Preparation of Dibenzazepine-containing Polymers and Use as Fluorescent Functional Additives for Estimating Plastic Blend

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Dibenzazepine-containing polymers were prepared by various polymerization methods and the effects of adding the obtained polymers to plastics were investigated. Dibenzazepine homopolymers were prepared by the oxidative polymerization of commercially available dibenzazepine derivatives and by the dehalogenative polymerization of corresponding dibromodibenzazepines. Dibenzazepine copolymers were prepared from dibromodibenzazepines. The addition of polymers to plastics afforded fluorescent function to them. The fluorescent behavior of a blend composite depended not only on the chemical structure of the polymers, but also on the plastic used as the matrix. The effects of adding dibenzazepine-containing polymer in plastic blends were investigated. When the compatibility of the plastic blend was higher, the fluorescence λ_{max} of the blend became shorter. This suggested that the method using a dibenzazepine-containing polymer is adaptive for estimating of the compatibility of the blend composite by the simple method.

Keywords Dibenzazepine-containing polymer, fluorescent additive, plastic blend, estimation of compatibility

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1 Introduction

Polymers containing diphenylamine a with bridging structure (Fig. 1) at their main chain, such as O,¹ S,²⁻⁴ SO,^{3,4} SO₂,⁴ -CH₂CH₂-,^{5,6} and -SiR₂-,⁷⁻¹⁰ often show interesting optical and

electrochemical properties, and thus have been researched. Our group has reported about Si unit-bridged diphenylamine-containing polymers as electric devices,¹¹⁻¹⁷ conjugation with DNA^{11,18,19} and carbonnanotubes.^{11,20}

On the other hand, diphenylamines with a bridging structure are expected to have thermal stability.⁷ Therefore, these compounds were selected as additives for plastics because these types of polymers seem to be useful as functional additives in plastics, by using a thermal melting process usually used in processing plastics. Usually, plastics are functionalized by additives. Therefore, many additives for plastics have been widely researched.

Poly(lactic acid) (PLA, Fig. 2) was used as the plastic. PLA is a synthetic biopolymer derived from biomass through bioconversion and polymerization,^{21,22} and therefore the modification and functionalization of PLA are widely researched.²³⁻³⁹ Our group has developed additives for PLA, such as a nucleating agent,^{40,41} a layered silicate,⁴² and a chemically modified poly(3-hydroxyalkanoate).⁴³ On the other hand, to make PLA with fluorescence function, we added

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Fig. 1 Chemical structure of poly(diphenylamine)s with a bridged structure and relative polymers.

Fig. 2 Chemical structure of plastics and the reaction scheme of the reactive blend (RB).

polymers containing diphenylamine with a monosilane-bridging unit (**PPhenaz**, Fig. 1).^{12,44,45}

However, it needs several steps to prepare phenazasiline-containing polymers because phenazasiline unit compounds are not usually purchased; therefore, simplification of the preparation process of the polymer is needed. In the present work, dibenzazepine was selected as diphenylamine with a bridged structure because some dibenzazepine derivatives are commercially available products.⁴⁶⁻⁴⁸ Thus, investigating the preparation of dibenzazepine-containing polymers and the use

of polymers as the functional additives for plastics are carried out.

By the way, plastics are sometimes used as blend composites of two or more kinds of plastics. For example, PLA's mechanical properties have been improved by a reactive blend (RB), which is a method of adding multifunctional isocyanates, such as lysine triisocyanate (LTI, Fig. 2) as compatibilizers. The present method is the addition of LTI as a reagent to the terminal hydroxyl group of polyesters, such as PLA, poly(ϵ -caprolactone) (PCL, Fig. 2),⁴⁹ and poly(butylenesuccinate)

(PBS, Fig. 2).⁵⁰ It is usually necessary for estimating compatibility to use difficult techniques, such as using AFM and measuring the physical properties. These estimation methods sometimes need a high level or complicated techniques or breaking samples; consequently, a blend estimation by a simple and easy method is needed. Therefore, the fluorometry was chosen as the estimation method of compatibility of plastic blends, because this is an easy and nondestructive method. The method for estimating compatibility by measuring fluorescence spectra has already been reported,¹² but that method needed two kinds of fluorescent additives (**PPhenaz-a** and **PAR-a**, Fig. 1). However, further simplification is needed. In this paper, it is described that the investigation of a simple method for estimating the compatibility of a plastic blend, by using dibenzazepine-containing polymers as a fluorescent probe, as in Fig. 3.

