COMPUTATIONAL STUDY ON THE MOLECULAR BEHAVIOUR OF HARD SEGMENTS OF MDI BASED POLYURETHANE.

By

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Declaration

The work described in this thesis was carried out by me under the supervision of Dr. Ranga S. Jayakody and Prof. Laleen Karunanayake. This has not been submitted in whole or in part to any university or any other institution for another Degree/Diploma.

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Bhagya Sharmali Wickramanayaka Karunarathna

2019

Certification of the supervisor

We certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University for the purpose of evaluation.

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Table of contents

List of Tables

List of Figures

LIST OF ABBREVIATIONS

MDI-BDO	4,4'-diphenylmethane diisocyanate and 1,4-butanediol
UV	Ultraviolet
TPU	Thermoplastic polyurethane
TDI	Toluene diisocyanate
MDI	Methylene diphenyl diisocyanate
NDI	1,5-naphthalene diisocyanate
PU	Polyurethane
PPDI	p-phenylene diisocyanate
Me-M-Me	Methanol capped methylenebisphenyl diisocyanate
HDO	Hexandiol
PDO	Propanediol
EDO	Ethylene glycol
DSC	Differential Scanning Calorimetry
PCL	Polycaprolactone
RDF	Radial Distribution Function
IR	Infrared
ESR	Electron Spin Resonance
ICT	Intramolecular charge transfer

SMILES	Simplified Molecular Input Line Entry System
STO	Slater-type orbitals
GTO	Gaussian-type orbitals
ESP	Electrostatic Surface Potential
PES	Potential Energy Surfaces
HASB	Hard – Soft – Acid – Base theory
MPA	Mulliken Population Analysis
APFD	Austin-Frisch-Petersson functional
TD-APFD	Time-dependent Austin-Frisch-Petersson functional
DFT	Density Functional Theory
TD-DFT	Time-dependent Density Functional Theory
MM	Molecular Mechanics
OPLS	Optimized Potentials for Liquid Simulations
OPLS-AA	All Atom Optimized Potentials for Liquid Simulations
UA	United Atom
OPLS-UA	United Atom - Optimized Potentials for Liquid Simulations
2D	Two dimensional
3D	Three dimensional

PME	Particle Mesh Ewald
RMSD	Root Mean Square Deviation
TS	Transition State
NBO	Natural Bond Orbital

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First and foremost, I want to thank my principal advisor Dr. Ranga S. Jayakody for encouraging my research and for allowing me to grow as a research scientist. His advices on both research as well as on my career have been priceless. I appreciate all his contributions of time and ideas to make my Ph.D. experience productive and stimulating. He has shown me, by his example, what a good scientist (and person) should be. I am also very grateful to Prof. Laleen Karunanayake, my Co- supervisor for his scientific advice and knowledge and many insightful discussions and suggestions. He is the most flexible supervisor I ever seen, and I specially thank to his kindness and wonderful attitudes towards his post graduate students.

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ABSTRACT

COMPUTATIONAL STUDY ON THE MOLECULAR BEHAVIOUR OF HARD SEGMENTS OF MDI BASED POLYURETHANE.

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Segmented polyurethanes show extraordinary physicochemical properties, mainly owing to the nature and the chemistry of the hard segment domains. There are yet many inexplicable physiochemical properties of MDI-BDO based hard polyurethane segments such as the geometry, *cis-trans* isomerism, electronic structure, chemical reactivity, dual fluorescence behaviour, the inter-hard-segment interactions, and the photo-response. In this study, it was attempted to develop and validate a model system that would facilitate further research on the structural and chemical properties of the MDI-BDO hard segments.

It was found that the *trans* isomer of urethane bond is more stable than the *cis* isomer and is argued here that thermal transformation from *trans* to *cis* not possible due to the high rotational energy barrier. The calculated Fukui indices show that *cis* and *trans* isomers are different in their chemical reactivity. The findings of this study suggest intermolecular and intramolecular pi-stacking and highly plausible two significant types of hydrogen bond types between hard segments.

In this study, a model system for MDI-BDO hard segment was developed and successfully validated via computational experiments. Further calculations done with the new model provided an indispensable understanding of the structure, *cis-trans* isomerism, reactivity, intermolecular interactions of the MDI-BDO hard segments. In summary, through the novel model, this study has opened new doors to the understanding of the

structural and chemical features of the hard segments of the MDI-BDO based polyurethane

We introduced a novel theoretical explanation on the dual fluorescence behaviour of MDI-BDO polyurethane hard segment upon irradiation. Even with the relatively small differences of absorbed energy, both *cis* and *trans* conformers undergo emissions with a relatively more significant difference in energy.*Cis* isomer undergoes larger geometrical relaxation at excited state by dissipating more energy as non-radiative relaxation and emit radiation with low energy. *Trans* isomer is having relatively small geometry relaxation at the excited state and emit radiation with high energy.

Trans to *cis* isomerization in the ground state is forbidden due to the high rotational barrier of 38 kcal/mol. With the presence of UV, *trans* to *cis* isomerization is possible by non-radiative relaxation through the conical intersection of first excited state and ground-state potential energy surfaces. It will let the molecule undergoes relaxation into either *cis* or *trans* configurations. Hence, the dual fluorescence nature of MDI-BDO can be observed via photoisomerization upon UV irradiation. This study was able to give a molecular level explanation to the dual fluorescence nature of the MDI BDO hard segments.

Keywords

MDI, MDI-BDO, Polyurethane, Photo isomerization, Dual fluorescence