

UGR 1.

Solvent Effects on the Reaction Rate of *m*-Methylphenolate with Acetic Anhydride

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Keywords

Computational chemistry, organic chemistry, nucleophilic acyl substitution, m-methylphenolate

Abstract

The nucleophilic acyl substitution reaction process between meta- substituted phenolates and acetic anhydride has been suggested to proceed as either concerted or step-wise. The first involves only one transition state between reactions and products, while the latter includes two high energy transition states and the formation of a relatively stable tetrahedral intermediate. Some experimental evidence has preferred the concerted process but nothing conclusive has been found (Ba-Saif, Luthra, Williams, J. Am. Chem Soc. 1987, 109, 6362). Previous research in our group has used the 6-31+G** basis set and B3LYP computational method to study this reaction process in the gas phase focusing on the electronics effect of substituents; m-nitrophenolate gives a concerted process while m-methylphenolate is step-wise. It is the goal of this research to determine how SM8 and SMD solvation models affect the step-wise reaction profile of m-methylphenolate with acetic anhydride in the aqueous phase. Preliminary tests using both models tracked solvation effects on three structures optimized in the gas-phase: transition state one, a putative tetrahedral intermediate, and transition state two. Calculations on these complexes using SMD and SM8 show a linear downward trend in energy with transition state two 11.0 and 12.4 kJ/mol more stable than the tetrahedral intermediate. Further research with optimization in the aqueous phase will be necessary to clarify these findings.

**Undergraduate Student/Award Consideration/Wittenberg University
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Academic Advisor: Justin Houseknecht

UGR 2.

One-Step Solvent-Free Synthesis and Grafting of Diazonium Salts onto Glassy Carbon Electrodes

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Abstract

The modification of glassy carbon electrodes is a versatile and efficient process that has been effected through chemical and electrochemical reduction, in addition to ultrasonic and ultraviolet wave exposure. From literature and previous research, it is known that an aryl amine can be converted into a diazonium ion by the reaction of a diazotizing reagent along with a weak acid, and that grinding glassy carbon electrodes in dry diazonium salts is sufficient to induce grafting onto their surfaces. Inspired by the findings, it was hypothesized that grinding glassy carbon electrodes in a water paste consisting of an aryl amine, *p*-toluenesulfonic acid, and sodium nitrite would allow for the synthesis of diazonium ions and subsequent surface attachment of aryl groups. The procedure was successfully implemented with four amines including *p*-nitroaniline, *m*-nitroaniline, 4-amino-3-nitrophenol, and 2-aminoanthraquinone. The result was confirmed by characteristic voltammetry of the attached groups and Raman spectroscopy of the reaction paste. Surface coverage resulting from the grafting of *p*-nitroaniline, calculated by integration of voltammetric peaks, exceeded 2 nmol/cm², which is greater than that obtained by grinding in dry diazonium salts. The coverage is also suggestive of the formation of more than a monolayer of attached groups. Despite the large coverage values, voltammetry of redox probes such as dopamine indicate that the electrode surfaces are still capable of electron transfer to solution species. Taken from the aspect of green chemistry, the procedure is particularly desirable because it produces no organic solvent wastes and does not require the isolation of any intermediates.

**Undergraduate Student/Award Consideration/Wittenberg University
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UGR 3.**Uncatalyzed Knoevenagel Condensation in Aqueous Medium
at Room Temperature**