2 Preparation of Dibenzazepine Homopolymers and Their Use as Functional Additives for Plastics

2-1 Preparation by oxidative polymerization⁵¹

As described above, dibenzazepine derivatives are expected as properties of diphenylamine, and some *N*-substituted dibenzazepine derivatives show physiological activity. Therefore, it should be easier to develop dibenzazepine-containing polymers than phenazasiline-containing polymers, because some dibenzazepine derivatives are commercially

available products.

First, the oxidative polymerization of dibenzazepine derivatives, which are commercial products, was carried out. Oxidative polymerization is known to be one of the most convenient polymerization methods,^{52,53} and poly(arylamine) type polymers were prepared by this method.^{13,54,55} Accordingly, **PAzep-as** were prepared by the oxidative polymerization of corresponding **Azeps**, as shown in Fig. 4, by referring to the literature.¹³ The prepared polymers are shown in Table 1. Generally, polymers prepared from oxidative polymerization were dedoped by dedoping reagents, such as hydrazine monohydrate (for the preparation of poly(diphenylamine)s¹³) and methanol (for the preparation of poly(thiophene)s⁵³). In this polymerization, hydrazine monohydrate was used as the dedoping reagent. Therefore, polymers with an *N*-aminoalkyl substituent were obtained by neutralizing their hydrochloride unit because hydrazine monohydrate was used as a dedoping reagent, and it worked not only as a dedoping reagent, but also as a base.

The fluorescence intensities of **PAzep-a**-added plastics were stronger than that of raw plastic, suggesting that **PAzep-as** are effective as fluorescent additives.

2-2 Preparation by dehalogenative polymerization^{56,57}

Oxidative polymerization is a convenient method for the preparation of polymers, but sometimes the juncture of the polymer was not controlled. Therefore, dehalogenative polymerization was adopted, because this method gives structurally well-defined π -conjugated polymers.^{58,59} In this way, dibromodibenzazepine derivatives (**Azep-Brs**) were prepared and polycondensations of **Azep-Brs** by Ni complexes⁵⁸ were carried out to obtain **PAzep-bs**, as shown in Fig. 5, and the prepared **PAzep-bs** are given in Table 2.

The absorption $\lambda_{\max}$ of a polymer with H on the side chain (**PAzep-b1**) is longer than that of *N*-alkyl substituted polymers, especially prepared by dehalogenative polymerization. This result was almost the same as that of poly(phenazasiline)¹⁵ and poly(diphenylamine).⁶⁰ However, the absorption $\lambda_{\max}$ of **PAzep-as** was different from that of **PAzep-bs**, suggesting that the optical properties of **PAzeps** depend on their preparation method.

Fig. 3 Scheme of estimating the compatibility of plastic blends in this paper.

Table 1 Prepared **PAzeps** by oxidative polymerization and used monomers

Polymer	R ¹	R
PAzep-a1	H	H
PAzep-a2	-CH ₂ CH ₂ CH ₂ NHMe ₂ Cl	-CH ₂ CH ₂ CH ₂ NMe ₂
PAzep-a3	-CH ₂ CH ₂ CH ₂ NH ₂ MeCl	-CH ₂ CH ₂ CH ₂ NHMe

Fig. 4 Oxidative polymerization scheme of **Azeps**.

