Chemical Bond Formation of Resin and Fluorescent Additive via Multifunctional Isocyanates

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Abstract

Chemical bond formation between polyester and a functional polymeric additive was tried by using multifunctional isocyanate (MFI) as a crosslinking agent. Reactions between desipramine, which is a monomer unit of functional polymeric additive, and MFI afforded generation of the corresponding urea type compounds. Accordingly, desipramine-containing copolymers (PAzep-Fl) were prepared as fluorescence functional additives. Chemical bond formations between polyester and PAzep-Fl via MFI were achieved by using liquid type poly(ε-caprolactone) (PCL) as a polyester. The GPC analyses of the composites suggest that chemical bonding occurs between PCL and PAzep-Fl via MFI. The fluorescence λmax of the composites had almost the same wavelength as that of chloroform solution of PAzep-Fl. These results suggest that the fluorescent function of PAzep-Fl is maintained even when a chemical bond is formed between polyester and PAzep-Fl via MFI.

Key words : Urea Bonding/Urethane Bonding/Diphenylamine with Bridged Structure/Fluorescent Additive

1. Introduction

The use of additives is the most promising method for resin modification due to its simplicity and variety. For example, to give fluorescence to transparent resins such as poly(lactic acid) (PLA) and polystyrene, we added polymers containing diphenylamine with a bridged structure, whose bridge unit was monosilane (phenazasiline: PPhenaz and PAR)¹ ² and ethylene (dibenzazepine: PAzep)³ ⁴ as shown in Fig. 1.

On the other hand, it can be expected that if both additives and resin are chemically bonded, the migration of additives can be suppressed. This led us to focus on desipramine for our research. Desipramine is a dibenzazepine derivative which has secondary

Fig. 1 Chemical structure of polymers containing diphenylamine with a bridged structure.
alkylamine on the N atom of its diphenylamine unit, and that has pharmaceutical applications such as an antidepressant\(^4,5\). When desipramine homopolymer (PAzep-a, Fig. 1) was blended with PLA and diphenylmethane 4,4’-diisocyanate (MDI, one of the multifunctional isocyanates (MFI), Fig. 2), a chemical bond formed between PAzep-a and PLA through MDI\(^3\). The difference is interesting when other MFIs are used. We have already reported that a chemical reaction occurred between polyester and MFI such as lysine diisocyanate (LDI, methyl 2,6-diisocyanatohezoxanoate, Fig. 2), and lysine triisocyanate (LTI, 2-isocyanate ethyl-2,6-diisocyanatohezoxanoate, Fig. 2)\(^6,7\), therefore, we checked if a similar reaction occurs between the monomer unit of a functional additive and MFI. So, chemical bond formation between polyester and functional additives via MFI was tried. As functional additives, desipramine-containing polymers, (PAzep-Fi, Fig. 2) were prepared, and liquid type poly(ε-caprolactone) (PCL, Fig. 2) was used as polyester.

2. Experimental

2.1 Reagents and Measurements

Desipramine hydrochloride (10,11-dihydro-5-[3-(methylamino)propyl]-5H-dibenz[b,f]azepine hydrochloride) and used MFI (MDI, LDI, LTI, hexamethylene 1,6-diisocyanate (HMDI), and dicyclohexylmethane-4,4’-diisocyanate (racemic type, H\(_{12}\)MDI)) were commercial products. Other chemicals were also used as purchased. NMR spectra were taken by using a Varian INOVA400 spectrometer, and IR spectra were taken by using a JASCO FT/IR-410 spectrometer. UV-visible spectra were measured with a JASCO V-570DS spectrometer, and fluorescence spectra were measured with a Hitachi F-4010 spectrometer.

2.2 Chemical Reaction between desipramine and MFI

2.2.1 Reaction between MDI

Under N\(_2\), MDI (0.26 g, 1.0 mmol) and desipramine (0.80 g, 3.0 mmol) obtained by the neutralization of desipramine hydrochloride by sodium hydroxide were dissolved in 5 mL of toluene and the reaction mixture was allowed to reflux for an hour. Then the mixture was poured into hexane. The precipitate was washed with ether and dried in a vacuum to give 0.72 g (0.92 mmol, 90\%) of (Azep-MDI) as a white powder.

