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Synthesis and Characterization of a Hydrolytically Stable Photochromic Copolymer Containing an N-alkylindolylfulgimide

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

SYNTHESIS AND CHARACTERIZATION OF A HYDROLYTICALLY STABLE
PHOTOCHROMIC COPOLYMER CONTAINING AN
N-ALKYLINDOLYLFULGIMIDE

A thesis submitted in partial fulfillment of
the requirements for the degree of
MASTER OF SCIENCE

in

CHEMISTRY

by

Samina Yasmeen

2016

To: Dean Michael R. Heithaus
College of Arts, Sciences and Education

This thesis, written by Samina Yasmeen, and entitled Synthesis and Characterization of a Hydrolytically Stable Photochromic Copolymer Containing an *N*-alkylindolylfulgimide, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

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Vice President for Research and Economic Development
and Dean of University Graduate School

Florida International University, 2016

DEDICATION

I dedicate my thesis work to my wonderful family, husband Muhammad Zubair Ahmad and children Areeb Khokhar, Arfee Khokhar, and Arham Khokhar. A special feeling of gratitude to my loving parents, Muhammad Yaseen and Shamium Akhtar whose words of encouragement and prayers are always with me. Very special thanks to my friends, Ms. Dora Mesa and Mrs. Tuzeen Kausar. Without their understanding, encouragement, support and love, the completion of this work would not have been possible.

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ABSTRACT OF THE THESIS

SYNTHESIS AND CHARACTERIZATION OF HYDROLYTICALLY STABLE

PHOTOCHROMIC COPOLYMER

CONTAINING AN *N*-ALKYLINDOLYLFULGIMIDE

By

Samina Yasmeen

Florida International University, 2016

Miami, Florida

Professor Watson J. Lees, Major Professor

Fulgides and fulgimides comprise one class of thermally irreversible photochromic organic compounds. Light dependent isomerization, has made these organic molecules promising materials for several applications, including optical memory devices, and switches. Hydrolytic stability of fulgides and fulgimides is crucial for their practical applications in biological systems and humid environments. Fulgimides, the most important derivative of fulgides, have a succinimide ring, which, unlike the anhydride ring, of fulgides, is resistant to hydrolytic degradation. A novel *N*-alkylindolylfulgimide was synthesized and copolymerized with acrylamide. The photochromic and hydrolytic properties of the copolymer in phosphate (pH 7.4) and acetate (pH 5.0) buffer solutions were characterized. The *N*-alkylindolylfulgimide based copolymer exhibited significantly enhanced hydrolytic stability (50 times better in phosphate buffer) and similar photochromic properties as a copolymer containing an *N*-arylindolylfulgimide.

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1. INTRODUCTION

1.1 Photochromism

Photochromism can be defined as “The reversible transformation of chemical species, induced in one or both directions by electromagnetic radiation, between two states having observable light absorption in different regions of the spectrum”.¹

For the most part, photochromic systems depend on unimolecular reactions.

Ordinarily, transformed chemical species “B” has at least one absorption band at a longer wavelength than the absorption bands of species “A”. Generally, the activation wavelength, λ_1 is in the ultraviolet region (190-400 nm), but may also be in the visible region 400-800 nm.¹

Figure 1. Photochromic reaction and absorption spectra of photochromic Compound.

Spiropyrans, azobenzenes, diarylethenes, fulgides, and fulgimides are traditional examples of organic photochromic molecules. Spiropyrans and azobenzenes are classified into T-type (thermally reversible) photochromes. The

photoinduced isomeric form is thermally unstable and colors slowly disappeared in the dark at room temperature.

On the other hand, fulgides and diarylethenes are classified into P-type (thermally irreversible, but photochemically reversible) photochromes. In the class of P-type photochromic molecules, the photoinduced isomeric forms are thermally stable in the dark at room temperature.²

1.2 Background

The phenomenon of photochromism was noted for the first time in 1867 when Fritzsche observed the bleaching of a colored tetracene solution in daylight, and its re-coloring at night.³ Since then, many photochromic compounds have been described. However, the general interest in photochromic compounds was moderate for about a century. During the 1950s, comprehensive synthetic and mechanistic studies were done, in particular by Hirshberg and Fischer *et al.*⁴ In the 1960s, research of photochromic compounds expanded rapidly. The main initiative of research was Hirshberg's idea of using the phenomenon of photochromism for photochemical erasable memory.⁵ However, the photodegradation of organic photochromic compounds limited the potential for their applications. Tremendous efforts were made in 70s-80s to improve the thermal irreversibility of photochromic

systems. The focus of research was to improve the thermal stability in existing molecules. Unfortunately, all attempts were unsuccessful.² Finally, in the mid-1980s the photogenerated colors of diarylethenes and furylfulgides were found to be stable at room temperature.⁶ In 2007, the most stable fulgide, trifluoromethyl dicyclopentyl indolylfulgide, was reported by Lees *et al.* to undergo 10,000 coloring and bleaching photochemical cycles before degrading by 13% (0.0013%/cycle). In terms of photochromic performance the indolylfulgide derivative is similar to the best diarylethene derivative (0.0007%/cycle).^{7,8}

Figure 2. Important classes of organic photochromic compounds.

Over the past decade, the basic palette of available photochromic compounds has not expanded significantly in photochromic devices. Generally, most of the effort has been devoted to improve the properties of established photochromic compounds.⁹ Spiropyrans, azobenzenes, diarylethenes, fulgides, and fulgimides.^{2,10}

Each class of photochromic molecules has a preferred application area. For instance, spiropyrans have a unique feature of increasing the dipole moment during the photoisomerization process from closed to open form.⁹ Spiropyrans

containing photochromic materials are usually considered a superior photochrome when interaction with charged surfaces and entities is desired.⁹ In 2015, Song *et al.*¹¹ introduced a spirooxazine containing high-performance photochromic sensor microchip used for the detection of eleven various multiplex metal ions. However, the low thermal stability of the *C* form of spiropyrans and spirooxazines has restricted their application in devices.¹²

Usually, azobenzenes containing materials are utilized in actuation and optical memory storage.⁹ The *E/Z* isomerization of azobenzenes leads to large structural changes, which can be transferred and amplified in suitable host material.⁹ Substituted photochromic azobenzenes are easy to synthesize and are compatible with aqueous environments.¹³ Recently, Liang *et al.*¹⁴ reported fully photoinduced molecular tweezers that use on photoswitchable DNA hybridized with azobenzene. For medical applications, one major issue of photochromic azobenzenes is the use of UV light to induce *E/Z* isomerization. High energy UV photons are detrimental because of their low penetration ability into biological tissues, and the severe cell damage among other unwanted side effects.⁹