Fig. 5 Preparation scheme of **PAzep-bs**.Table 2 Optical properties of **PAzep-bs**

Polymer	X	R	Absorption $\lambda_{\text{max}}/\text{nm}^a$	Fluorescence $\lambda_{\text{max}}/\text{nm}^{a,b}$
PAzep-b1	$-\text{CH}_2\text{CH}_2-$	H	344 ^c	409 ^c
PAzep-b2	$-\text{CH}_2\text{CH}_2-$	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$	321	411
PAzep-b3	$-\text{CH}_2\text{CH}_2-$	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{NHMe}$	321 ^c	406 ^c
PAzep-b4	$-\text{CH}_2\text{CH}_2-$	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{NMeBoc}$	321	404
PAzep-b5	$-\text{CH}_2\text{CH}_2-$	Me	332 ^c	395 ^c

a. CHCl_3 solution.b. Excited at absorption λ_{max} .c. CHCl_3 soluble part. X = $-\text{SiMe}_2-$: **PPhenaz-Me**X = $-\text{SiMe}_2\text{SiMe}_2-$: **PDSiAzep**X = $-\text{SiMe}_2\text{OSiMe}_2-$: **PSiO**

Fig. 6 Polymers for comparing optical properties.

The optical properties of poly(*N*-alkyldiphenylamine)s with a bridged structure were compared. A comparison of the polymers' optical properties with **PAzep-b5** is shown in Fig. 6.¹⁷ The absorption λ_{max} of the polymer was in the order $\text{Si} > \text{CH}_2\text{CH}_2 > \text{SiOSi} > \text{SiSi}$, as shown in Table 3. To investigate the effect of the structure, the X-ray data of the monomers were compared.^{17,61} The sums of the angles around the N of the diphenylamine unit are also given in Table 3. As shown in the table, the sums of the bond angles around the N atom of the corresponding monomers were in the order **PPhenaz-a** > **PAzep-5b** > **PSiO** > **PDSiAzep**. These results suggest that the absorption λ_{max} of this type of polymers also depends on the flatness around the N atom of the monomer unit.

The addition of **PAzep-b** to plastic gave the same fluorescence

Table 3 Comparison between the absorption λ_{max} of polymers and the flatness of the N atom of corresponding monomers

Polymer	X	Absorption $\lambda_{\text{max}}/\text{nm}^a$	Sum of bond angles around the N atom of relative monomeric compound/deg
PAzep-b5	$-\text{CH}_2\text{CH}_2-$	332 ^b	351.5 ^c
PPhenaz-Me	$-\text{SiMe}_2-$	361 ^{b,d}	358.5 ^d
PDSiAzep	$-\text{SiMe}_2\text{SiMe}_2-$	274 ^d	337.8 ^d
PSiO	$-\text{SiMe}_2\text{OSiMe}_2-$	315 ^d	341.2 ^d

a. CHCl_3 solution.b. CHCl_3 soluble part.

c. Data of **Azep-2-HCl** from Ref. 61. Two types of crystals were observed. The angle shown in the table was the average value (the angles were 354.7° and 348.3°).

d. Data from Ref. 17.

Fig. 7 Fluorescence spectra of PLA with 0.005 phr **PAzep-b5** (solid line) and without **PAzep-b5** (dotted line).

as by the addition of **PAzep-a**. The fluorescence spectra of **PAzep-b**-added PLA and raw PLA are shown in Fig. 7. The efficiency of the fluorescent additive of **PAzep-b** seems to be higher than that of **PAzep-a**. The change of this efficiency

Fig. 8 Preparation scheme of **PAzep-FIs**.Table 4 Prepared **PAzep-FIs** and optical properties of polymers

Polymer	R'	R''	CHCl ₃ solution absorption $\lambda_{\text{max}}/\text{nm}^a$	CHCl ₃ solution fluorescence $\lambda_{\text{max}}/\text{nm}^{a,b}$	Cast Film fluorescence $\lambda_{\text{max}}/\text{nm}^{a,c}$
PAzep-FI-a8	H	-C ₈ H ₁₇	352	417	439
PAzep-FI-a12	H	-C ₁₂ H ₂₅	347	418	436
PAzep-FI-b8	Me	-C ₈ H ₁₇	346	420	434
PAzep-FI-b12	Me	-C ₁₂ H ₂₅	353	426	438

a. CHCl₃ solution.b. Excited at absorption λ_{max} .c. Cast from CHCl₃.Table 5 Prepared PLA/PCL blend composites and their fluorescence λ_{max}

