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**Chemistry of Dihydrophenanthrene Ketal and its Application in
Polymer Curing**

by

Abdul Munam

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Master of Science

The Department of Chemistry

Carleton University

Ottawa, ON Canada

January, 2000

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The Faculty of Graduate Studies and Research
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In partial fulfillment of the requirements
For the degree of Master of Science

Prof. G. Buchanan, Chairman of the Department of Chemistry

Prof. Z. Y. Wang, Thesis Supervisor

Carleton University

January 14th, 2000

Abstract

Curing is a common process to increase the temperature and solvent resistance of polymers. The use of masked polyol chemistry for curing polyurethane was tested using two masked-polyol precursors, dihydrophenanthrene-based 6-membered ketal and 7-membered ketal. The use of the masked-polyol chemistry was rationalized based on the generation of the hydroxyl group upon heating and its subsequent in-situ reaction with the isocyanate group without producing any volatile by-product.

The synthesis of dihydrophenanthrene-based ketal was done using commercially available phenanthrenequinone in three steps. The dihydrophenanthrene-based ketal underwent thermal ring opening and yield phenanthrene-based alcohol in high yield. The deriving force for the ring opening was the formation of stable 9,10-disubstituted phenanthrenes. In an attempt to lower the temperature of the thermal ring-opening reaction, the effect of ketal size, substituent and the use of catalysts were examined.

A novel acrylate monomer containing the “masked alcohol” moiety was synthesized and copolymerized in a different feed ratio with acrylate monomer (e.g. methyl methacrylate). Copolymers were used to prepare a film by blending with a diisocyanate prepolymer to establish a one-component heat curing polyurethane system. The polymer films, after being heated for 2 to 4 hours at 140 °C and 160 °C, were found to be insoluble in organic solvents. The urethane peak at 1690 cm^{-1} in the IR spectrum and the insolubility of the polymer film indicated the crosslinking due to reaction between the in-situ thermally generated hydroxyl group and the isocyanate group of the prepolymer.

Acknowledgements

This thesis would not have been completed or even started without the help and guidance of many people. I first want to express my gratitude to my supervisor, Dr. Z. Y. Wang, for his constant support and guidance throughout this thesis. I am grateful to Dr. Jane Gao for her help and guidance.

I would also like to thank everyone who were or are in the lab, students and postdocs, for making it a great place to work. Furthermore, I would especially like to thank Dr. Sean Meng for discussion and technical help. Special thanks goes to my very good friends Mansur Elahi, Syed Zubair Ali and Maria De Rosa for their help with the computer skills.

My appreciation also goes to the supporting staff of the department of chemistry, especially to Keith Bourque for running the 400 MHz NMR spectra.

Above all, thanks to my mother, Zakia Khatoon, and my late brother Monis Hasan Khan for their constant support throughout my whole life. I dedicate this thesis to them.

Thank you all.

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Symbols and Abbreviations

$\text{\AA}$	Angstrom
δ	Chemical Shift (ppm)
λ	Wavelength
Δ	Heat
λ_{max}	Maximum Peak Wavelength
AIBN	2,2'-Azobisisobutyronitrile
aa	Axial - Axial
ae	Axial - Equatorial
BCB	Benzocyclobutene
BTEAC	Benzyltriethylammonium Chloride
DSC	Differential Scanning Calorimetry
DABCO	1,4-Diaza[2,2,2]bicyclooctane
DBTDL	Dibutyltin Dilurate
DMAc	N,N-Dimethylacetamide
ee	Equatorial - Equatorial
GPC	Gel Permeation Chromatography
HRMS	High Resolution Mass Spectroscopy
Hz	Hertz
IR	Infrared Spectroscopy
2-IEMA	2-Isocyanatoethyl Methacrylate
J	Coupling Constant
k	Rate Constant

MA	Methacrylate
MMA	Methyl Methacrylate
MS	Mass Spectrometry
mp	Melting Point
MHz	Mega Hertz
MW	Molecular Weight
M_w	Weight - Average Molecular Weight
M_n	Number- Average Molecular Weight
NMR	Nuclear Magnetic Resonance
¹H NMR	Proton Nuclear Magnetic Resonance
¹³C NMR	Carbon 13 Nuclear Magnetic Resonance
PMMA	Poly (Methyl Methacrylate)
ppm	Parts Per Million
TG	Thermogravimetry
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
T_g	Glass Transition Temperature
T_m	Melting Temperature
T_d	Onset Temperature for 5% Weight Loss
T_{onset}	Onset Temperature
T_{max}	Temperature at Maximal Peak Height
THF	Tetrahydrofurane
T_{RO}	Ring-opening Temperature