On the other hand, diarylethenes undergo large electronic changes upon irradiation with UV light. Photoinduced electronic changes has been utilized in the application of diarylethenes based materials to control the electronic coupling and energy transfer pathways in multicomponent systems.⁹ In 1998, Kawata *et al.*¹⁵ introduced the use of diarylethenes in nondestructive readout memory devices. The data were stored in three dimensional photochromic diarylethenes memory. A reflection confocal microscope was used as a readout system. The readout laser

light had a longer wavelength than the absorption edge of the colored isomer.⁸ Diarylethenes are also known for their high opened-to-closed quantum yield (0.86), and photochemical and thermal stability. However, the closed-to-opened quantum yield is low, the extinction coefficients of both forms are low, and the refractive index changes are not large.³

Fulgides and fulgimides are a promising class of organic photochromic compounds. In comparison with fulgides, fulgimides are known for their enhanced thermal stability and copolymerization ability.^{16,17} Fulgimides are preferably used for modulating the structure and function of biomolecules. For example, under photoirradiation a fulgimide attached to a biomolecule can alter the molecular structure and modulate the activity. Fulgides and fulgimides have potential applications in molecular switches, optical storage, optical data processing, waveguides, security and printing, eyewear and leisure products.²¹

1.3 Chemical processes involved in organic photochromism

Photochromism is a special case of a photochemical reaction, almost any type of photochemical reaction may be used to produce photochromism with appropriate molecular design. For example, pericyclic reactions take place in spiropyrans, spirooxazines, diarylethenes, fulgides, and fulgimides.¹⁸ In spirooxazine, upon irradiation with UV light, the ring opens because a bond breaks between the spiro-carbon and the oxygen. As a result the spiro-carbon becomes sp^2 hybridized and planar, then develops a conjugate system by aligning its p -orbital with the rest of the molecule. The newly formed conjugated system has the ability to absorb photons of visible light, and therefore appears colored. After

irradiation with visible light, the bond between the carbon and oxygen atoms reforms. Then, the spiro-carbon becomes sp^3 hybridized again, and the molecule returns to its colorless state.

Photochromic reactions of diarylethenes and fulgides operate by a 6π -electrocyclization. *Cis/trans* isomerization of azobenzene is an example of a photochromic reaction.¹⁹ Photochemical reactions of some of the typical families of photochromic compounds are shown in Scheme 1.^{2,20,21}

1.4 Fulgide and fulgimide

The general structure of fulgides and fulgimides are presented in Figure 3.

Figure 3. General structures of fulgides and fulgimides.

Fulgides, the acidic anhydride of 1,3-butadiene-2,3-dicarboxylic acid, and its derivatives were first discovered by Stobbe in 1905.^{22,23} The name “fulgide” was originally given to the bismethylene succinic anhydride, which comes from the Latin *fulgere* meaning to glitter or shine. In fact, some derivatives of fulgide exhibit a variety of characteristic colors upon exposure to light.²⁴ The photochromic fulgides and fulgimides should have an aromatic ring or a double bond as one of

Scheme 1. Photochromism of photochromic compounds

Spirooxazines:

Diarylethenes:

Indolyl fulgides and indolyl fulgimides:

fulgides X=O, fulgimides X= N-R

Azocompounds:

the substituents, R_1 , R_2 , R_3 or R_4 at the exomethylene carbon. The aromatic ring or the double bond results in a 1,3,5-hexatriene structure that can undergo 6π -electrocyclization. The *E/Z* isomeric forms depend on the arrangement of the substituents (R_1 , R_2 and anhydride ring). One of the isomers, either *E* or *Z*, may undergo a 6π -electrocyclization with UV light to produce a colored cyclic isomer, *C* form, Figure 4.

Figure 4. *E*, *Z* and *C* isomers of fulgide

In 1988, Matsushima synthesized several heteroaromatic fulgides, and studied their thermal and photochemical stability in poly(methyl methacrylate) (PMMA) films, Figure 5.^{25,26} Among these different fulgide derivatives, 3-indolylfulgide was recognized to have high thermal and photochemical stability, large quantum yields, large molar absorption coefficients, and an absorption maxima in the visible region. The succinimide derivatives of fulgides are fulgimides, which were first introduced by Heller.^{27,28} Fulgimides are one of the most important derivatives of fulgides. The 3-indolylfulgimides were recognized to have the same advantageous properties as the corresponding fulgides.²⁹ Unlike fulgides, fulgimides are hydrolytically stable in protic solvents and the succinimide ring of fulgimides allows another substituent to be attached via the nitrogen atom while keeping the promising photochromic properties. These properties lead to the application of fulgimides in erasable optical recording materials and photoswitchable optical devices. In general, fulgimides

can be synthesized by a variety of methods, but most often they are prepared from their precursor fulgides.^{30, 31}

Figure 5. Examples of heterocyclic fulgides synthesized by Matsushima *et al.*^{25,26}

1.4.1 Photochemical reaction of fulgides and fulgimides

The photochemical reaction of fulgides and fulgimides involves a pericyclic reaction. According to Heller, the C-form is formed by an excitation of electrons from n to π^* . The orbitals are rearranged by a conrotatory movement in accordance with the Woodward-Hoffmann selection rules.⁹ However, Becker proposed a different mechanism after using microsecond and nanosecond laser flash photolysis. Becker suggested that the photocyclization reaction of a fulgide is a result of π to π^* rather than n to π^* excitation,¹⁰ Figure 6. The π to π^* excitation was confirmed by the picosecond laser photolysis studies of Partheopouls and Rentzepis,³⁴ and Kurita and Takeda.³⁶

1.5 Synthesis

1.5.1 Synthesis of fulgides

Generally fulgides are synthesized by a Stobbe condensation, which involves the condensation of an aryl aldehyde or ketone with a succinate derivative to form a half ester, followed by acid hydrolysis of the half ester and dehydration of the

Figure 6. Conrotatory ring closure of a fulgide.

resulting diacid, Scheme 2.²⁷ The first step of a Stobbe condensation is the formation of an ester enolate by deprotonation of the α -carbon of the diethyl

succinate. The next step is the formation of a β -alkoxy ester intermediate, followed by lactone formation via intramolecular acyl substitution reaction. Then, the lactone ring is opened to an acid via an elimination reaction under basic conditions. The remaining ester is then hydrolyzed and the resulting diacid dehydrated to obtain the photochromic fulgide, Scheme 3.²⁷ A significant hurdle in the implementation of a Stobbe condensation in the chemical industry is its low yield.^{32,33} Therefore, a modified synthetic route or new synthetic strategy needs to be developed.³⁴

Scheme 2. Synthesis of fulgide by Stobbe condensation.

Scheme 3. Mechanism of Stobbe condensation.