2.2.2 Reaction between H\(_{12}\)MDI

Under N\(_2\), H\(_{12}\)MDI (0.60 g, 2.3 mmol) and desipramine (0.20 g, 0.8 mmol) were dissolved in 2 mL of toluene and the reaction mixture was stirred at 100\(^\circ\)C for 24 hours. Then the mixture was poured into hexane. Decantation of the mixture and drying the residue under vacuum gave 0.26 g (0.33 mmol, 43\%) of Azep-H\(_{12}\)MDI.

2.2.3 Reaction between HMDI

Reaction of HMDI (0.17 g, 1.2 mmol) and desipramine (0.90 g, 3.4 mmol) by the same preparation method as Azep-H\(_{12}\)MDI afforded 0.52 g (0.74 mmol, 52\%) of Azep-HMDI.

2.2.4 Reaction between LDI

Reaction of LDI (0.17 g, 0.8 mmol) and desipramine (0.60 g, 2.3 mmol) by the same preparation method as Azep-H\(_{12}\)MDI afforded 0.58 g (0.78 mmol, 97\%) of Azep-LDI.
2.2.5 Reaction between LTI
Reaction of LTI (0.11 g, 0.41 mmol) and desipramine (0.47 g, 1.8 mmol) by the same preparation method as Azep-LTI afforded 0.23 g (0.22 mmol, 52%) of Azep-LTI.

2.3 Preparation of PAzep-Fl
2.3.1 Preparation of 2,8-dibromo-10,11-dihydro-5-[3-(N-methylamino)propyl]dibenzo[b,f]azepine hydrochloride (Azep-Br)

Desipramine hydrochloride (6.10 g, 20 mmol) was dissolved in a mixture of carbon tetrachloride and chloroform (50:50 vol./vol., 200 mL), and the flask was put into an ice bath. Then, N-homosuccinimide (7.51 g, 42 mmol) was added to the flask. The reaction mixture was stirred overnight, then, temperature of the reaction mixture became room temperature. The mixture was washed in brine and dried over MgSO₄. After removal of MgSO₄ by filtration, the solvent was removed by evaporation. After evaporation of the solvent, the crude product was purified by recrystallization from hexane to give 7.76 g (17 mmol) of Azep-Br. The yield was 84%. ¹H-NMR (CDCl₃): δ 9.5 (br, 1H), 7.2-7.3 (m, 4H), 6.93 (d, 2H, J = 8.3 Hz), 3.78 (t, 2H, J = 6.8 Hz), 3.08 (s, 4H), 2.90 (t, 2H, J = 7.3 Hz), 2.47 (s, 3H), 2.0-2.2 (m, 2H) ppm. ¹³C-NMR (CDCl₃): δ 146.23, 136.06, 132.61, 129.56, 121.56, 116.07, 47.90, 47.14, 32.58, 31.51, 24.00 ppm.

2.3.2 Preparation of poly(10,11-dihydro-5-[3-(N-methylamino)propyl]dibenzo[b,f]azepine-2,8-diy1-alt-9,9-diodicyclfluorene-2,7-diyl) (PAzep-Fl-a)

2 M Na₂CO₃ (aq) (10 mL) was added under N₂ to toluene solution (10 mL) containing Azep-Br (0.47 g, 1.0 mmol) and 9,9-diodicyclfluorene-2,7-diboronic acid (0.49 g, 1.0 mmol). Then, Pd(PPh₃)₄ (59 mg, 0.05 mmol) was added to the suspension, and stirred at 90 ℃ for 72 hours. The reaction mixture was poured into water and extracted by chloroform. The organic layer was removed by filtration, and then the obtained powder was washed in brine and dried over MgSO₄. The NH unit of PAzep-Fl was converted to N-Boc by the same method as Boc-PAzep-Fl-a. Using 0.47 g of Azep-Br (1.0 mmol), 0.60 g of 9,9-diodicyclfluorene-2,7-diboronic acid (1.0 mmol), and 59.8 mg of Pd(PPh₃)₄ (0.05 mmol) afforded 0.31 g (0.41 mmol unit) of PAzep-Fl-b as an orange powder. The yield was 40%. ¹H-NMR (CDCl₃): δ 7.1-7.9 (m, 12H), 3.7-4.0 (m, 2H), 2.6-2.8 (m, 2H), 2.41 (s, 3H), 1.7-2.1 (m, 6H), 0.5-1.5 (m, 46H). Anal. Calcd for (C₃₀H₂₃N₂·0.7H₂O)₁₅Br: C 82.69%; H 9.77%; N 3.51%; Br 2.63%. Found: C 82.53%; H 9.46%; N 3.25%; Br 2.65%.

