthesized by two methods. A method is the polymerization of monomers with the polymerizable groups, and the another is the chemical modification of polyimides or their precursors. Horie et al.[1] reported a photosensitive polyimide containing epoxy group which was synthesized by the reaction of polyimide having pendant hydroxy group with epichlorohydrin. In general, it is difficult to obtain quantitative conversion in polymer reactions. Thus, the approach to synthesize photosensitive polyimides using functional diamine monomers has an advantage from the viewpoint of molecular design. In general, synthetic methods of the diamines contain several process such as protections of amino group, introduction of polymerizable groups, and deprotections. Ueda et al.[2] reported a synthesis of the diamine containing a vinyl ether group by a chemoselective reaction of a diamine with hydroxy group in the two-step process. Although chemoselective reaction is excellent methods for the synthesis of the functional diamines, there is no report on the one-step chemoselective synthesis of functional diamines.

This paper reports on successful synthesis of functional diamines with cationically polymerizable groups such as propargyl, vinyl ether, and a spiro ortho ester groups[3,4] by the one-step chemoselective reaction of **1** using DBU as a strong organic base.

A typical procedure for the reaction of **1** with alkyl halides is as follows; the reaction of **1** (0.143 g 0.5 mmol) with propargyl bromide (**2a**) (0.143 g 1.2 mmol) was carried out using DBU (0.181 g 1.2 mmol) in dimethylslufoxide (DMSO 1 ml) at 50 °C for 48 h. The reaction mixture was diluted with ethyl acetate, washed twice with water and dried using $MgSO_4$. After $MgSO_4$ was filtered off, the solvent was then evaporated *in vacuo* to obtain a product. The product thus obtained was recrystallized from chloroform/n-hexane to obtain the purified product in 96% yield (mp: 58.7-60.0 °C).[5] In the IRspectrum of the product (**3a**), the absorption peak at 3500, 1690 cm^{-1} due to the carboxy group of **1** was not observed at all, and the absorption peaks appeared at 1693 cm^{-1} due to the C=O stretching and at 1195 cm^{-1} due to a C-O-C stretching of a ester group. In the ^{1}H-NMR spectrum of **3a**, the signals due to the propargyl ester moiety were observed at 3.40 and 4.81 ppm with the expected intensity ratios, and the signals due to the amino group was observed at 6.51 ppm with the reasonable intensity ratio. These results proved that the reaction of **1** with **2a** using DBU proceeded chemoselectively to provide the targeted diamine **3a** as shown in Scheme 1.



Scheme 1. Chemoselective synthesis of functional diamines.

Table 1. Synthesis of various diamine monomer[a]

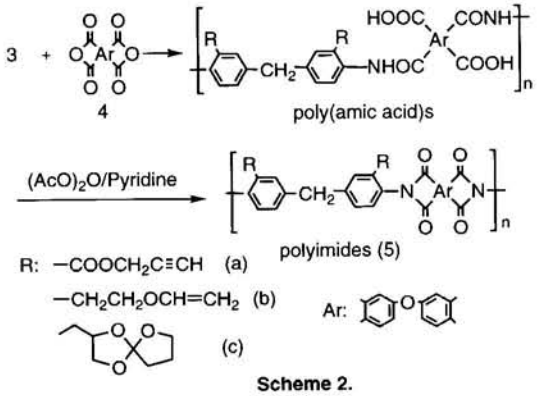
Run	Alkyl halide	Temp / °C	Time / h	Yield / %
1	**2a**	rt	24	79
2	**2a**	rt	48	96
3	**2b**	rt	24	4
4	**2b**	50	24	72
5	**2b**	70	48	88
6	**2c**	rt	24	20
7	**2c**	50	24	65
8	**2c**	70	12	91

[a] The reaction was carried out with 1 (0.5mmol) and alkyl halides (1.2 mmol) using DBU (1.2 mmol) in DMSO (1.0 ml).