In 1996, Yokoyama *et al.* reported a trifluoromethylindolylfulgide with remarkable thermal stability.³² The first synthetic step was the reaction of 1,2-dimethylindole with trifluoroacetyltrifluoromethanesulfonate. The trifluoroacetylindole was obtained in 42% yield. Then 1,2-dimethyl-3-

trifluoroacetylindole was condensed with dimethylisopropylidene succinate via a Stobbe condensation. The fulgide was obtained in 3% yield by hydrolysis under basic condition followed by dehydration with imidazole-trifluoroacetate, Scheme 4. The overall yield of the final product, indolyfulgide, was only 1%. The low yield of the final product is a hurdle to the further application of the synthetic route.³²

Scheme 4. Synthetic scheme of indolyfulgide by Yokoyama *et al.*

In 2001, Lees *et al.*¹⁷ introduced a versatile synthetic route for the synthesis of fulgides. The synthetic strategy was improved by modification of the Stobbe condensation. In the first step, diethyl isopropylidenesuccinate was obtained in 75% yield. The synthesis involved the reaction of diethyl succinate with acetone. In the second step, 1,2-dimethyl-3-trifluoroacetylindole was obtained with 96% yield by reacting 1,2-dimethylindole with trifluoroacetic anhydride. Next, 1,2-dimethyl-3-trifluoroacetylindole was reacted with diethyl isopropylidenesuccinate in the presence of a strong base, lithium diisopropylamide (LDA), at -78 °C in toluene. A mixture of *cis/trans* lactones was obtained in 38% yield. The mixture of *cis/trans* lactones was hydrolyzed with NaH followed by the addition of water to form the dicarboxylic acid intermediate. Then acetic anhydride was used to dehydrate the dicarboxylic acid intermediate resulting in trifluoromethylindolyfulgide with 83% yield from the lactones. The new methodology allowed the preparation of a variety of indolyfulgides with reasonable

yield. The application of the new methodology was expected to improve the yield of fluorinated as well as non-fluorinated indolylfulgide derivatives.

Scheme 5. Synthesis of trifluoromethylindolylfulgide by Lees *et al.*

1.5.2 Synthesis of fulgimides

There are three different synthetic pathways to fulgimides. In synthetic route I, the key intermediate, succinamic acid, was obtained by reaction of the parent fulgide with a primary amine. Subsequent dehydration of the succinamic acid yields the photochromic fulgimide. In synthetic pathway II, the key intermediate, succinamic acid, was obtained by reacting the succinic half-ester with a Grignard salt of the amine followed by subsequent dehydration to produce photochromic fulgimide. In synthetic pathway III, the first step was the synthesis of non-*N*-substituted fulgimide from parent fulgide, followed by the addition of a substituent at the nitrogen of the imide ring, Scheme, 6.³⁵

It was previously reported that synthetic pathway I was the highest yielding and the most common for the synthesis of fulgimides. Lees *et al.*³⁶ adopted synthetic pathway I to synthesize a series of fluorinated indolylfulgimides from the

Scheme 6. Synthetic pathway of fulgimide from fulgide

parent fulgide, Scheme 7.¹⁷ The parent fulgide was treated with an aniline derivative in the presence of LDA or NaH to obtain the succinamic acid intermediate. Then, the fulgimide was obtained by dehydration of the succinamic acid intermediate with acetic anhydride. The reported yield was up to 64%.

Scheme 7. Synthesis of fulgimide by Lees *et al.*

A new procedure for the synthesis of imides under mild reaction conditions was first developed by Toru³⁷ and then Rentzepis applied it to the synthesis of a series of fulgimide derivatives in 80%³⁸ yield, Scheme 8. The synthesis involves the treatment of an anhydride with an amine, producing the amic acid intermediate. A Lewis acid and hexamethyldisilazane (HMDS) were used as dehydrating agents to produce the fulgimide. The proposed mechanism of cyclization is that the Lewis

acid and HMDS promotes silylation of the amic acid to a labile trimethylsilyl ester derivative followed by thermal deoxysilylation to give the imide.

Scheme 8. Synthetic route of fulgimide by Rentzepis *et al.*

In search of developing an environment friendly method with the use of less solvents for the synthesis of fulgimides, Lee *et al.*³⁹ explored a fast, efficient and low cost synthetic method using microwave technology. A thienylfulgimide was synthesized in a conventional microwave oven. In the first step of the synthesis, the mixture of a thienylfulgide and a bromo-amine was reacted under microwave irradiation. Then, the succinamic acid intermediate was formed that subsequently underwent the dehydration process by acetic anhydride providing a fulgimide in a 85% yield, Scheme 9

Scheme 9. Synthesis of fulgimide by Lee *et al.*

Smet *et al.*⁴⁰ adopted a third synthetic pathway for the synthesis of furylfulgimide. The parent furylfulgide was reacted with ammonia in acetone, and provided a non *N*-substituted furylfulgimide with 58% yield. The non *N*-substituted furylfulgimide was reacted with 4-vinylbenzylbromide in the presence of Cu-

powder. The product *N*-*p*-methylstyryl furylfulgimide was obtained in 68% yield, Scheme 10.

Scheme 10. Synthesis of fulgimide by Smet *et al.*

1.5.3 Synthesis of copolymer containing fulgide or fulgimide

Most of the optoelectronic devices, for example 3D optical memory devices, demand photochromic material at higher concentrations and in the robust medium such as beads, films and moldable materials..⁴¹ Rentzepis *et al.*^{42,43} synthesized a series of indolyfulgide and indolyfulgimide containing copolymers. The linear and crossed linked copolymers were made by treating fulgides or fulgimides with methyl methacrylate (MMA). Polymerization was carried out via a free radical mechanism with azobisisobutyronitrile (AIBN). The linear copolymers were soluble in organic solvents but the cross linked copolymers were insoluble in any solvent. Both types of polymers exhibit similar photochromic properties as their corresponding monomers, Schemes 11 and 12.

1.6 Photochromic properties of indolyfulgides and indolyfulgimides

The photochromic properties of fulgides and fulgimides such as UV-Vis absorption spectra, photochromic quantum yield, and photochemical and thermal stability are very similar when they are compared in solution and in solid polymer films. The measurement of these properties determines the best photochromic

Scheme 11. Linear-copolymer containing indolyfulgide and indolyfulgimide

Scheme 12. Cross-linked copolymer containing indolyfulgimide

system for each application.^{27,44} Many experimental studies on the synthesis of new fulgides and investigations of their photochromic properties have been conducted, but only a few studies have focused on their thermal stabilities.⁴⁵ Fulgimides are known for their excellent photochromic properties as well as being highly resistant to solvolytic degradation in comparison to fulgides.