UV-vis	Ultraviolet-Visible
b	Broad
bs	Broad Singlet
bd	Broad Doublet
bt	Broad Triplet
d	Doublet
dd	Doublet of Doublet
dt	Doublet of Triplet
dq	Doublet of Quartet
m	Multiplet
md	Multiplet of Doublet
q	Quintet
t	Triplet
tq	Triplet of Quartet
s	Singlet

Chapter 1

Introduction

The term curing comes from cure (solidification). This terminology is based on the change in physical properties of the material during the process of solidification, which is when a “soft” material becomes “hard” during cure. Polymer curing refers to a process during which a polymer is transformed and it can take place during or after processing. Several reactions can take place during polymer curing, some of which are chain extension, grafting, dehydration, and crosslinking. Curing leads to the formation of insoluble and infusible polymers. The polymer chains are connected at several points (crosslinks), hence forming a three-dimensional network. A crosslinked network is obtained from either a linear polymer containing a functional group capable of reacting with itself, or a functionalized polymer and a crosslinking agent. Crosslinked polymers may also be obtained from a monomer with an average functionality greater than two.

Infusible materials obtained from polyfunctional and low molecular weight materials are mostly used in adhesives, paints, and compression molding. However, linear polymers with reactive functional groups are first processed (by extrusion or compression molding) and then cured to obtain an infusible material; typical examples being the vulcanization of rubber and the preparation of glass fibers.

The need for polymers with high thermal stability and good mechanical properties at high temperatures has greatly increased with their applications in aerospace and electronics. The polymers meeting such stringent requirements are aromatic rigid-rod polymers, whose main drawback is their poor solubility and infusibility due to high glass transition (T_g) or melting temperature (T_m). Introduction of a flexible linkage such as an

ether, methylene, or small pendant group improves the processability of the polymer. However, the glass transition temperature of a polymer is also depressed by the presence of flexible groups, and hence lowers its use temperature. The decomposition temperature is also lowered by the presence of aliphatic groups.

Polymer curing allows the combination of the most desirable properties for the preparation of thermally stable polymer. The introduction of a crosslinking site at the end chain of oligomers has received much attention because of the higher melt-flow properties of the oligomer compared to those of the high molecular weight polymer. In addition, the cured polymer shows the same or improved properties compared to that of the linear high molecular weight polymer (i.e. thermal stability, mechanical properties and resistance to solvent).¹

The curing system has to meet several requirements. First of all, the curing agents have to remain inactive during polymerization. The reaction should also take place above the T_g of the polymer, but below its decomposition temperature. Furthermore, the product of reaction should have a thermal stability comparable or higher than the initial polymer. Finally, the curing reaction has to be specific and proceed rapidly.

1.1. Curing Chemistry

The curing chemistry relies on the presence of functional groups that would not react during polymerization, but would react under different conditions (i.e. higher temperature or irradiation). Other systems, using “masked” functional groups, have also been developed for functional groups that are too reactive (i.e. isocyanate). In such systems the masking agent is liberated before the desired reaction takes place.

The last type of curing system is based on the presence of a latent group in the polymer. The curing chemistry will be presented here with respect to the evolution or not of by-products during the curing reaction.

I.1.1. Curing Systems With Volatile By-Products

Polyimides are known for their high thermal stability and their poor processability. The typical synthesis of polyimides is accomplished by reacting dianhydride with diamine. A polyamic acid is first obtained. The polyimide is then obtained by removing water to form the imide groups. The polyimide precursor (polyamic acid) is more easily processed than polyimides thus allowing the possible acquisition of polyimide materials by condensation of a polyamic acid. However the evolution of water during the reaction could lead to the presence of voids in the material which would impair its mechanical properties (Scheme I.1).

Scheme I.1. Polyimides from polyamic acid precursor.

Polyurethane is traditionally prepared from a diisocyanate and a diol, which constitutes a two-component heat curing polyurethane. The two components must be kept separate because of the high reactivity of isocyanate towards alcohol. Masking the isocyanate group with a phenol or an oxime has developed one-component heat-curing polyurethane. The resulting system is not thermally stable. This is evident upon heating; the isocyanate is regenerated and then reacts with the alcohol. The main drawback with this system is the release of toxic by-product (e.g. phenol) during the curing reaction (Scheme I.2).

