

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

By

**BAGGYA SHARMALI WICKRAMANAYAKA
KARUNARATHNA**

Ph.D.

2019

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

By

BAGGYA SHARMALI WICKRAMANAYAKA

KARUNARATHNA

Thesis submitted to the University of Sri Jayewardenepura for
the award of the Degree of Doctor of Philosophy

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.

.....

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.

.....

Dr. Ranga S. Jayakody

Project Supervisor

Department of Chemistry,

Faculty of Applied Sciences,

University of Sri Jayewardenepura.

Date:

.....

Prof. Laleen Karunanayake

Project Supervisor

Dean,

Faculty of Applied Sciences,

University of Sri Jayewardenepura.

Date:

Table of contents

1. Introduction.....	1
1.1. Polyurethane structure.....	1
1.2. Applications of polyurethanes.....	2
1.3. Isocyanates.....	3
1.4. Polyols.....	5
1.5. Chain Extenders.....	6
1.6. MDI-BDO Hard segment.....	8
1.7. Intermolecular interactions of polyurethane chains.....	8
1.8. Photophysical and Photochemical Processes of MDI-BDO hard segment.....	9
1.9. UV-Vis spectroscopy.....	10
1.10. Fluorescence spectroscopy.....	11
1.11. Dual fluorescence nature of the material.....	12
1.12. Overview of the research problem.....	13
2. Literature Review.....	15
2.1. Structure of MDI-BDO.....	15
2.2. Hydrogen bond interactions in the polyurethane polymer matrix.....	17
2.3. Polyurethane upon UV irradiation.....	20
2.4. Dual fluorescence nature of polyurethane upon UV irradiation.....	22
2.5. Photoisomerization.....	23
3. Methodology.....	29

3.1.	Computational Quantum Mechanics	29
3.1.1.	Predicting Molecular Geometry	30
3.1.2.	Geometry optimization	30
3.1.3.	Optimization Algorithm	32
3.1.4.	Level of Theory	33
3.1.5.	Basis set	34
3.1.6.	Electrostatic surface potential map	36
3.1.7.	Potential Energy Surface Scan	36
3.1.8.	2-Dimensional potential energy surface	37
3.1.9.	3-Dimensional potential energy surface	37
3.1.10.	Dipole Moments	38
3.1.11.	Chemical Reactivity	39
3.1.12.	IR- spectroscopy	41
3.1.13.	UV-Visible Spectra	42
3.1.14.	Natural Bond Order analysis	43
3.1.15.	Emission spectrum calculation	44
3.1.15.1.	Frank-Condon Principle	44
3.2.	Classical Computational Methods	48
3.2.1.	Molecular Dynamics Simulations	48
3.2.2.	Force Field	49
3.2.3.	Model construction	50

3.2.4.	Energy minimization.....	51
3.2.5.	Integration Algorithms.....	51
3.2.5.1.	Newton's equations.....	51
3.2.5.2.	The Verlet algorithm.....	52
3.2.5.3.	The Velocity Verlet algorithm.....	53
3.2.6.	Canonical ensemble (NVT).....	53
3.2.7.	Isothermal-isobaric ensemble (NPT).....	53
3.2.8.	Simulation temperature.....	54
3.2.9.	Thermostats.....	54
3.2.9.1.	Berendsen thermostat.....	54
3.2.9.2.	Nose-Hoover temperature coupling.....	55
3.2.10.	Periodic Boundary Conditions (PBC).....	57
3.2.11.	Constraint MD.....	60
3.2.12.	Particle Mesh Ewald (PME).....	60
3.2.13.	Glass Transition Temperature Calculation.....	61
3.2.14.	Hydrogen bond analysis.....	62
3.2.15.	Hydrogen bond autocorrelation.....	63
3.2.16.	Root mean square deviations Calculations.....	64
4.	Results and Discussion.....	65
4.1.	Geometry optimization.....	65
4.2.	Potential energy scan along H ₃₈ N ₈ C ₆ O ₇ dihedral.....	69