1.6.1 UV-Visible absorption spectra

The identification of photochromic molecules is best documented by UV-Visible spectroscopy (UV-Vis). The *E/Z* forms and the *C* form of fulgides/fulgimides exhibit different absorption spectra. Generally, the absorption maxima of the *E* form and *Z* form are similar to each other while the absorption maximum of the *C* form is bathochromic to the absorption maxima of the *E/Z* isomers. When a mixture of *E/Z* forms of a fulgimide is irradiated with visible light, a conrotatory ring-closing reaction occurs in agreement with the Woodward and Hoffmann rules and the *C* form appears in the visible region of the spectrum.²⁷ In heteroatomic fulgides, the *C* form has a bathochromic shift because of the electron-donating ability of the heterocyclic groups. The red shift suggests the extended conjugation of heteroatoms with a carbonyl group of the fulgimide.⁴⁶

Indolylfulgides have three thermally stable isomers, *E*, *Z*, and *C* form; each with a distinct UV-Vis absorption spectrum. The three isomers can transform according to the photochromic reactions associated with P type photochromism.⁴⁷ Through these reactions, the *E/Z* forms transform to the *C* form under UV light with limited efficiency. Irradiation with visible light transforms the *C* form to either *E* or *Z* form via an electrocyclic ring-opening reaction. In 1984, Ilge *et al.*⁴⁸ investigated

Figure 7. UV-Vis absorption spectra of a photochromic fulgide.

Figure 8. Absorption maxima of furanyl, thienyl and pyrrolylfulgides in toluene.

the effect of heterocyclic substituent, on the absorption maxima of the cyclic form of fulgides. Absorption maxima tended to red shift with the electron-donating ability of the heterocyclic group, Figure 8.

1.6.2 Quantum yield

The quantum yield is a measure of the efficiency of the photochromic reaction and can be defined as “The number of molecules that undergo the photochromic reaction per photon absorbed”.⁴⁹ Fast and effective photochromic reactions are possible with low energy light sources if the quantum yields are high. Once a new photochromic molecule is synthesized, light-induced conversion efficiencies as well as the reaction times are normally determined by measuring absolute quantum yield.⁴⁹ Quantum yields of the *E*, *Z* and *C* forms of fulgides/fulgimides can be measured in various solvents and in different polymers.⁵⁰ Rentezpis *et al.*¹² measured the solvent polarity dependance of quantum yields for 2-indolylfulgides.

Quantum yields of both ring closing (coloration) and ring opening (decoloration) depend upon the polarity of the solvent. In a polar solvent, such as acetonitrile, the quantum yield was 0.1. In a nonpolar solvent, such as hexanes, the quantum yield was found to increase by a factor of 2. The reason for the low quantum yield in polar solvents is because in the excited state the molecule has a large dipole moment, which is stabilized by the polar solvent and thus the reaction becomes uphill in terms of the activation energy.¹²

Yokoyama and Kurita demonstrated the effect of electron-donating substituents on the quantum yield. The quantum yield of photocyclization reaction decreased in the order H-, MeS-, MeO-, and Me₂N-. The compound having a Me₂N- substituent at the 5th position is highly resistant towards ring opening (bleaching reaction).^{27,35}

Figure 9. Effect of substituent on quantum yield.

1.6.3 Thermal stability

Some optoelectronic devices are expected to maintain viability at 50°C for prolonged periods. Therefore, it is very important that the isomers of photochromic

compounds should be thermally stable at elevated temperature. Practically, photochromic compounds have found limited application in optical information storage devices because of the lack of thermal stability of the colored form.⁵¹ Among all the subclasses of fulgides, indolylfulgides have attracted special attention because of their enhanced photochemical and thermal stability. The isomeric forms of photochromic indolylfulgides (*E*, *Z* and *C* forms) when dissolved in deuterated chloroform, hexanes or acetonitrile and kept in the dark, did not show thermal decomposition at room temperature even after one month. The *C* form of trifluoromethyl substituted indolylfulgides were found to be very stable, because no change in absorption spectra was observed at 80°C even after one month. However, the *Z* form underwent thermal decomposition at 80°C.^{52°,53} Lees *et al.* proposed that a 1,5 hydrogen shift is the rate determining step of thermal degradation. It was postulated that thermal stability could be improved by replacing the isopropylidene group with a cycloalkylidene group, and a series of cycloalkylidene indolylfulgides were synthesized with improved thermal stability.⁵⁴

1.6.4 Photochemical stability

The photochemical stability is defined as “The percentage of the molecules still retaining photochromic properties after a certain number of ring-closing/ring-opening cycles”.²⁹ The ultimate result of photochemical degradation is the loss of performance over time. Photochemical stability is an important property of photochromic compound for applications in memories and switches. It is difficult to obtain a photochromic compound having high photochemical stability. Matsushima *et al.*^{25,26} studied the photochemical stability of some heterocyclic fulgides. The

indolyl and pyrazolyl derivatives showed improved photochemical stability as compared with the furanyl, thienyl and pyrrolyl derivatives, Figure 10.

Figure 10. Examples of heterocyclic fulgides synthesized by Matsushima *et al.*^{25,26}

Mechanistic studies of the photochemical decomposition of indolylfulgides were undertaken by Yokoyama.³² According to the proposed mechanism, the decomposition pathway is a 1,5 hydrogen migration from one of the methyl groups to the carbonyl oxygen on the anhydride ring. A nonphotochromic compound is obtained by the subsequent tautomerization of the resulting compound, Figure 11. Fluorinated indolylfulgides display better photochemical stability as compared to their non-fluorinated analogues.^{36,53} The most promising fulgide for applications in memories and switches is a photochromic trifluoromethyl substituted indolylfulgide reported by Yokoyama and Takahashi.³²

1.6.5 Hydrolytic stability

Hydrolytic stability is a crucial factor for practical applications of photochromic compounds in humid environments or aqueous biological systems and thus

Figure 11. Proposed mechanism of 1,5 sigmatropic rearrangement and tautomerization.

fulgimides are the most suitable fulgide derivative.^{55,56} Fulgides are unstable in hydrolytic media because of their succinic anhydride ring, while fulgimides with a succinimide ring have improved hydrolytic stability²⁴. Lees *et al.*¹⁷ compare the hydrolytic stability of fulgides and fulgimides. When indolylfulgides were dissolved in a 70:30 (ethanol:water) mixture at room temperature, the fluorinated indolylfulgides showed a significant loss in absorbance. In contrast, indolylfulgimides were more resistant to hydrolysis. In general, the *Z* form of indolylfulgimides maintained at least 90% absorbance at $\lambda_{\max}$ after 360 h in the ethanol and water mixture. Slow *C* to *Z* isomerization of the *C* form makes the measurement of the hydrolytic stability of the *C* form complicated. However, the fulgimides kept 55 % of their original absorbance at the *C* form $\lambda_{\max}$ after 2 weeks in a 70:30 (ethanol:water) mixture at room temperature.¹⁷

Fulgimides maintained photochromic activity in aqueous mixtures, such as 1:1 (ethanol:water). The *Z*, *E* and *C* forms of a fulgimide synthesized by Matsushima *et al.* kept their photochromic properties in aqueous mixtures, Figure 12. Photochemical reversibility of this fulgimide was examined without substantial solvolysis in 1:1 aqueous ethanol solution.⁴⁴

Figure 12. Hydrolytically stable fulgimide synthesized by Matsushima *et al.*

1.6.6 Application of photochromic fulgimides

Photochromic fulgimides have been applied in several areas, for example regulating energy transfer with light and for 2D molecular memories. Port *et al.*^{57,58} found that energy transfer could be regulated photochemically after synthesizing a molecule in which intramolecular energy transfer was dependent upon the form of the photochromic fulgimide. A covalently attached photochromic indolylfulgimide was sandwiched between an anthracene, donor group, and coumarin, acceptor group, in a photoswitchable donor-switch-acceptor energy transfer system, Figure 13.