Syntheses of the functional diamines with vinyl ether or spiro ortho ester moiety were investigated using **2b** or **2c** (Table 1). Although the reaction of **1** with **2b** proceeded hardly at room temperature for 24 h (Run 3), increasing of the reaction temperature and time enhanced the reaction, and **3b** was obtained in 88% yield at 70 °C for 48 h in DMSO (Run 5). The diamine with spiro ortho ester moiety, **3c** was also prepared easily in 91% yield from the reaction of **1** with **2c** at 70 °C for 12 h (Run 8). These mean that the reactivity of the used halides is in the following order: **2b<2c<2a**. The spectral data of **3b**[6] and **3c**[7] proved that the reaction of with **2b** or **2c** proceeded chemoselectively without the protection of amino group. It is worthy of remark that the O-alkylation proceed selectively in the presence of free amino groups. Because in our previous study[8] on chemoselective reaction of aniline and benzoic acid with benzyl chloride using DBU under the similar conditions, about 20% of N-alkylation of aniline was observed as the side reaction. In the case of the reaction of **1** with the used halides, DBU seemed to

react with carboxy group to produce -COO⁻DBUH⁺ salt quantitatively, then the carboxylate anion react with the halides in a mode of nucleophilic substitution to give the targeted diamines with polymerizable groups. The N-alkylation of **1** would not proceed due to inductive effect of *o*-carboxy group which decrease the nucleophilicity of the amino group.

To estimated the usefulness of the prepared diamines with bulky functional groups at *o*-position, the synthesis of polyimides by polyaddition with tetracarboxylic dianhydrides following chemical cyclization was conducted. As an example, **3a** with propargyl ester group was reacted with 4,4'-oxydiphthalic anhydride (**4**) in DMSO at room temperature for 8 h to produce a poly(amic acid)s in high yield. The poly(amic acid)s was then converted toward polyimide (**5a**) by cyclization with acetic anhydride/pyridine at 90 ℃ for 24 h. The structure of **5a**[9] was identified by IR and ^{1}H-NMR spectra, and the degree of imidization of the obtained polyimide was estimated by ^{1}H-NMR to be 100%. The number average molecular weight (Mn) estimated by GPC was 3400.



Scheme 2.

Table 2. Synthesis of various polyimides

Diamine	Polyaddition[a] Time h	Imidization[b] Temp °C	Time h	Yield % [c]	D.I. % [d]	Mn x10^{-3} [e]	Mw/Mn[c]
3a	8	90	24	50	100	3.42	1.31
3b	8	rt	5	83	94	11.6	1.52
3c	6	rt	12	59	89	5.10	1.24

[a] The reaction was carried out with various diamines (0.5mmol) and tetracarboxylicdianhydride (0.5 mmol) in DMSO (1.0 ml) at rt. [b] Used acetic anhydride / base as dehydrating agent. [c] Insoluble parts in methyl alcohol. [d] Degree of imidization determined by ^{1}HNMR. [e] Estimated by GPC based on polystyrene standards.

The polyimides **5b** and **5c** were synthesized easily from the reaction of **3b** or **3c** with **4** (Table 2). Therefore, it was found that the new diamines have good reactivity in polyaddition with tetracarboxylic dianhydrides followed by cyclization toward polyimides.

In summary, the functional diamines with cationically polymerizable groups were successfully synthesized in one-step process by the chemoselective reaction of **1** with **3** using DBU under mild conditions. The diamines are useful materials for the synthesis of photosensitive polyimides. The study on synthesis, characterization and photoinitiated cationic polymerization of the prepared polyimides are now in progress.