Sample	PLA, wt%	PCL, wt%	Added PAzep-FI ^a	LTI/ phr	Fluorescence $\lambda_{\text{max}}/\text{nm}^b$
PLA-a	100	0	PAzep-FI-a (0.01)	0	412
PLA-aT	100	0	PAzep-FI-a (0.01)	0.5	405
PCL-a	0	100	PAzep-FI-a (0.01)	0	435
PCL-aT	0	100	PAzep-FI-a (0.01)	0.5	415
PLA-b	100	0	PAzep-FI-b (0.01)	0	421
PLA-bT	100	0	PAzep-FI-b (0.01)	0.5	412
PCL-b	0	100	PAzep-FI-b (0.01)	0	438
PCL-bT	0	100	PAzep-FI-b (0.01)	0.5	429

a. The figures in parenthesis show the added ratio (phr).

b. Excited at absorption λ_{max} of **PAzep-FI** in CHCl₃.

seems to be because of the following reasons. The first is that there are no structure defects in **PAzep-b**. The other is that **PAzep-a** was dedoped by the dedoping reagent, but sometimes a small amount of dopant remained in the polymers, so the dopant reduced the efficiency as the fluorescence additive.

3 Preparation of Dibenzazepine Copolymers and Their Use as Functional Additives for Plastics

3-1 Preparation of dibenzazepine copolymers^{62,63}

Azep-Brs can be useful not only as a monomer of dibenzazepine homopolymers, but also as a monomer of dibenzazepine copolymers, because many copolymers have been prepared from corresponding dibromide by cross-coupling reactions.⁵⁸ Therefore, the preparation of dibenzazepine-containing copolymers (**PAzep-FI**) by using **Azep-Br** as monomers, and their use as a functional additive for plastics were investigated.

The preparation scheme of **PAzep-FI** is shown in Fig. 8. **PAzep-FIs** were prepared from the Suzuki-Miyaura coupling reaction^{9,58} of corresponding dibromodibenzazepines (**Azep-2-Br-HCl** and **Azep-3-Br-HCl**) and 9,9-dialkylfluorene-2,7-diboronic acid; the resulting polymers are shown in Table 4. The obtained **PAzep-FI** was soluble in the usual organic solvents, such as chloroform and THF. These IR and NMR spectra suggest that most of dibromodibenzazepines' (**Azep-2-Br-HCl** and **Azep-3-Br-HCl**) ammonium unit was converted to amine unit by the polymerization process, because the polymerizations were carried out under the basic condition. Neutralization of the polymers is also suggested by elemental analysis of the Cl content of the polymers.

The optical properties of **PAzep-FIs** are given in Table 4. The absorption and fluorescence λ_{max} of the solution suggest that long alkyl chains do not affect their optical properties in the same way as **PAzep-b**⁵⁷ and **PPhenaz**.¹⁵ The fluorescence λ_{max} of the cast film was longer than that of the CHCl₃ solution.

3-2 Using **PAzep-FIs** as functional additives^{63,64}

For use as functional additives, **PAzep-FIs** were added to plastics; the blend ratio is given in Table 5. PLA and PCL were chosen as the plastics because PCL was used for modifying PLA.⁴⁹ As shown in Table 5 and Fig. 9, the fluorescence λ_{max} of **PAzep-FI** added PLA was almost the same as **PAzep-FI** in CHCl₃. This suggests that **PAzep-FI** has good dispersibility in PLA, similar to **PPhenaz**.^{44,45} On the other hand, the fluorescence λ_{max} of **PAzep-FI**-containing PCL was almost in the same region as that of **PAzep-FI** cast film, suggesting that π -stacking by aggregation⁶⁵⁻⁶⁷ of **PAzep-FI** occurred in PCL because of its poor dispersibility in PCL. These results suggest that the compatibility of **PAzep-FI** to the plastic depended on the plastic used, as shown in Fig. 10. This type of aggregation behavior of the π -conjugated functional additive was observed when PCL was used as a matrix plastic.⁶⁸