Figure 13. Photoswitchable energy transfer compound containing a fulgimide.

The rate of access to stored information is very important in 2D molecular memories, and depends on the rate of photochromic isomerization from the closed to the open forms and the dye fluorescence lifetime. Fulgimide architecture for 2D molecular memories was introduced by Rentizepis *et al.*⁵⁹. A photochromic fulgimide linked with a strongly fluorescing oxazine dye was used to access the stored information in 2D molecular memories, Figure 14.

Figure 14. Molecular memory by Rentzepis.

Moore *et al.*⁶⁰ reported that photochromic fulgimide can perform sophisticated logic operations. A complex system in which the photochromes were covalently linked together in a single molecular device was developed. The output of the one molecular switch was transmitted to the other chromophore by photoinduced isomerization. The dyad of porphyrin-fulgimide (P-FG) is an example of this molecular device, Figure 15.

2. OBJECTIVES OF RESEARCH

The overall aim of this research is to synthesize, purify and characterize a photochromic copolymer. The selected *N*-alkylindolylfulgimide containing copolymer is expected to have improved thermal and hydrolytic stability relative to

an *N*-arylimidylfulgimide. Kanaoka *et al.*⁶¹ reported that *N*-ethylmaleimide (*N*-alkylimide) is 25 times more stable than *N*-phenylmaleimide (*N*-arylimide) in a phosphate buffer at pH 7.0.

Figure 15. Molecular device of porphyrin-fulgimide dyad .⁶⁰

2.1 Synthesis of a polymerizable photochromic fulgimide monomer

A photochromic monomer *N*-alkylimidylfulgimide **1** was synthesized with polymerizable vinylbenzyl group attached on the nitrogen atom of the imide ring.

2.2 Synthesis of a linear fulgimide 1-co-PAA copolymer.

Photochromic monomer *N*-alkylimidylfulgimide **1** was copolymerized with acrylamide (AA) providing a linear copolymer. The *N*-alkylimidylfulgimide linear copolymer was synthesized to improve the thermal stability of the *C* form relative to the previously prepared *N*-arylimidylfulgimide linear copolymer.

2.3 Characterization

Photochromic fulgimide **1** and its copolymer **1-co-PAA** were characterized by measuring UV-Vis spectra, and thermal and photochemical stability.

3. EXPERIMENTAL AND PROCEDURE

3.1 General Remarks

All commercially available materials were used without further purification. Compounds were purified by flash chromatography using 230-400 mesh silica gel. A Cary 300 spectrophotometer was used to record UV-Vis spectra. A Bruker 400MHz NMR spectrometer was used to record NMR spectra. The ^1H and ^{13}C NMR samples were internally referenced to TMS or residual solvent. Photochemical stability was measured with an Oriel 1000 W Hg (Xe) arc lamp as the light source. A band pass filter was used for 365 nm light and a cut off filter was used for >515 nm light.

3.2 Synthesis of *N*-alkylindolylfulgimide

3.2.1 Synthesis of dimethyl isopropylidenesuccinate

The 2-Nitropropane (76.60 g, 0.860 mol) was dissolved in 2.4 L of acetonitrile, followed by addition of dimethyl maleate **3** (135.70 g, 0.942 mol) and 1,8-Diazobicyclo[5.4.0]undec-7-ene (DBU) (201.56 g, 1.32 mol). The reaction mixture was left to react for 16 h at room temperature and then concentrated *in vacuo*. The residue was quenched with 600 mL of HCl. The mixture was extracted with 1.5 L of ethyl acetate and washed twice with 600 mL of water (2 x 600 mL). The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by vacuum distillation to yield 128.48 g (73%) of dimethyl isopropylidenesuccinate **4**. ¹H NMR (CDCl₃, 400 MHz) δ 3.66 (s, 3H), 3.61 (s, 3H), 3.47 (s, 2H), 2.23 (s, 3H), 1.83 (s, 3H).

3.2.2 Synthesis of 1,2-dimethylindole

The 2-Methylindole **5** (15.40 g, 0.117 mol) was dissolved in 200 mL of dimethylformamide (DMF) and left to react at room temperature for 30 min. The mixture was then cooled to 0 °C followed by addition of NaH (6.01 g of 60% dispersed in oil, 0.150 mol) and left to react for 10 min. After 10 min, methyl iodide

(8.0 mL, 0.129 mol) was added. The reaction mixture was left to react under argon gas at room temperature for 5 h. The mixture was then concentrated *in vacuo*. The concentrated residue was dissolved in ethyl acetate 500 mL and extracted with water (3 x 200 mL) and brine (1 x 200 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The product, 1,2-dimethylindole **6**, was obtained in 92% yield (15.65 g). ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, *J* = 7.4 Hz), 7.37 (d, *J* = 7.9 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.1 Hz, 1H), 6.22 (s, 1H), 3.73 (s, 3H), 2.48 (s, 3H).

3.2.3 Synthesis of 3-acetyl-1,2-dimethylindole

The 1,2-dimethylindole **6** (9.50 g, 65.4 mol) was dissolved in 160 mL of acetic anhydride (170 g, 1.7 mol). The reaction mixture was reflux under argon for 36 h. The reaction mixture was concentrated *in vacuo* and the residue was recrystallized from hexanes/CH₂Cl₂. The product, 3-acetyl-1,2-dimethylindole **7**, was obtained in 71% yield (6.75 g). ¹H NMR (CDCl₃, 400 MHz) δ 7.95 (d, *J* = 7.1 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 3.72 (s, 3H), 2.80 (s, 3H), 2.70 (s, 3H).

3.2.4 Synthesis of Cis/trans indolelactones

Dimethyl isopropylidenesuccinate **4** (23.9 g, 128.35 mmol) was dissolved in 60 mL of dry hexanes and cooled to -78 °C. Lithium diisopropylamide (LDA) (76 mL of a 2 M solution in THF, 152 mmol) was transferred to an additional funnel via a cannula. The LDA was added dropwise to the reaction mixture, and the reaction mixture was left to react for 30 min at -78 °C under argon. The 3-acetyl-1,2-dimethylindole **7** (7.01 g, 38.8 mmol) was dissolved in 200 mL of dry hexanes. The solution of 3-acetyl-1,2-dimethylindole was added dropwise to the reaction mixture of LDA and dimethyl isopropylidenesuccinate **4**. The reaction mixture was left to react at room temperature for 2 d. The solution was concentrated *in vacuo* and the residue was dissolved with 200 mL of water and acidified with 5% H₂SO₄ to pH 2. The aqueous layer was extracted with ethyl acetate (3 x 100 mL). The organic layer was washed with brine (2 x 100 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (2:1 hexanes/ethyl acetate) and the resulting mixture of *cis*/*trans* indolelactones **8** was obtained in 21% yield (2.28 g). Mixture of *cis* and *trans* lactones was separated during column chromatography by collecting different fraction. *Trans* lactone: ¹H NMR (CDCl₃, 400 MHz) δ 7.81 (d, *J* = 7.8 1H), 7.29-7.27 (m, 1H), 7.20 (td, *J* = 7.0, 1.1 Hz, 1H), 7.15 (td, *J* = 7.4, 1.5 Hz, 1H), 4.47 (s, 1H), 3.85 (s, 3H), 3.63 (s, 3H),