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Abstract

Knoevenagel condensation, a carbonyl condensation between aldehydes and active methylene molecules (Deb, Bhuyan, 2005), is an important method for carbon-carbon bond formation (Jones, 1967; Tietze, Beifuss, 1991). Knoevenagel condensation products can serve as reactants for Diels-Alder reactions as well as the synthesis of heterocyclic compounds (Deb, Bhuyan, 2005). The conventional method requires base catalysts such as an amine, ammonia or sodium ethoxide in organic solvent (Deb, Bhuyan, 2005). Due to the strong basicity of traditional catalysts, several environmentally benign catalysts have been studied by researchers. Those catalysts include Lewis acids, surfactants, zeolites and heterogeneous catalysts (Deb, Bhuyan, 2005). Microwave, clays, ionic liquids, biotechnology catalysts, ultrasound, solvent-free grinding, and solid phase have all been shown to catalyze the reaction as well (Menegatti, 2012). Following Deb and Bhuyan's research, a greener method of uncatalyzed Knoevenagel condensation in water at room temperature was proposed (Deb, Bhuyan, 2005). Using water as the only solvent and no catalyst, various aromatic aldehydes and several active methylene molecules were reacted. Several successful reactions were reported, including ethyl cyanoacetate and 3-methyl-1-phenyl-2-pyrazoline-5-one (Edaravone). All of the products were quantitatively (e.g. percent yield) and qualitatively (e.g. IR, ¹H-NMR etc.) analyzed after reactions.

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Academic Advisor: Dr. David Finster

UGR 4.

Synthesis of Cadmium Selenide Quantum Dot Nanoparticles

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Abstract

Quantum dots are nanoparticles which are made from semiconductor materials that are small enough to exhibit properties that differ from the properties of bulk semiconductor materials. This poster describes a synthetic method of producing CdSe quantum dot nanoparticles where it is very easy to control the size of the nanoparticle. This method is safer, easier, and faster than other methods for producing CdSe quantum dots. It was found that the emission spectra of the CdSe quantum dots may have more than one emission process and that the end size of the CdSe quantum dot nanoparticle depends on the temperature and time the reaction is allowed to proceed.

**Undergraduate Student/Award Consideration//Wittenberg University
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UGR 5.

**Quantitative Raman Enhancement of Copper Chlorophyllin
by Silver Colloids**

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Abstract

The objective was to quantitatively analyze the level of Raman signal from copper chlorophyllin on silver colloids due to Surface-Enhanced Raman Spectroscopy (SERS). The reducing agent for the colloid and/or size of the colloid, use of salt, polymer concentration, and pH all influenced the signal level. The first step in this research was to synthesize suitable colloids to be used for SERS. Silver nitrate was reduced using six different reducing agents in order to create different colloid sizes. These colloids were characterized through the use of UV-Vis spectroscopy with maximum absorption wavelengths ranging from 350nm-800nm. To characterize how monodisperse the colloids were the peak width was calculated (FWHM). The second step of the research was to prepare samples for SERS analysis by adhering copper chlorophyllin to the colloids. Salt (NaCl) concentration, use of a polymer (polyvinyl acrylate), pH, and type of colloid were all varied to find maximum enhancement. The amount Raman signal enhancement as a function of pH contradicts a literature source¹, as effect of pH upon the observed signal is opposite than what was previously reported.