4.2.1.	C-N bond length change over the change of H38N8C6O7 dihedral angle	
		74
4.2.2.	Lone pair occupancy	76
4.3.	<i>Cis</i> and <i>trans</i> isomers	79
4.3.1.	Vibrational Frequencies of <i>trans</i> and <i>cis</i> conformations.....	80
4.3.2.	Dipole moment.....	83
4.3.3.	Chemical Reactivity.....	84
4.4.	The ground-state properties of MDI-BDO	89
4.4.1.	Electrostatic potential map of MDI-BDO	89
4.4.2.	Hydrogen bond interactions of MDI-BDO at ground state.....	91
4.4.2.1.	Hard segment - Hard segment interactions.	91
4.4.2.2.	Infrared spectroscopy for hydrogen-bonded MDI-BDO dimer.....	97
4.4.2.3.	Hard segment-Soft segment interactions.....	99
4.4.3.	Molecular dynamics simulations.....	105
4.4.3.1.	Construction of MDI-BDO molecular model system	105
4.4.3.2.	The density of the MDI-BDO molecular model system	106
4.4.3.3.	Dynamic stability of the MDI-BDO molecular model.....	107
4.4.3.4.	Glass transition temperature	108
4.4.3.5.	Hydrogen bond interaction dynamic in MDI-BDO molecular model.	110
4.4.3.6.	Change in Dihedral angle (C14C15C16) over the simulation period.	113
4.4.3.7.	The change in the dihedral angle with temperature.....	114

4.5.	The differences in chromophore characteristics of <i>cis</i> and <i>trans</i> MDI-BDO isomers.....	115
4.5.1.	The UV absorption of MDI-BDO.....	115
4.5.2.	The differences in Fluorophore characteristics of <i>cis</i> and <i>trans</i> MDI-BDO isomers. 123	
4.5.2.1.	Fluorescence of MDI-BDO	123
4.5.2.2.	The Stokes shift	125
4.5.2.3.	Geometrical changes during non-radiative relaxation.....	127
4.5.2.4.	Non-radiative relaxation in Molecular orbitals perspective	129
4.6.	<i>Trans</i> to <i>cis</i> isomerization at the ground state.....	133
4.7.	<i>Trans</i> to <i>cis</i> isomerization upon UV irradiation.....	140
4.8.	The dual fluorescence nature of MDI-BDO.....	144
5.	Conclusions.....	146
6.	References	
	Appendix 1	
	Appendix 2	
	Appendix 3	
	Appendix 4	

List of Tables

Table 1. NBO analysis data of trans to cis isomerization.	71
Table 2. Hydrogen bond parameters and Type of intermolecular hydrogen bonds for MDI-BDO dimer.....	95
Table 3. Hydrogen bond parameters and type of intermolecular hydrogen bonds for MDI-BDO trimer	95
Table 4. Hydrogen bond parameters and type of intermolecular hydrogen bonds for MDI-BDO dimer.....	96
Table 5. Hydrogen bond parameters and type of intermolecular hydrogen bonds for MDI-BDO-PCL dimer.	104
Table 6. Hydrogen bond parameters and type of intermolecular hydrogen bonds for MDI-BDO-PCL trimer.....	104
Table 7. Excited states transitions of trans MDI-BDO	116
Table 8. Excited sates transitions of cis MDI-BDO isomer.....	117
Table 9. The relative contribution of transition in trans conformer	119
Table 10. The relative contribution of transition in cis conformer.	119
Table 11. HOMO-LUMO transition (a) trans (b) cis.....	120
Table 12. Calculated emission energy of cis and trans isomers.....	123
Table 13. The potential energy of cis and trans isomers at each energy level.....	124
Table 14. The dihedral angle of OCNH at the excited state and relaxed excited state.	128
Table 15. Differences of LUMO orbital energies between excited state and excited optimized state.	130
Table 16. HOMO - LUMO energy gap at the excited optimized state.....	130

Table 17. Potential energies of most stable configurations of H38N8C6O7 and H49N22C23O24 dihedrals	136
Table 18. The HNCO dihedral angles and the potential energies of the conformations of Trans MDI-BDO and Transition state of MDI-BDO.....	139