2.56 (s, 3H), 2.25 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H). *Cis* lactone: ^1H NMR (CDCl_3 , 400 MHz) δ 8.14 (d, $J = 7.8$ Hz, 0.3H), 7.52 (d, $J = 7.8$ Hz, 0.7H), 7.23-7.17 (m, 1H), 7.13 (t, $J = 7.8$ Hz, 1H), 7.06 (t, $J = 7.1$ Hz, 1H), 4.27 (s, 0.7H), 4.11 (s, 0.3H), 3.63 (s, 3H), 3.01 (s, 2H), 2.87 (s, 1H), 2.58 (s, 2H), 2.43 (s, 1H), 2.37 (s, 3H), 1.96 (s, 3H), 1.88 (s, 2H), 1.78 (s, 1H).

3.2.5 Synthesis of methylindolylfulgide

Cis/trans indolelactones **8** (2.90 g, 8.50 mmol) was dissolved in 250 mL of DMF at 0 °C. Sodium hydride (60% dispersion in oil, 0.84 g, 21 mmol) was added to the solution of *cis/trans* indolelactones **8**. The reaction mixture was warmed to room temperature and left to react for 1 h. Then, the reaction mixture was cooled back to 0 °C. After cooling, water (2.5 mL, 139 mmol) was added. Then the reaction mixture was stirred overnight and concentrated *in vacuo*. The residue was dissolved in 150 mL of water and washed with ethyl acetate (3 x 100 mL). The aqueous layer was acidified with 10% HCl to pH 2 and the mixture was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated *in vacuo* to obtain the crude diacid intermediate **9**. The intermediate diacid **9** was dissolved in 100 mL of toluene, followed by the addition of acetic anhydride (50 mL, 0.53 mol). The reaction mixture was heated to reflux for 2 h under argon and then concentrated *in vacuo*. The residue was

dissolved in water (200 mL) and extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with CH₂Cl₂ and recrystallized from CH₂Cl₂/hexanes to obtain 0.78 g (27%) of methylindolylfulgide.

¹H NMR (CDCl₃, 400 MHz) δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.26-7.24 (m, 1H), 7.15 (td, *J* = 7.3, 1.1 Hz, 1H), 3.69 (s, 3H), 2.81 (s, 3H), 2.20 (s, 6H), 0.94 (s, 3H).

3.2.6 Synthesis of indolylfulgimide

Methylindolylfulgide **10** (0.050 g, 0.16 mmol) and vinylbenzylamine **11** (0.032 g, 0.24 mmol) were dissolved in 3.2 mL of CH₂Cl₂, and left to react at 40 °C for 3 h. After solvent evaporation, 3.2 mL of acetyl chloride was added to the succinamic acid **12** and left to react for 1 h at room temperature. The mixture was concentrated *in vacuo*. The residue was neutralized with saturated NaHCO₃ over ice (10 mL). The crude product was extracted with CH₂Cl₂ (3 x 15 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by column chromatography (1:1 hexanes/ethyl acetate) to obtain a mixture

of *E/Z* isomers of *N*-alkylindolyfulgimide **1**. The mixture of isomers was dissolved in toluene (4 mL) and illuminated with 365 nm light to obtain the closed *C* form. Purification by column chromatography (1:1 hexanes/CH₂Cl₂) yielded 0.010 g (15%) of *N*-alkylindolyfulgimide **1C**. *C* form: ¹H NMR (CDCl₃, 400 MHz) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.69 (m, 4H), 6.53 (d, *J* = 8.9 Hz, 1H), 5.72 (d, *J* = 18.1 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.61 (s, 2H), 2.87 (s, 3H), 2.40 (s, 3H), 1.74 (s, 3H), 1.24 (s, 3H), 1.15 (s, 3H).

3.2.7 Preparation of linear copolymer **1-co-PAA**

The *C* form of *N*-alkylindolyfulgimide **1C** (4.5 mg, 0.010 mmol) was dissolved in 2 mL of THF. With stirring, acrylamide (0.35 g, 4.9 mmol) and azobisisobutyronitrile (AIBN) (1% of acrylamide) were added to the solution. The mixture was sealed in a glass ampoule under vacuum and kept at 50 °C for 48 h. After 48 h, a violet polymeric gel was formed. The polymeric gel was dissolved in 30 mL of nanopure water and then transferred to a dialysis bag (M.W. cutoff: 6000-8000). Dialysis was performed 4 times in 3.5 L of water. The copolymer solution was dried *in vacuo* to provide the *C*-form copolymer **1-co-PAA**.

3.3 Characterization

3.3.1 Spectral determination

A concentrated stock solution of the *C* form of *N*-alkylindolylfulgimide **1C** in toluene (25 mL) was prepared from 10 mg of purified solid sample. A freshly prepared stock solution was diluted with toluene (10 mL) to make five dilute solutions ranging from 0.20 to 0.50 mM. Absorbance of each sample was recorded by a UV-Vis spectrophotometer. The extinction coefficient of the *C* form was determined from the slope of a plot of absorbance vs concentration. The five diluted solutions of the *C* form were irradiated with visible light >515 nm light to quantitatively convert the *C* form to the *E* form. Absorbance of each sample was recorded by a UV-Vis spectrophotometer. The extinction coefficient of the *E* form was determined.

3.3.2 Thermal and hydrolytic stability

Monomer based study: The thermal stability of the *N*-alkylindolylfulgimide **1** monomer was measured by a UV-Vis spectrophotometer. A solutions of the *C* form was prepared in toluene (10 ml) with an absorbance of 0.54 at λ_{max} of the *C* form. Each of 7 ampoules were filled with 1.2 ml of *C* form solution and sealed. The ampoules were then wrapped in aluminum foil and incubated in a water bath maintained at 80 °C. Ampoules were removed at specific time and opened and UV Vis absorbance was determined. Same procedure was repeated except that a stock solution of the *C* form was irradiated with visible light to produce the *E* form prior to being transferred to ampoules. A freshly prepared solution of *C* form and

corresponding copolymer was irradiated with visible light with cut off filter > 515 nm to obtain the *E* form.