1. Schnitzer, C.S.; Reim, C. L.; Sirois, J. J. *J. Chem. Educ.*, **2010**, 87, 429 – 431.

**Undergraduate Student/Award Consideration//Wittenberg University

Research Advisor: Dr. Raymond Dudek

Academic Advisor: Dr. Raymond Dudek

UGR 6.**Computer Simulations of Peptide Translocation by ClpY Nanomachines**

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Abstract

Protein misfolding is a common problem within the cellular environment. As proteins become misfolded, they have a propensity to aggregate, which has been linked to several neurodegenerative diseases such as Alzheimer's and Parkinson's disease. Clp ATPases, members of the AAA+ (ATPases associated with various cellular activities) superfamily, assist in the bacterial protein quality control system to remove misfolded proteins. These nanomachines are hexameric ring structures which couple the energy produced by ATP hydrolysis with large scale conformational changes to perform unfolding, translocation and degradation of targeted substrate proteins (SPs). Flexible pore loops residing in the central channel have a highly conserved GYVG motif. Upon ATP hydrolysis, the loop undergoes a ~10Å motion along the pore axis. The tyrosine amino acid of each loop has been proposed to act as a "paddle", binding the SP when ATP is bound at the subunit, and pulling it through the pore as ATP is hydrolyzed. These ATPases are highly versatile, degrading any misfolded SP within the cell provided it has a degradation tag for recognition. In this study, we probe the dependence of the translocase activity on the SP sequence. We performed molecular dynamics simulations of the well-characterized ClpY ATPase and two substrate proteins to determine whether the pore loop will "slip" when it encounters a sequence of amino acids without side chains. The SP is a SsrA-SsrA fusion peptide with random coil structure. In the mutant variant, five internal amino acids of the peptide were substituted by a contiguous stretch of Glycine amino acids. Translocase activity of both SP's was examined, and our results suggest that slipping occurred in the mutated SP.

**Undergraduate Student/Award Consideration/Central State University
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Academic Advisor: Dr. Ibrahim Katampe

UGR 7.

Flame Retardant Composite Materials

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Abstract

Polyurethane is a versatile polymer that can be used for many applications in industries and commercial products. Despite polyurethanes multiple uses, it is a highly flammable thermoplastic polymer which can seriously restricts its usage in the fields with the requirement of fire safety. In this study, Melamine was used as the flame retardant to improve the flame retardancy of polyurethane films because of their potential barrier effect in polymer matrix. Also it is an environmentally friendly additive that releases less dense smoke and toxic fumes also it releases nitrogen gas as a product under combustion which is 78% of the air we breathe. UL-94 Vertical Flame Test for thin materials was used to show that the addition of melamine increases the thermal properties of polyurethane film. The detailed burning behaviors and mechanisms under combustion should be further studied.

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Academic Advisor: Dr. Suzanne Seleem

UGR 8.

**Laser Flash Photolysis of Aromatic Compounds in the Solid State
and Solution**

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Abstract

The photochemistry of several aromatic compounds, such as corannulene and pyrene, in the solid state and solution was studied. Laser flash photolysis of aromatic compounds in solution and the solid state made it possible to detect their triplet excited state. Furthermore, the laser flash photolysis demonstrated that the triplet excited states were much shorter lived in the solid state than in solution. The effect of the crystal lattice on the excited state of these compounds will be discussed in terms of size, shape, and calculation of carbon bonds.

**Undergraduate Student/Award Consideration/ Central State University
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Academic Advisor: Dr. Suzanne Seleem

UGR 9.

**The Crisis of Water Contamination: Heavy Metal Detection
Utilizing Electrochemistry**

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Keywords

Contamination, Sensors, Electrochemistry

Abstract

Heavy metals in water are an important environmental concern due to its high toxicity to a wide spectrum of living organisms at the level of parts per billion (ppb). Many parts of the world have contamination in the ground water and drinking water with heavy metals such as lead and arsenic. There is a pressing need to detect trace amounts of these heavy metals on-site with low cost and portable sensors for real world analysis. Our research group has been working on the use of Square Wave Anodic Stripping Voltammetry (SWASV) to detect heavy metals lead and arsenic with inexpensive bare gold and bare silver electrodes. Our results have found that the gold electrode overall gave the best detection in the ppb range for arsenic and lead and enhanced signal of over 30%. Additionally, the sensitivity of optimized SWASV parameters such as deposition time will be displayed as well.

**Undergraduate Student(s)/Team Award Consideration/Wright State University
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Academic Advisor: Dr. Suzanne Lunsford

UGR 10.