4 Estimating the Compatibility of a Plastic Blend by Measuring the Fluorescence Spectra

4-1 Investigation of effect of addition of LTI^{63,64}

As described above, **PAzep-FI** was effective as a fluorescent additive, and plastics are sometimes used as blend composites of two or more kinds of plastics, like in Fig. 2. The present method involves the addition of LTI as a reagent to the terminal hydroxyl group of polyesters. To investigate the effect of **PAzep-FI** on the blend composite, **PAzep-FI** was blended to a PLA/PCL/LTI blend.⁴⁹ First, the effect of adding **PAzep-FI** to one kind of plastic/LTI blend was investigated. The blend ratio and fluorescence λ_{max} of the blend composites are given in Table 5. As shown in Fig. 11 and Table 5, the fluorescence λ_{max} became shorter upon the addition of LTI. This effect seems to be explicable as follows: in **PAzep-FI-a**, which has a reactive

Fig. 9 Comparison of the fluorescence spectra of **PAzep-FIs**.

Fig. 10 Supposed dispersion scheme of **PAzep-FIs** in PLA or PCL.

secondary amine unit, the distance between the **PAzep-FI** molecules seems to become longer because of chemical bond formation of the NH unit of **PAzep-FI-a** and the plastics *via* LTI. The reason for this is that a network type structure was formed by the reaction of polyester and LTI, as shown in Fig. 12(a). This network structure causes the distance of **PAzep-FI** molecules to increase compared with the absence of LTI. Therefore, a larger effect of the addition of LTI was observed when PCL was used as a matrix plastic than when PLA was used.

However, when **PAzep-FI-b**, which has a non-reactive tertiary amine on its side chain, was used as a fluorescent additive, the effect of adding LTI was lower. This can be explained as follows. As shown in Fig. 12(b), when LTI was added to the plastic/**PAzep-FI-b** blend composite, a network-type structure was formed by the reaction of polyester and LTI. This network structure seems to cause the distance of **PAzep-FI-b** molecules to increase compared with the absence of LTI, because **PAzep-FI-b** seems to be incorporated into the plastic/LTI network.

Therefore, the addition of LTI causes a shorter fluorescence $\lambda_{\max}$. However, the difference in the wavelength by the addition of LTI was smaller than that of **PAzep-FI-a** as a fluorescent additive, because chemical bond formation between **PAzep-FI-b** and PCL did not occur. These were also suggested by measuring the molecular weight of the blend composites and their impact strength.

4-2 Estimating the compatibility of a plastic blend by measuring the fluorescence spectra^{63,64}

Next, the effect on the fluorescent properties of adding **PAzep-FI** to PLA/PCL/LTI blend composites was investigated. The blend ratios and their fluorescent properties are given in Table 6 and typical fluorescence spectra are shown in Fig. 13, and the others are shown in Figs. S1 and S2. The fluorescence $\lambda_{\max}$ of the plastic vs. PLA ratio was plotted as shown in Fig. 14. The solid line and dotted line indicate the fluorescence $\lambda_{\max}$ of **PAzep-FI-a** and **PAzep-FI-b**, respectively. When the PLA/PCL blend ratio was the same, the fluorescence $\lambda_{\max}$ of LTI-containing plastics was shorter than that of the plastics in the absence of LTI. This result suggests that **PAzep-FI** was effective as a probe for estimating the compatibility, whereas **PPhenaz** without **PAR** was not effective for estimating the compatibility of a plastic blend.⁴⁵