Copolymer based study: The hydrolytic stability of the copolymer **1-co PAA** in 50 mM sodium phosphate buffer (pH 7.4) and 50 mM sodium acetate buffer (pH 5.0) were measured by a UV-Vis spectrophotometer. A solution of the *C* form was prepared in buffer (10 ml) with an absorbance of 0.57 at $\lambda_{\max}$ of the *C* form. Each of 7 ampoules were filled with 1.2 ml of *C* form solution and sealed. The ampoules were then wrapped in aluminum foil and incubated in a water bath maintained at 37 °C. The same procedure was repeated except that a stock solution of the *C* form was irradiated with visible light to produce the *E* form prior to being transferred to ampoules. Ampoules were removed at specific time and opened and UV Vis absorbance was measured.

3.3.3. Photochemical stability

To measure the photochemical stability of *N*-alkylindolylfulgimide **1** and its copolymer, *C* form monomer of compound **1** in toluene and the *C* form of copolymer in 50 mM sodium phosphate buffer (pH 7.4) and 50 mM sodium acetate buffer (pH 5.0) were quantitatively converted to solutions of *E* form by irradiating with visible light >515 nm. The initial absorbance of the *E* form solutions was 0.91 at $\lambda_{\max}$. The *E* form solution was irradiated to the photostationary state (PSS) with 365 nm light for monomer and 375 nm light for **1-co-PAA**. The UV-Vis spectrophotometer was used to determine the absorbance at $\lambda_{\max}$ of the *C* forms in the visible region. The time taken to achieve 90% of the coloration reaction (*E* to *C* form) at $\lambda_{\max}$ of PSS was then measured. Then, the transformation time of

decoloration reaction of *C* form solutions to *E* form solution was measured. The same solutions of *C* form at PSS were then irradiated with visible light >515 nm again until the absorbance at λ_{max} of the *C*-form, solutions were < 1%. Once, the duration of the coloration and decoloration were established, the freshly prepared solutions were converted back and forth with an automated filter switch. All the solutions were stirred and capped during reaction to avoid evaporation of the solvents. After a designated number of irradiation cycles, the samples were fully converted to PSS with prolonged irradiation and the absorbance was recorded with a UV-Vis spectrophotometer. The photochemical stability was determined by comparison with the initial absorbance at the PSS of *C*.

4. RESULTS AND DISCUSSION

4.1 Synthesis of *N*-alkylindolylfulgimide 1

A new *N*-alkylindolyfulgimide **1**, with a vinylbenzyl attached on the succinimide ring, was synthesized from the precursor indolyfulgide **10**. Indolyfulgide **10**, was synthesized from commercially available 2-methylindole **5**. After methylation of 2-methylindole **5** and subsequent acetylation of 1,2-dimethylindole **6** the product 1,2-dimethyl-3-acetylindole **7** was obtained. Dimethyl isopropylidenesuccinate **4** was reacted with indole **7** to yield *cis/trans* indolelactones **8** via a Stobbe condensation. The indolelactones **8** were then hydrolyzed to a dicarboxylic acid **9** by using NaH and then water. After completion of the reaction the dicarboxylic acid **9** was dehydrated in refluxing acetic anhydride to obtain methyl indolyfulgide **10** in 27% yield. Indolyfulgide **10** was then used as a starting material for the synthesis of *N*-alkylindolyfulgimide **1**. The anhydride ring of methylindolyfulgide **10** was opened via addition of vinylbenzylamine **11**. The resulting succinamic acid **12** was then dehydrated in acetyl chloride to yield the open form *N*-alkylindolyfulgimide **1E**. The *N*-alkylindolyfulgimide **1E** was irradiated with UV light to obtain the closed form of *N*-alkylindolyfulgimide **1C**. The linear copolymer **1-co-PAA** was synthesized from *N*-alkylindolyfulgimide **1C** and acrylamide via free-radical polymerization with AIBN as the initiator. The linear copolymer was photochromic and soluble in water.

4.2 Characterization

4.2.1 UV-Vis absorption spectra

The UV-Vis absorption spectra of *C* and *E* forms of *N*-alkylindolylfulgimide **1** in toluene, and **1-co-PAA** in phosphate and acetate buffer were determined, Table 1. After copolymerization, the resulting copolymer displayed a similar UV-Vis absorption spectrum as the corresponding monomer. In phosphate buffer, the λ_{max} of the **1-co-PAA**, *C* and *E* forms, exhibited a 17 and 7 nm bathochromic shift relative to the fulgimide **1** monomer in toluene, respectively. It has been proposed

Figure 16. UV-Vis absorption spectra of *N*- alkylindolylfulgimide **1** in toluene.

Figure 17. UV-Vis absorption spectra of 1-co-PAA in buffer.

that the *C* form has a near planar structure which can establish an extended conjugated system. The charge separated *C* form has strong interactions with protic solvents causing a decrease in the energy of the electronic transitions that results in a shift of the absorption band to longer wavelength.^{12,66}

Table 1. Extinction coefficients at λ_{max} for fulgimides in toluene

Compound (Medium)	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{mol}^{-1} \text{ L cm}^{-1}$)	
	<i>E</i> -form	<i>C</i> -form
<i>N</i> -Alkyindolylfulgimide 1 (Toluene)	365 (6.1×10^3)	571 (5.3×10^3)
<i>N</i> -Arylindolylfulgimide 2 (Toluene) ⁶⁵	367 (6.6×10^3)	574 (6.0×10^3)
1-co- PAA (Acetate buffer)	368	591
1-co- PAA (Phosphate buffer)	372	588
2-co- PAA (Acetate buffer) ⁶⁵	377	596
2-co- PAA (Phosphate buffer) ⁶⁵	379	590

4.2.2 Thermal and hydrolytic stability

Figure 18. The E form decomposition in 50 mM phosphate (pH 7.4) and 50 mM acetate buffer (pH 5.0). Data for 2-co-PAA from ref.65.

Figure 19. The C form decomposition in 50 mM phosphate (pH 7.4) and 50 mM acetate buffer (pH 5.0). Data for 2-co-PAA from ref. 65.

Figure 20. Decomposition of N-alkylfulgimide 1 and N-arylfulgimide 2 in toluene at 80 °C. Data for N-arylfulgimide 2 from ref. 65.