2.3.3 Preparation of poly(10,11-dihydro 5-[3-(N-methylamino)propyl]dibenzo[b,f]azepine-2,8-diy1-alt-9,9-diodocyclfluorene-2,7-diyl) (PAzep-Fl-b)

PAzep-Fl-b was prepared by the same method as PAzep-Fl-a. Using 0.47 g of Azep-Br (1.0 mmol), 0.60 g of 9,9-diodocyclfluorene-2,7-diboronic acid (1.0 mmol), and 59.8 mg of Pd(PPh₃)₄ (0.05 mmol) afforded 0.31 g (0.41 mmol unit) of PAzep-Fl-b as an orange powder.

3. Results and Discussions
3.1 Chemical bond formation between desipramine and MFI

We tried to achieve a chemical bond between desipramine-containing polymers and resins by using MFI. First, reactions between desipramine and MFI
were carried out as shown in Fig. 3 as a model reaction, referring to the literature on the reaction of diphenylamine and isocyanate$^8$. Azep-MDIs were obtained with over 40% yield. ESI-MS (Fig. 4 (a)) of the products suggested the generation of urea moiety. Then, further structural analysis was performed. IR spectra of urea are shown in Fig. 4 (b). As shown in the figure, a new signal was observed at about 1630 cm$^{-1}$ that was not observed in desipramine. The 1630 cm$^{-1}$ signal is assigned as a urea unit. $^1$H and $^{13}$C($^1$H) NMR spectra of Azep-MDI are shown in Fig. 5. In Azep-H$_{12}$MDI or Azep-LDI, the two signals assigned as NH of a urea unit were observed in $^1$H NMR spectrum. Azep-LDI has asymmetrical structures originated from LDI, therefore, two peaks assigned as NH units seem to be observed. In Azep-H$_{12}$MDI, since H$_{12}$MDI was racemate, it is thought that it originates in the space structure of the cyclohexyl group of Azep-H$_{12}$MDI. In Azep-LTI, starting MFI (LTI) has low symmetry, three peaks are observed in the NH signal.
assigned as urea units. On the other hand, in Azep-MDI and Azep-HMDI, only one kind of NH signal was observed because of high symmetry of starting MFI. As shown in the figure, when asymmetrical MFI was used, the signals assigned as the aromatic unit, urea unit (-NMe, C=O), and bridging ethylene unit of the obtained Azep-MDI were also multiplexed.