Synthesis of a Haplomyrtin Precursor from a TIPS Protected Intermediate

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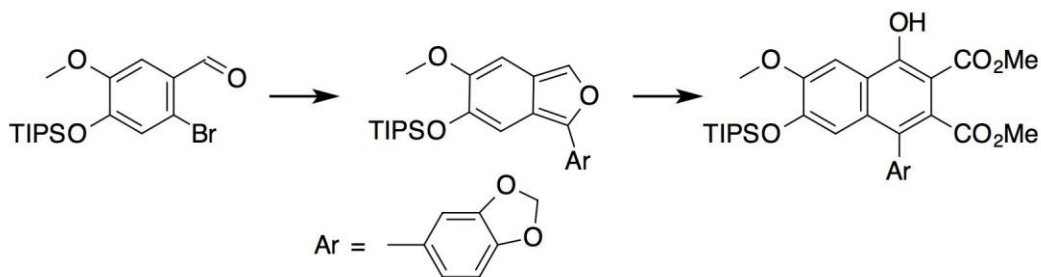
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Keywords

TIPS protected, Haplomyrtin, Diels-Alder, Cycloaddition

Abstract

Previous synthetic efforts directed at Haplomyrtin focused on the use of a benzyl protective function in the preparation of an intermediate 2-phenylbenzofuran. The use of a TIPS protective group affords a distinct advantage in this preparation. Thus, the reaction of 6-bromovanillin with triisopropylsilylchloride produces 2-bromo-4-triisopropylsilyloxy-5-methoxybenzaldehyde. Protection of the benzaldehyde function as the cyclic ethylene ketal is followed by a lithium halogen exchange reaction and a subsequent reaction of the lithium intermediate with piperonal to produce a non-isolatable alcohol. Immediate reaction of the alcohol with an acid catalyst in the presence of dimethyl acetylenedicarboxylate (DMAD) produces the Diels-Alder product dimethyl 1-(1,3-benzodioxol-5-yl)-4-hydroxy-6-methoxy-7-triisopropylsilyloxynaphthalene-2,3-dicarboxylate, a Haplomyrtin precursor.



**Undergraduate Student/Award Consideration/Wright State University

Research Advisor: Dr. William Feld

Academic Advisor: Dr. William Feld

GR 1.**Low-Temperature Crystallization of Biomimetically Synthesized TiO₂ Nanomaterials**

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Abstract

Titania is a widely utilized metal oxide in many commercial and defense applications due to its unique physico-chemical properties such as photosensitivity, biocompatibility and nontoxicity. Indeed, nanosized titania has emerged as an important material for several advanced technologies including energy harvesting (i.e., photovoltaics) and the photocatalytic degradation of organic pollutants in water, air, and on surfaces. In this research, TiO₂ materials were biomimetically synthesized, utilizing peptides/polymers (e.g. polyethylene imine (PEI), protamine, and lysozyme) to initiate and mediate the precipitation of titania from an aqueous Ti-containing precursor. Biomimetic approaches for creating TiO₂ represent an attractive alternative to traditional high temperature (> 500°C) synthesis methods, as biomimetically generated titania contains functional organic constituents. Unfortunately, biomimetic mineralization techniques typically produce amorphous or poorly-crystalline titania materials or require specialized, recombinantly produced proteins to produce highly-crystalline rutile or anatase TiO₂. In this study, we have investigated the devitrification of biomimetically synthesized titania materials under relatively mild conditions that mimic natural microbial environments. The production of highly-crystalline titania under such benign conditions is advantageous, as the organic component of the bio-hybrid material is preserved and available for further use, such as halamine formation. This processing route yielded bio-hybrid /nano TiO₂ materials with photocatalytic activity exceeding that of the commercial standard, Degussa P25. Furthermore, the synthesized materials exhibit multimodal detoxification capabilities due to the presence of oxidizing halamines.

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Academic Advisor: Dr. Kevin Myers

GR 2.