List of Figures

Figure 1. Commonly used diisocyanate compounds	4
Figure 2. Commonly applied chain extenders	7
Figure 3. Chemical structure of MDI-BDO hard segment of polyurethane	8
Figure 4. A simple Jablonski diagram to illustrate the processes that can be occurred in excited states	10
Figure 5. Variation of emission spectrum of the polyurethane film with time	23
Figure 6. Example of paths taken when an angle changes in geometry optimization. (a) The path took by optimization using a Z-matrix or redundant internal coordinates. (b) The path took by an optimization using Cartesian coordinates.	31
Figure 7 . The atom numbering of two dihedrals (scan coordinates) of double dihedral potential energy scan.....	38
Figure 8. Franck–Condon principle energy diagram.	46
Figure 9. 2D representation of periodic boundary conditions applied to a cubic principle cell (grey). The velocity of each constituent atom is depicted by the vector. Atoms leaving the principle cell are replaced by their image from the opposite cell. Short range interactions occur within the sphere defined by r_{cut}	58
Figure 10. Structural formula of MDI-BDO with the atom numbering scheme used in this work shown	67
Figure 11. Optimized geometry of MDI-BDO	67
Figure 12. The highest occupied molecular orbital diagram of MDI-BDO.....	68
Figure 13. Potential energy surface for the scan of the H38N8C6O7 dihedral angle.....	69
Figure 14. The conformations of MDI-BDO and the orbital diagrams of conformers (a) Global minima – trans (b) Transition state (c) Local minima – cis	73

Figure 15. C6-N8 bond length vs. H38N8C6O7 dihedral angle	75
Figure 16. C6-O7 bond length vs. H38N8C6O7 dihedral angle.....	75
Figure 17. Occupancy of nitrogen lone pair electrons vs. H38N8C6O7 dihedral	76
Figure 18. Variation of C6-N8 bond length and stabilization energy for π bonding electrons (C6-O7) and nitrogen lone pair electrons	77
Figure 19. The DFT optimized structures of MDI-BDO. (a) Trans isomer. (b) Cis isomer.....	79
Figure 20. IR spectrums of trans and cis MDI-BDO isomers (a) Trans MDI-BDO (b) Cis MDI-BDO.....	82
Figure 21. Dipole moment vector of MDI-BDO molecule. (a) Trans isomer (b) Cis isomer.....	84
Figure 22. f+ Reactivity indices of MDI-BDO molecule	86
Figure 23. f- Reactivity indices of MDI-BDO molecule	87
Figure 24. f0 Reactivity values of MDI-BDO molecule.....	87
Figure 25. Dual Descriptor of MDI-BDO molecule	88
Figure 26. (a) HOMO of the trans isomer (b) HOMO of the cis isomer (c) LUMO of trans isomer (d) LUMO of the cis isomer	88
Figure 27. (a) Electrostatic surface potential map of MDI-BDO molecular structure. (b) Electron density map of MDI-BDO molecular structure.....	90
Figure 28. Graphical representation of the possibilities of intermolecular hydrogen bond interactions between MDI-BDO molecules	92
Figure 29. Hydrogen-bonded MDI-BDO molecular clusters (a) Dimer (b) Trimer (c) Tetramer	94

Figure 30. Predicted IR spectra of MDI-BDO (a) Monomer (b) Hydrogen bonded dimer	98
Figure 31. Structure of long-chain monomers (a) MDI (b) BDO and (c) PCL	99
Figure 32. Possibility of the intermolecular hydrogen bond interaction between hard segments and soft segments in MDI-BDO-PCL	100
Figure 33. DFT optimized structures of hydrogen-bonded MDI-BDO-PCL molecular clusters (a) Dimer (b) Trimer	103
Figure 34. MDI-BDO multi molecular model system.	106
Figure 35. Variation of the Density of MDI-BDO over time	107
Figure 36. RMSD of MDI-BDO model system over time.....	108
Figure 37. Density vs. temperature of MDI-BDO	109
Figure 38. Specific volume vs. temperature of MDI-BDO.....	109
Figure 39. RMSD vs. time at different temperatures	110
Figure 40. Variation of the number of hydrogen bond pairs over temperature	111
Figure 41. (a) Continues autocorrelation functions of A type of hydrogen bond interactions versus temperature (b) Continues autocorrelation functions of B type of Hydrogen bond interactions versus temperature (c) Average H-bond life time versus temperature for type A and B Hydrogen bond interactions	113
Figure 42. The distribution of total number of C14C15C16C19 dihedral angles (TotD) at 303 K.....	114
Figure 43. Distribution of total number of C14C15C16C19 dihedral angles (TotD) at different temperatures.	115
Figure 44. The absorbance of cis and trans MDI-BDO isomers.....	118
Figure 45. Calculated frontier molecular orbitals for trans isomer of MDI-BDO	121