The stability of the *C* and *E* forms of *N*-alkylindolylfulgimide **1** was studied in toluene at 80 °C. The *E* and *C* forms, were very stable, degradation rate was $<1 \times 10^{-3} \text{ h}^{-1}$. Figure 20. The *C* form showed improved stability compared with a previously studied *N*-arylindolylfulgimide.⁶⁵ The hydrolytic stability of **1-co-PAA** was studied in acetate and phosphate buffer at 25 and 37 °C. In both buffers the *E* form of **1-co-PAA** exhibited enhanced stability relative to the *C* form. In acetate buffer at 37 °C, the hydrolytic stability of the *E* form of **1-co-PAA** is increased by the factor of 3 in comparison to *C* form. In phosphate buffer, hydrolytic stability of *E* form of **1-co-PAA** is increased by the factor of 4 in comparison to the *C* form. In addition, both forms of **1-co-PAA** were slightly stable in acetate buffer than in phosphate buffer Table 2. The degradation rate of the **1-co-PAA** *C* form is 50 fold slower than that of the **2-co-PAA** *C* form in phosphate buffer at pH 7.4 and 37 °C. . It was reported that *N*-ethylmaleimide (*N*-alkylimide) is 25 times more stable than *N*-phenylmaleimide (*N*-arylimide) in a phosphate buffer at pH 7.0.⁶¹ The rate of degradation of **1-co-PAA** in phosphate is slightly higher than in acetate buffer, which shows that this pH range has only a limited effect on the rate of hydrolysis. It has been previously reported that rate of hydrolysis of *N*-alkylmaleimide is base catalyzed in pH range between 7 and 9, and is independent of the pH below pH 4. However the introduction of phenyl on nitrogen provides an effective positive charge on the imide carbonyl, which results in an increase in the rate of hydrolysis. Between pH 5 and 7.4.⁶²

Table 2. Decomposition of fulgimides at 80 °C and copolymers at 37 °C

Compound (Medium) ^{``}	Decomposition rate ($\times 10^3, \text{h}^{-1}$) ^a	
	Open forms	Close forms
<i>N</i> -Alkylfulgimide 1 (Toluene)	0.02	0.21
<i>N</i> -Arylfulgimide 2 (Toluene) ⁶⁵	< 0.01	0.82
1-co-PAA (Acetate buffer)	0.11	0.34
1-co-PAA (Phosphate buffer)	0.23	1.1
2-co-PAA (Acetate buffer) ⁶⁵	0.71	1.0
2-co-PAA (Phosphate buffer) ⁶⁵	0.51	56

^a Data fit to a single exponential decay.

4.2.3 Photochemical Stability

Figure 21. Photochemical decomposition of 1-co-PAA and 2-co-PAA in 50 mM phosphate (pH 7.4) and 50 mM acetate buffer (pH 5.0). Data for 2-co-PAA from ref. 65.

The photochemical stability of *N*-Alkylindolylfulgimide and its corresponding copolymer were studied in toluene and buffers, respectively. In toluene, *N*-alkylindolylfulgimide **1** underwent 507 photochemical cycles before degrading by 20%, Figure 22. The decomposition rate of the monomer **1** is 0.03% per cycle,

Figure 22. Photochemical decomposition of *N*-alkylfulgimide 1 and *N*-arylfulgimide 2 in toluene. Data for *N*-arylfulgimide 2 from ref. 65.

which is similar to that of *N*-arylindolyfulgimide 2.⁶⁵ The decomposition rates of the copolymer were faster in buffers than the monomer in toluene. The copolymer degradation rate is almost similar in acetate buffer as in phosphate buffer, Figure 21. In phosphate buffer **1-co-PAA** underwent 76 cycles before degrading 23%, Table 3. The degradation rates are higher in aqueous solutions. These results are consistent with previous studies which reported that the large dipole molecule of the C form have strong interaction with the polar solvents. This strong interaction lower the transformation process by increasing the activation energy of the reaction. Consequently, fulgimides copolymers have lower quantum yields (longer cycling time) in polar solvents vs nonpolar solvents.^{12,55,63,65} The lower quantum yield increase the cycling time and thus the sample needs to be illuminate for a longer time for a given number of cycles. This results in increased degradation rate.

Table 3. Photochemical stability of fulgimides and copolymers at room temperature

Compound (Medium)	Cycling time (s)		Photochemical decomposition		
	<i>C-E</i>	<i>E-C</i>	Cycles	A/A ₀	% Per Cycle
<i>N</i> -Alkylfulgimide 1 (Toluene)	12	60	507	0.83	0.03
<i>N</i> -Arylfulgimide 2 (Toluene) ⁶⁵	20	100	871	0.81	0.02
1-co-PAA (Acetate buffer)	200	420	65	0.79	0.32
1-co-PAA (Phosphate Buffer)	155	190	76	0.77	0.30
2-co-PAA (Acetate buffer) ⁶⁵	720	720	40	0.80	0.50
2-co-PAA (Phosphate Buffer) ⁶⁵	120	300	105	0.78	0.20

5. CONCLUSION AND FUTURE DIRECTIONS

5.1 Conclusion

A novel *N*-alkylindolylfulgimide molecule having a vinylbenzyl group attached to the nitrogen atom of the imide ring, **1**, was synthesized and copolymerized with acrylamide, **1-co-PAA**. Copolymer **1-co-PAA** exhibited significantly enhanced hydrolytic stability and similar photochemical properties as **2-co-PAA** containing an *N*-arylindolylfulgimide **2**. The previously reported copolymer of *N*-arylindolylfulgimide was unstable in phosphate buffer. Therefore, the stability of fulgimides was improved by replacing the aryl group with an alkyl group. The degradation rate of the least stable *C* form of **1-co-PAA** was 50 times slower than that of **2-co-PAA** in phosphate buffer at pH 7.4. However, in acetate buffer at pH 5.0 the decomposition rate was 3 times slower. The **1-co-PAA** in *E* form exhibited enhanced stability relative to the *C* form in both buffers. The **1-co-PAA** was more

stable in acetate buffer than in phosphate buffer for both forms. The photochemical stability of **1-co-PAA** both in acetate and phosphate buffer.

5.2 Future research

The future work involves two objectives. First, synthesis of crosslinked copolymer and second, applications of the aqueous soluble copolymer in aqueous environment need to be investigated.

The *N*-alkylindolylfulgimide has enhanced hydrolytic stability in phosphate buffer. An *N*-alkylindolylfulgimide with doubly substituted vinylbenzyl group can be synthesized. The methyl group on the indolyl ring needs to be replaced with vinylbenzyl chloride. A synthetic scheme is proposed, Scheme 13.

Additionally, fulgimides have the potential to be copolymerized with polymers. This crosslinked copolymer can be used as a hydrogel. The photochromic fulgimide copolymers have many applications. For example, it can be used to turn “on” and “off” enzyme activity. The light-induced activity is a safe method for biological systems. The enzyme will be immobilized in polymer, and upon irradiation of the light photochromic compound will be transformed and enzyme will react with substrate, Figure 23.

Figure 23. Enzyme immobilization by using photochromic copolymer

The trifluoromethyl dicyclopropyl indolylfulgide is known for its excellent thermal stability.⁶⁴ Derivation of this fulgide to the fulgimide by proposed scheme 15 might result in highly stable trifluoromethyl dicyclopropyl *N*-alkylindolylfulgimide **4** in aprotic solvents, Scheme 15.

Scheme 13. Proposed synthetic pathway of disubstituted *N*-Alkylindolylfulgimide 3.

Scheme 14. Polymerization of disubstituted *N*-Alkylindolyfulgimide.

Scheme 15. Proposed synthetic pathway of trifluoromethyl dicycloproyl *N*-Alkylindolyfulgimide 4.

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