Effect of Alkyl Chain Length on the Thermal Properties of Poly(arylene ether)s Derived From *N*-Alkyl-*N*-Phenyl-3,5-Difluorobenzene sulfonamides

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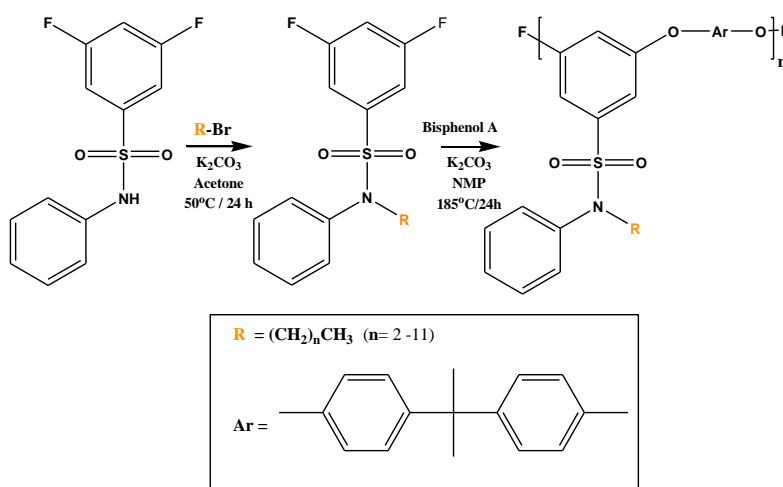
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Keywords

PAE, Sulfonamide, *N*-alkyl derivatives, Glass transition temperature

Abstract

Meta-activated nucleophilic aromatic substitution leads to poly(arylene ether)s, PAE, in which the activating group resides in a pendant position relative to the polymer backbone. The nitrogen atom in the strongly activating sulfonamide provides a point of chemical diversity that can be exploited to tailor the physical properties of the resulting polymers. Using *N*-phenyl-3,5-difluorobenzene sulfonamide group as the starting material a series of *N*-alkyl derivatives, with chain lengths of 3 to 12 carbon atoms, were prepared and characterized followed by conversion to the corresponding PAE. The effect of alkyl chain length on the thermal stability and glass transition temperatures, T_g , values was determined.



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Research Advisor: Dr. Eric Fossum

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GR 3.**Determination of the Intracellular Fate and Trafficking of Chelerythrine, a Potent BH3 Mimetic and Na⁺/K⁺ ATPase Inhibitor, in Human Lens Epithelial Cell Cultures via Surface-Enhanced Raman Spectroscopy (SERS)**

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Abstract

Chelerythrine (CET) is a quaternary benzophenanthridine alkaloid (QBA) and potent pro-apoptotic capable of inhibiting the Na⁺/K⁺ ATPase (NKA) in human lens epithelial cell (HLEC) lines. Despite the medicinal use of CET and other structurally related QBAs for centuries, the mechanism and intracellular fate of CET is largely speculated and unknown. To this end, this study aimed to track the intracellular distribution and quantitatively determine the degree of accumulation of CET within various cellular compartments via surface-enhanced Raman spectroscopy (SERS)-based nano-sensing. HLECs were treated with 50 μM of CET in 300 mOsM phosphate buffered saline solution for 30 minutes at 37 °C. Cytosolic, crude and purified (*i.e.*, free of nuclear material) plasma membrane, and whole cell extracts were obtained and incubated with Creighton colloidal silver nanoparticles (AgNPs) for SERS sensing. The SERS analysis rapidly detected the presence of a large amount of intracellular CET while concurrently yielding the concentration of free CET in each extract via a linear calibration function of the integrated band area of the 659 cm⁻¹ phonon mode. The CET concentration within the cytosol of HLECs was found to be near passive diffusion equilibrium, suggesting rapid transmembrane transport as a cationic monomer. However, when normalized for total protein content, the CET content was found to be nearly 100 fold higher in the plasma membrane than cytosolic extracts. These data suggest and provide further support to the recent observations indicating that CET expeditiously enters and distributes inside the cell and with a potential high affinity for P-type ATPases, such as the NKA.

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Academic Advisor: Dr. Ioana E. P. Sizemore

GR 4.