Scheme I.2. One component heat-curing polyurethane using masked isocyanates.

Polyimides² and poly (aryl ethers)s³ have been crosslinked with triazene terminated polymers. The dimethyl phenyl triazene end-group decomposes to an aryl radical, nitrogen, and an aminyl radical. The aryl radical reacts with an aromatic ring of

the oligomer to form a σ -complex that reacts with the aminyl radical to produce a crosslink and liberate dimethylamine (Scheme I.3).

Scheme I.3. Cross-linking of polyaromatics by bis (triazenes).

I.1.2. Curing System Without Volatile By-Products

I.1.2a. Carbon Based Systems

Several carbon-based systems have been developed. The curing results from self-coupling reaction to the crosslinking end-group. Acetylene has been used to crosslink polyimides.⁴ However; it has not been determined unambiguously whether the curing reaction proceeds by cyclotrimerization⁵ or polymerization⁶ of the acetylene group. (Scheme I.4).

Scheme I.4. Curing reaction of acetylene.

Upon thermolysis, paracyclophane ring opens to a diradical which can then polymerize or dimerize (Scheme I.5).⁷ Paracyclophane has been used to crosslink Poly (aryl ether)s⁸ and polyquinolines.⁹

Scheme I.5. Thermolysis of paracyclophane.

Thermal activation of benzocyclobutene (BCB) generates a highly reactive diene (o-quinodimethane), which could then enter into a wide variety of reactions such as dimerization, oligomerization, and Diels-Alder cycloaddition (Scheme I.6). The benzocyclobutene group has been introduced as an end group¹⁰ or a pendant group.¹¹ Thus, it has been incorporated into high-performance polyimides,¹² aromatic polyamide,¹³ poly (arylene ether)s¹⁴ and polystyrene.¹⁵

Scheme I.6. Thermal reaction of benzocyclobutene.

Biphenylene has been used for the crosslinking of polyquinolines.¹⁶ However, the degree of crosslinking was not always high enough to change the polymer properties.¹⁷ This is due to the fact that dimerization of biphenylene leads only to chain extension. Crosslinking was obtained only from the reaction of biphenylene with quinoxaline. Better results were obtained when a mixture of acetylene and biphenylene-terminated polymer led to a crosslinked material via the formation of phenanthrene group (Scheme I.7).¹⁸

Scheme I.7. Crosslinking reactions with biphenylene.

I.1.2b. Non-Carbon Based Systems

Polyimides and polyamides have been thermally crosslinked by trimerization of nitriles¹⁹ and cyanamides.²⁰ The resulting cured material showed higher thermo-oxidative stability than that cured with norbornene. This was due to the presence in the cured material of methylene groups when cured with norbornene.

Epoxides react with a wide variety of functional groups (i.e. amine, alcohol, carboxylic acid or anhydride and with itself). The reaction with primary amines is used to produce crosslinked networks. The epoxide is introduced in the polymer at the end-chain or as a pendant group, and an amine or a diamine is used as the crosslinking agent.

The curing chemistry leading to void-free materials, is mostly based on self-coupling or polymerization of the crosslinking agents and Diels-Alder reaction. The only crosslinking agent that reacts with nucleophiles is the epoxide. Since the thesis work

investigates the use of dihydrophenanthrene based ketal (masked-polyol) as curing agent, a brief overview of phenanthrene preparation and its reactivity is necessary.

I.2. Phenanthrene

I.2.1. Synthesis of Phenanthrene

The simple aromatic hydrocarbons used as starting materials or the preparation of more complex products comes from two main sources, namely coal and petroleum. Coal is an enormously complex substance made up primarily of large arrays of highly unsaturated benzene like rings linked together. When heated to 1000 °C in the absence of air, thermal break down of coal molecules occurs and a mixture of volatile products called coal tar distills off. Further fractional distillation of coal tar yields benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, and a host of other aromatic compounds. Phenanthrene was discovered in coal tar almost simultaneously by Oster Mayer, Fittig,²¹ and by Glaser.²² Coal tar is today still the most important raw material for the preparation of phenanthrene. Even phenanthrene of correct melting point obtained from coal tar shows the presence of small amounts of anthracene in its spectrum.²³

Numerous synthesis of phenanthrene have been carried out, and it has also been observed as a product of many pyro-condensations. It is produced, according to Graebe,²⁴ when toluene, dibenzil, 9-methylfluorene or stilbene (I-1) are passed through red-hot tubes; o,o'-ditolyl (I-2) over red-hot platinum wire also yields phenanthrene.²⁵

Scheme I.8. Phenanthrene from stilbene and o,o'-ditolyl.