Figure 46. Calculated frontier molecular orbitals for cis isomer of MDI-BDO	122
Figure 47. Franck–Condon principle energy diagram.	125
Figure 48. Rationalization of the Stokes shifts (a) Small geometry relaxation in the excited state produces a small Stokes shift. (b) Large geometry relaxation in the excited state produces a large Stokes shift	127
Figure 49 The change in geometry during the excited state non radiative relaxation. (a) Trans MDI-BDO at excited state. (b) Trans MDI-BDO at relaxed excited state. (c) Cis MDI-BDO at excited state. (d) Cis MDI-BDO at relaxed excited state.	129
Figure 50. Rationalization of the strong emission and small Stokes shift of trans isomer of MDI-BDO: the geometry relaxation and the frontier molecular orbitals (MOs) involved in the vertical excitation and the emission of trans MDI-BDO. Excitation and radiative processes are marked as solid lines and the nonradiative processes are marked by dotted lines.	131
Figure 51. Rationalization of the weak emission and large Stokes shift of cis isomer of MDI-BDO: the geometry relaxation and the frontier molecular orbitals (MOs) involved in the vertical excitation and the emission of cis MDI-BDO. Excitation and radiative processes are marked as solid lines, and the non-radiative processes are marked by dotted lines.	132
Figure 52. Structural formula of two dihedrals of double dihedral potential energy scan	134
Figure 53. Energy profile of MDI-BDO for rotation around H38N8C6O7 and H49N22C23O24 at ground state.....	134
Figure 54 Contour maps of MDI-BDO the potential energy surfaces at ground state (S0) as function of dihedral angles H38N8C6O7 and H49N22C23O24	135

Figure 55. The most stable conformations in potential energy surface of MDI-BDO at ground state. (a) Both dihedral 1 and 2 at trans configuration. (b) Dihedral 1 at trans configuration and dihedral 2 at cis configuration. (c) Dihedral 1 at cis configuration and dihedral 2 at trans configuration. (d) Both dihedral 1 and 2 at cis configuration.	137
Figure 56. The rotational energy barrier between stable trans MDI-BDO and transition state	139
Figure 57. Schematic diagram of isomerization of MDI-BDO.....	140
Figure 58. Potential energy surface for ground state (S_0) and excited state (S_1) of MDI-BDO	142
Figure 59. Contour maps of MDI-BDO potential energy surfaces as a function of dihedral angles H38N8C6O7 and H49N22C23O24 (a) Excited state (S_1)(b) Ground state (S_0)	143
Figure 60. Schematic diagram of the photoisomerization process of MDI-BDO exhibits two different molecular structural configurations, trans and cis. The molecule can be switched between trans and cis by absorption of light as depicted by the dashed arrows	145

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

Acknowledgement

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.

I would also like to extend my special thanks to the Advance Material research Center (AMRC) at the Faculty of Applied Sciences, University of Sri Jayewardenepura and University Research Grants for financial support, and Department of Chemistry for providing required facilities to carry out my research successfully.

The group has been a source of friendships as well as good advice and collaboration. I also have to thank the members of my computational lab, M. Erandi, P. Shenani, H. Virangi , C. Rukshan and other members for their helpful career advices and suggestions in general.

I would like to thank my parents and to my beloved husband, Sameera Edirisinghe, whose love and guidance are with me in whatever I pursue.

ABSTRACT

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

Bhagya Sharmali Wickramanayaka Karunarathna

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