Growth of Sparingly-Soluble Minerals: The Effect of Varying Ratio and Impurity Concentration

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Keywords

mineral growth kinetics; calcite; magnesite; AFM

Abstract

A fundamental understanding of mineral growth kinetics is necessary to predict mineral reactivity in geologic environments. Here, we use hydrothermal atomic force microscopy to measure reaction rates and morphological evolution of sparingly-soluble minerals while systematically varying the concentrations of their constituent cations and anions in solution. We find that calcite, a calcium carbonate mineral, grows via a kink site nucleation limited mechanism, while magnesite, a magnesium carbonate mineral with the same structure as calcite, does not due to the slower rate of water exchange for magnesium ions. We have also determined strontium inhibits calcite growth by preventing calcium attachment to the surface. A theoretical model used to explain this behavior was also developed.

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GR 5.

Synthesis of Main Chain Alkoxy Substituted DP-PPV and Application of HWE to DP-PPVs

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Keywords

OLEDs, photoluminescent polymers, and PPVs/DP-PPVs

Abstract

In the interest of the synthesis of polymers that have the potential to possess inherent light emitting properties (LEDs) the synthesis of a novel 1,4-bis(chloromethyl)benzene monomer, 5-benzyloxy-1,4-dichloromethyl-2,3-diphenyl benzene **1** was done. Monomer **1** was polymerized via the Gilch polymerization method to yield, poly(5-benzyloxy-2,3-diphenyl phenylene vinylene) **2**. Polymer **2** was characterized by TGA, DSC, GPC, UV-Vis and fluorescence studies, and was found to have a $T_{d5\%}$ of 267°, M_w/M_n of 7136 Da/6603 Da, an absorbance maximum at 406 nm and an emission maximum at 509 nm. The Horner-Wadsworth-Emmons variant of the Wittig was applied in the synthesis of poly(2,3-diphenyl-1,4-phenylenevinylene) (DP-PPV) **3** from 1,4-bis(diethoxyphosphorylmethyl)-2,3-diphenyl benzene **4**, which was synthesized via the Michaelis-Abuzov reaction, and 2,3-diphenylterephthaldehyde **5**.

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Research Advisor: Dr. William Feld
Academic Advisor: Dr. William Feld

GR 6.

Novel Oxyalkylene Linked Polyimides

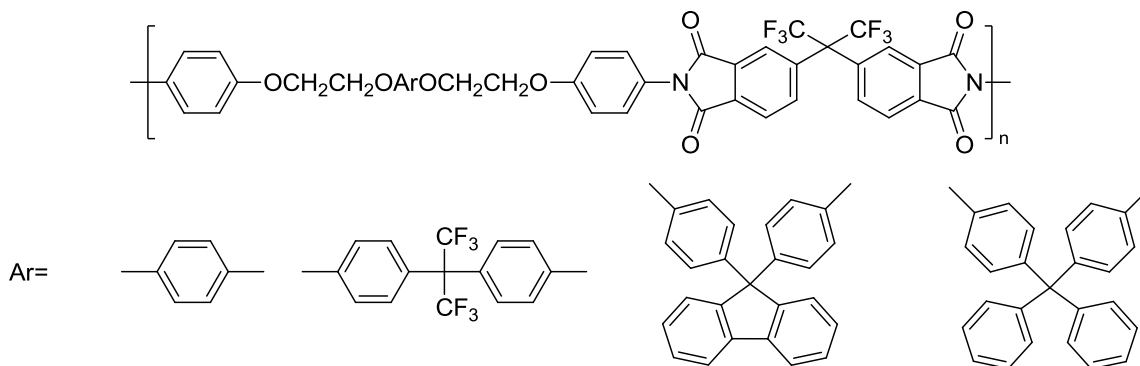
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Keywords