The fluorescent properties of **PAzep-FI** were also measured in solution; the results are shown as $\times$ in Fig. 14, and their fluorescence spectra are shown in Fig. S3. As described above, the fluorescence $\lambda_{\max}$ of a CHCl_3 solution of **PAzep-FI** was almost the same wavelength as that of **PLA-a** and **PLA-b**, suggesting that **PAzep-FI** has good compatibility to PLA. However, the fluorescence $\lambda_{\max}$ of a methanol solution of **PAzep-FI** was almost the same wavelength as **PAzep-FI** cast film as well as **PCL-a** and **PCL-b**. This suggests that **PAzep-FIs** were aggregated in PCL as in methanol, such as poly(alkylthiophene) and poly(alkylthiazole).⁶⁶ In addition, we also measured the fluorescence spectra in a mixed solvent of chloroform and methanol with various weight ratios. As shown in the figure, the fluorescence $\lambda_{\max}$ in a mixed solvent was almost the same wavelength as the fluorescence $\lambda_{\max}$ in PLA/PCL blend without using LTI. This result suggests that the

Fig. 11 Fluorescence spectra of **PAzep-FIs** in PLA or PCL and the effects of adding LTI.

Fig. 12 Supposed dispersion of **PAzep-FIs** in PLA or PCL with LTI.

measurement of solvatochromism of a fluorescent additive is an easy way to check whether the additive is suitable as a reagent for estimating the compatibility of a plastic blend.

5 Conclusions

Prepared dibenzazepine-containing polymers afford fluorescent properties to plastics. Furthermore, in a plastic blend, the fluorescence spectra of dibenzazepine-containing polymers (**PAzep-FIs**) depended on the compatibilities of the blend. This fluorescent behavior was effective for estimating the

compatibility by the fluorescence spectra. The method described in this paper needs only one fluorescent additive; therefore, it is expected that this method of estimating compatibility will be simplified, whereas two kinds of polymers were needed for estimating by using phenazasiline-containing polymers.¹² Therefore, **PAzep-FIs** are functional materials for estimating plastic blends. This paper has discussed estimating the compatibility of a PLA/PCL blend, but the versatility of this method will be improved by adapting it to another blend system. This method should be effective for another blend system because not only **PAzep-FI-a** (reactive with isocyanate), but also **PAzep-FI-b** (non-reactive with isocyanate) was effective

for estimating the compatibility of the PLA/PCL/LTI blend system. In addition, improvements of the detectability of compatibility by these fluorescent spectra will be an expected measurement method by further molecular design.

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Table 6 Prepared PLA/PCL blend composites and their fluorescence $\lambda_{\max}$

Sample	PLA, wt%	PCL, wt%	Added PAzep-FI ^a	LTI/phr	Fluorescence $\lambda_{\max}/\text{nm}^b$
Blend-a1	90	10	PAzep-FI-a (0.01)	0	426
Blend-a1T	90	10	PAzep-FI-a (0.01)	0.5	413
Blend-a2	85	15	PAzep-FI-a (0.01)	0	432
Blend-a2T	85	15	PAzep-FI-a (0.01)	0.5	413
Blend-a3	70	30	PAzep-FI-a (0.01)	0	429
Blend-a3T	70	30	PAzep-FI-a (0.01)	0.5	415
Blend-b1	90	10	PAzep-FI-b (0.01)	0	436
Blend-b1T	90	10	PAzep-FI-b (0.01)	0.5	422
Blend-b2	85	15	PAzep-FI-b (0.01)	0	436
Blend-b2T	85	15	PAzep-FI-b (0.01)	0.5	426
Blend-b3	70	30	PAzep-FI-b (0.01)	0	436
Blend-b3T	70	30	PAzep-FI-b (0.01)	0.5	433

a. The figures in parenthesis show the added ratio (phr).

b. Excited at absorption $\lambda_{\max}$ of PAzep-FI in CHCl_3 .

7 Supporting Information

A detailed explanation of phr is given. Fluorescence spectra of PAzep-FI-containing plastic blend composites and the fluorescence spectra of PAzep-FI in a mixed solvent are shown. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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Fig. 14 Relationship between the fluorescence $\lambda_{\max}$ and the weight ratio of a matrix plastic or solvent.

Fig. 13 Fluorescence spectra of PLA:PCL = 85:15 blend composite with PAzep-FIs.

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