### 3.2 Preparation of desipramine-containing polymers

As a desipramine-containing polymers, PAzep-Fls (Fig. 2) were prepared as a fluorescent additive for polyester. The preparation scheme of PAzep-Fl is as shown in Fig. 6. Azep-Br was prepared from commercial desipramine hydrochloride by the reported method for bromination of N-methyldiphenylamine in 9). PAzep-Fl were prepared from the Suzuki coupling reaction of 9,9-dialkylfluorene-2,7-diboronic acid and Azep-Br. The obtained PAzep-Fl was soluble in the usual organic solvents such as chloroform. The NMR peak observed at about 2.8 ppm originated from -CH2N+H2Me in Azep-Br moved to about 2.6 ppm when the polymerization was carried out. As shown in Fig. 7, the IR spectra suggest that the absorption band at about 2300-
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2800 cm\(^{-1}\) originated from the ammonium unit of Azep-Br is disappeared by preparation of PAzep-Fl. These IR and NMR spectra suggest that most of Azep-Br’s ammonium unit was converted to amine unit by the polymerization process because the polymerizations were carried out by the basic condition. This is suggested by elemental analyses of Cl of PAzep-Fl. It is difficult to measure the molecular weight of PAzep-Fl by GPC because of the existence of the NH unit; therefore, conversion of the NH unit in PAzep-Fl to a NBoc unit was tried by the reported method\(^{12}\). As shown in Fig. 7, a new band at about 1700 cm\(^{-1}\), originating from the -NBoc unit, was observed by the reaction. The degrees of polymerization of Boc-PAzep-Fl-a and -b were determined as 6.2 and 4.6 respectively, by GPC analyses, therefore, \(M_n\) of PAzep-Fl were estimated to be about 4000 as shown in Table 1. The optical properties of desipramine-fluorene copolymers (PAzep-Fl and Boc-PAzep-Fl) are also shown in Table 1. As shown in the table, the introduction of a larger alkyl side chain had no effect on absorption and fluorescence \(\lambda_{\text{max}}\). This suggests that introducing the length of alkyl side chain of desipramine-fluorene copolymer has no effect on the \(\pi\)-conjugated main chain like poly(phenazasiline)\(^{13}\). The absorption \(\lambda_{\text{max}}\) of chloroform solution of PAzep-Fl and Boc-PAzep-Fl was about 350 nm, which is shorter than that of phenazasiline-fluorene copolymer (377 nm)\(^{14}\).

### Table 1 Molecular weight and optical properties of PAzep-Fl.

<table>
<thead>
<tr>
<th>polymer</th>
<th>(M_n \times 10^4)</th>
<th>DP(^{b})</th>
<th>UV (\lambda_{\text{max}})(^{c})</th>
<th>PL (\lambda_{\text{max}})(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAzep-Fl-a</td>
<td>4.2(^{a})</td>
<td></td>
<td>352</td>
<td>417</td>
</tr>
<tr>
<td>Boc-PAzep-Fl-a</td>
<td>4.7 (1.4)(^{d})</td>
<td>6.2</td>
<td>351</td>
<td>418</td>
</tr>
<tr>
<td>PAzep-Fl-b</td>
<td>3.6(^{a})</td>
<td></td>
<td>347</td>
<td>418</td>
</tr>
<tr>
<td>Boc-PAzep-Fl-b</td>
<td>4.0 (2.3)(^{d})</td>
<td>4.6</td>
<td>331</td>
<td>419</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined by GPC (eluent = CHCl\(_3\), polystyrene standards). The figures in parentheses are \(M_n/M_w\).

\(^{b}\) The average degree of polymerization was calculated from GPC data and the molecular weight of the repeating unit.

\(^{c}\) CHCl\(_3\) solution.

\(^{d}\) Determined from DP of corresponding Boc-PAzep-Fl.

\(^{e}\) \(M_w/M_n\) was shown in the parentheses.

The difference seems to come from the difference of the flatness around the N atom of the diphenylamine unit. This is measured from X-ray analyses of the corresponding monomer unit\(^{15,16}\). Chloroform solutions of both PAzep-Fl and Boc-PAzep-Fl show fluorescence \(\lambda_{\text{max}}\) at about 420 nm.

### 3.3 Chemical bond formation between PAzep-Fl and PCL

The composites are prepared by the reactions between hydroxy-terminated liquid type PCL, MFI (10 phr) and PAzep-Fl (1 phr) to achieve chemical bond formation between the resin and the functional additive. The composition of the materials is shown in Table 2, and the obtained composites are viscous liquids. Determination of chemical bond formation was carried out by measurement of the molecular weight of the composite by GPC. As described above, MFI and desipramine (monomer unit of PAzep-Fl) react to give the urea type compound Azep-MFI, and we already reported chemical bond formation between PCL and MFI\(^7\). So, in this project, we expected chemical bond formation between PAzep-Fl and PCL via MFI. The molecular weight of the final composite containing PAzep-Fl can be measured by GPC, although the molecular weight of PAzep-Fl couldn’t be measured by GPC, because the NH unit of PAzep-Fl in the final composite will be converted to urea unit. If a reaction occurs between PCL and MFI, the molecular weight of the obtained composite will be larger than starting PCL because of the formation of urethane (PCL + MFI, Fig. 8). When PAzep-Fl was added to the polyurethane type composite (PCL + MFI), the molecular weight of the obtained composite (PAzep-Fl + MFI + PCL, Fig. 8) will be larger than that of the polyurethane type composite (PCL + MFI)
because of urea bond formation (PAzep-Fl + MFI, Fig. 8). As shown in Table 2, the molecular weight of the composite with PAzep-Fl was larger than that without PAzep-Fl. In addition, molecular weight of the composite with MFI was larger than that without MFI from comparison between MFI-containing composite (sample-1, sample-3, sample-5, sample-7, and sample-9) and sample-11 (without MFI). Moreover, the composite has low solubility resulting from the addition of PAzep-Fl to the composite, because of formation of a cross-linked structure by introduction of PAzep-Fl. This suggested that MFI reacts with both PCL and PAzep-Fl as shown in Fig. 8.