diamines, 6FDA, polyimides

Abstract

Flexible oxyalkylene ether linkages within the polyimide backbone have been shown to decrease T_g but do not have a deleterious effect on thermal stability. Several diamine compounds with oxyalkylene ether linkages were synthesized by the usual reaction of diols, hydroquinone bis(2-hydroxyethyl) ether, 2,2-bis[4-(2-hydroxyethoxy)phenyl]hexafluoropropane, and 4,4'-(9-fluorenylidene)bis(2-phenoxyethanol), with p-fluoronitrobenzene followed by chemical reduction. The diamines were converted to polyimides by using 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in a one-pot, amic-acid/imidization procedure in m-cresol. The fully closed imides could be casted into transparent, creasable films and exhibited a 5% weight loss at $>400^\circ$ and appeared to exhibit a thermal transition ranging from 186 - 231° by DSC. Currently, another diamine synthesized from 4,4'-bis(2-hydroxyethoxy)-tetraphenyl methane, will be reacted with 6FDA to produce a polyimide which will provide comparison for thermal properties.



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Research Advisor: Dr. William Feld

Academic Advisor: Dr. William Feld

GR 7.

Aryl Alkoxy Polyethers

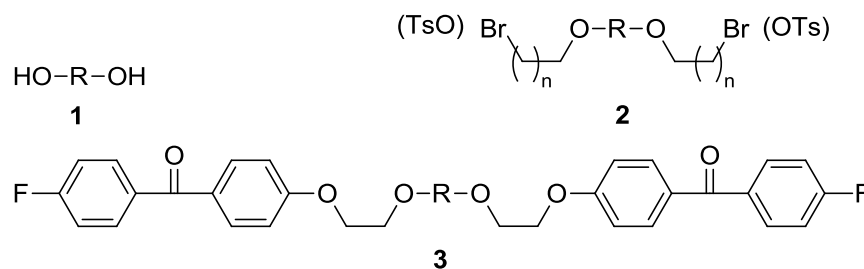
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Keywords

dibromo compounds, ditosylates, poly(ether)s, poly(ether ether ketone)s

Abstract

The ready availability of diphenol compounds **1** has led to the synthesis of a series of building blocks for use in the preparation of unique monomers. The reaction of aromatic bis(hydroxyethoxy) compounds with p-toluenesulfonyl chloride or the use of α,ω -dibromoalkanes leads to a series of monomers exemplified by **2**. Subsequently, the reaction of appropriate dibromides or ditosylates **2** with 4-fluoro-4'-hydroxybenzophenone leads to a series of unique PEEK related monomers illustrated by **3**. Polymerization of these monomers can be conducted in NMP using K_2CO_2 as a base and toluene as an azeotroping agent.



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F 1.

Flipping Organic Chemistry with Just-In-Time Teaching

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Abstract

The undergraduate organic chemistry curriculum requires levels of analysis, synthesis, and critical thinking for which most students are under-prepared. As instructors it is our responsibility to provide the optimal environment for students to achieve these important learning goals. The “flipped classroom” is an effective model to achieve the higher order learning goals inherent in organic chemistry. The flipped classroom described here was implemented in conjunction with Just-In-Time Teaching (JiTT). The initial class contained fifty-one students at Wittenberg University. Students prepared for class by following detailed reading guides, completing online homework, and commenting on the material with which they struggled using the course management system. Class was approximately half answers to their direct questions and half group problem solving. Students worked in groups of 3-4 to create both visual (pen strokes on the iPad) and auditory solutions using the *Explain Everything* app. Challenges and successes of this approach will be discussed including a four-fold reduction in students obtaining a D, F, or W in Organic I.

F 2.

Comprehensive Safety Instruction for an Undergraduate Chemistry Program

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Abstract

Optimal safety instruction at the college level for chemistry courses is described in some detail in the Supplements to the ACS CPT Guidelines. To meet these requirements it is best to develop a comprehensive safety program that spans the four-year curriculum so that students appreciate that safety is a part of all lab activities. This program reveals that safety issues presented in various courses in a four-year program become more complicated as advanced courses are addressed. This poster will outline a program that includes safety instruction in all lab courses.