References and Notes

1 H. S. Yu, T. Yamashita, and K. Horie, *Macromolecules*, **29**, 114 (1996).

2 I. Suzuki, J. Sugiyama, M. Ueda, H. Okunoyama, and M. Kakuta, *Polymer Preprints, Japan*, **42**, 2, 484 (1993).

3 K. Bodenbenner, *Ann.*, **625**, 183 (1959).

4 T. Endo and W. J. Bailey, *J. Polym. Sci., Polym. Lett. Ed*, **18**, 25 (1980).

5 Spectral data of **3a**: IR (KBr, cm^{-1}); 3480, 3376 (ν N-H) 3290 (ν C-H) 2940 (ν C-H) 2124 (ν C≡C) 1693 (ν C=O) 1624 (ν C=C aromatic) 1587 (σ N-H) 1195 (ν C-O-C) ^{1}H-NMR (60 MHz, DMSO-d_6, TMS); δ ppm: 3.40 (s, 2.0 H, ≡CH) 3.61 (s, 2 H, -CH_2-) 4.85 (s, 4.0 H, -OCH_2-) 6.51 (s, 3.9 H, -NH_2) 6.82 (d, J= 8.0 Hz, 2.0 H, Ar-H) 7.10 (d, J= 8.0 Hz, 2.0 H, Ar-H) 7.59 (s, 2.2 H, Ar-H). Anal. Found: C, 69.90; H, 5.30; N, 7.48%. Calcd for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.73%.

6 Spectral data of **3b**: IR (KBr, cm^{-1}); 3484, 3376 (ν N-H) 3028 (ν C-H vinyl) 2954 (ν C-H) 1692 (ν C=O) 1621 (ν C=C) 1587 (σ N-H) 1502 (ν C=C aromatic) 1247 (ν C-O-C ether) 1194 (ν C-O-C ester) ^{1}H-NMR (200 MHz, DMSO-d_6, TMS); δ ppm: 3.64 (s, 2 H,) 3.98 (t, J= 4.2 Hz, 2.0 H, $COOCH_2$) 4.01 (dd, J= 6.6 Hz, 1.6 Hz, 4.0 H, C=CH_2) 4.24 (dd, J= 1.6 Hz, 14.2 Hz, 2.0 H, C=CH_2) 4.40 (t, J= 4.2 Hz, 4.0 H, CH_2OC) 6.51 (m, 6.0 H, CH, NH_2) 6.71 (d, J= 8.4 Hz, 2.0 H, Ar-H) 7.09 (d, J= 8.4 Hz, 2.0 H, Ar-H) 7.56 (s, 2.0 H, Ar-H). Anal. Found: C, 64.66; H, 6.17; N, 6.80%. Calcd for $C_{23}H_{26}N_2O_6$: C, 64.78; H, 6.15; N, 6.57%.

7 Spectral data of **3c**: IR (KBr, cm^{-1}); 3466, 3366 (ν N-H) 1688 (ν C=O) 1630 (ν C=C aromatic) 1589 (σ N-H) 1194 (ν C-O-C ester) 1050 (ν C-O-C spiro ortho ester) ^{1}H-NMR (200 MHz, $CDCl_3$, TMS); δ ppm: 1.90~2.27 (m, 8.0 H, -CCH_2CH_2-) 3.73 (s, 2 H, -CH_2-) 3.82~4.02 (m, 6.0 H, -CH_2-O-C-CH_2-) 4.09~4.67 (m, 8.0 H, -$COOCH_2$CH-, -C-O-CH_2-) 5.67 (br, 4.1 H, NH_2) 6.60 (d, J= 8.4 Hz, 2.0 H, Ar-H) 7.07 (d, J= 8.4 Hz, 2.0 H, Ar-H) 7.69 (s, 2.0 H, Ar-H). Anal. Found: C, 60.24; H, 5.64; N, 4.99%. Calcd for $C_{29}H_{34}N_2O_{10}$: C, 61.04; H, 6.01; N, 4.91%.

8 Unpublished data.

9 Spectral data of **5a**: IR (film, cm^{-1}); 3280 (ν ≡C-H) 2128 (ν C≡C) 1780, 1726 (ν C=O imide, ester) 1380 (ν C-N) ^{1}H-NMR (200 MHz, DMSO-d_6, TMS); δ ppm: 3.50 (s, 1.9 H, CH_2) 4.31 (s, 1.9 H, CH in propargyl) 4.86 (s, 3.9 H, CH_2 in propargyl) 7.20~8.40 (m, 12 H, Ar-H).