PAzep-Fls are prepared as fluorescent functional additives. So, the fluorescence properties of the composites were investigated. As shown in Table 2, the fluorescent $\lambda_{\text{max}}$ of the composites were almost same as that of the solution.

Although the densities of PAzep-Fl-b (1.03 g/cm$^3$) and PCL (1.08 g/cm$^3$) were different, PAzep-Fl has good dispersibility with PCL without aggregation of PAzep-Fl or sinking into PCL. Some of the $\pi$-conjugated compound aggregated to the surface of the blend composite because $\pi$-conjugated compound had only low compatibility with solid type PCL. However, it is thought that the reason why PCL and PAzep-Fl have good compatibility is because the obtained PAzep-Fl-containing composite was liquid.

4. Conclusions

Desipramine was an effective unit for chemical bond formation with polyester via MFI. Selection of additive or resin is also important for the development of adhesives. Although in this paper, PAzep-Fls were prepared as desipramine-containing functional polymers, it is expected that combining them with other functional units will lead to the important developments in various fields.

**Table 2** Prepared PAzep-Fl-containing composites and their data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PAzep-Fl-b</th>
<th>Used MFI (10 phr)</th>
<th>f</th>
<th>$M_w \times 10^{-3}$</th>
<th>$M_w/M_n$</th>
<th>PL $\lambda_{\text{max}}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1</td>
<td>1 phr</td>
<td>MDI</td>
<td>2</td>
<td>5.4</td>
<td>1.9</td>
<td>416</td>
</tr>
<tr>
<td>sample 2</td>
<td>0 phr</td>
<td>MDI</td>
<td>2</td>
<td>4.4</td>
<td>1.9</td>
<td>-</td>
</tr>
<tr>
<td>sample 3</td>
<td>1 phr</td>
<td>H$_2$MDI</td>
<td>2</td>
<td>4.9</td>
<td>1.7</td>
<td>420</td>
</tr>
<tr>
<td>sample 4</td>
<td>0 phr</td>
<td>H$_2$MDI</td>
<td>2</td>
<td>3.4</td>
<td>1.9</td>
<td>-</td>
</tr>
<tr>
<td>sample 5</td>
<td>1 phr</td>
<td>HMDI</td>
<td>2</td>
<td>5.6</td>
<td>2.2</td>
<td>416</td>
</tr>
<tr>
<td>sample 6</td>
<td>0 phr</td>
<td>HMDI</td>
<td>2</td>
<td>5.0</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>sample 7</td>
<td>1 phr</td>
<td>LDI</td>
<td>2</td>
<td>4.1</td>
<td>2.2</td>
<td>418</td>
</tr>
<tr>
<td>sample 8</td>
<td>0 phr</td>
<td>LDI</td>
<td>2</td>
<td>4.0</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>sample 9</td>
<td>1 phr</td>
<td>LTI</td>
<td>3</td>
<td>6.8</td>
<td>4.5</td>
<td>415</td>
</tr>
<tr>
<td>sample 10</td>
<td>0 phr</td>
<td>LTI</td>
<td>3</td>
<td>6.4</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td>sample 11</td>
<td>1 phr</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>2.3</td>
<td>416</td>
</tr>
</tbody>
</table>

- Determined by GPC (eluent = CHCl$_3$, polystyrene standards). The figures in parentheses are $M_w/M_n$.
- Cast film.

Fig. 8 Scheme of chemical bond formation between PAzep-Fl and PCL via MFI.
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References