Phenanthrene also produced by zinc-dust distillation of morphine, morphenol, and other natural products.²⁶ Phenanthrene is formed when coumarone and benzene are passed through red-hot tubes.²⁷ The phenanthrene synthesis of Pschorr²⁸ starts from the condensation product (I-3) of o-nitro-benzaldehyde and phenylacetic acid. The nitro-group in o-nitrobenzaldehyde is reduced to the amino-group, and the latter is diazotized. The ring is closed with copper powder to give phenanthrene-9-carboxylic acid (I-4) and on distillation, phenanthrene is obtained (Scheme I.9).

Scheme I.9. Phenanthrene via Pschorr's synthesis.

Phenanthrene has also been prepared from *o*-phenylbromostyrene with aluminum chloride (Scheme I.11).³⁰

Scheme I.11. Phenanthrene from *o*-phenylbromostyrene.

Phenanthrene is obtained quantitatively from 9-fluorenylcarbinol with phosphorus pentoxide.³¹ This synthesis has also been carried out with the isotope ^{14}C in the carbinol-group and yielded phenanthrene with ^{14}C in the 9-position (Scheme I.12).³²

Scheme I.12. Phenanthrene from 9-fluorenylcarbinol.

Phenanthrene is also formed in addition to chrysene by the action of aluminum chloride on tetraphene.³³ Aldehyde (I-5) cyclizes with hydrobromic acid to phenanthrene ($\text{R} = \text{H}$). This synthesis can be used for the preparation of alkyl Phenanthrene ($\text{R} = \text{CH}_3$

or C_2H_5) (Scheme I.13). The nitrile (I-7) can be cyclized under the same condition. Hydrolysis and decarboxylation give phenanthrene or alkyl phenanthrene (Scheme I.14).³⁴

**Scheme I.13. Phenanthrene
from compound I-5.**

**Scheme I.14. Phenanthrene
from compound I-7.**

Diphenyldialdehyde (I-9) reacts with hydrazine to give the azine (I-10) which readily splits off nitrogen and forms phenanthrene (Scheme I.15).³⁵

Scheme I.15. Phenanthrene synthesis from diphenyldialdehyde.

Many naturally occurring compounds of biological interest contain a phenanthrene moiety.³⁶ Some 9,10-disubstituted phenanthrene have been synthesized for

the studies of their photophysical properties and the use as a fluorescent label in polymer.^{37, 38} A number of other known synthetic routes to phenanthrene include Wagner-Meerwin rearrangement of fluorenyl derivatives,³⁹ ring expansion of fluorenones with diazoalkanes,⁴⁰ cyclization of naphthalene derivatives,⁴¹ cyclization of biphenyl derivatives,⁴² reaction of aryl pinacols with triflic acid,⁴³ and by double succinylation of benzene.⁴⁴

All these syntheses are of course, only of importance for the preparation of phenanthrene derivatives since phenanthrene itself is best obtained from coal tar.

1.2.2. Oxidation

Phenanthrene is more susceptible to oxidation, and the point of first attack in each reaction is at the 9- and 10- positions. On oxidation with chromic acid in glacial acetic acid or in suspension in sulphuric acid, it yields 9,10-phenanthrenequinone (I-11).⁴⁵ The only factor which seems to limit the yield of 9,10-phenanthrenequinone is the sensitivity of this compound to further oxidation with hydrogen peroxide yield diphenic acid (I-12) (Scheme I.16).⁴⁶

Scheme I.16. Oxidation of phenanthrene.

9, 10-Phenanthrenequinone is orange-red crystals, with a melting point of 206 °C-207 °C and is practically insoluble in water. It is soluble in benzene, toluene, ether, glacial acetic acid and hot alcohol. It is very stable to heat and can be sublimed. The two side rings exert a stabilizing influence on the o-quinonoid systems. 1,2-, 3,4- and 1,4-phenanthrenequinone have been prepared by indirect routes.⁴⁷

Oxidation of phenanthrene with osmium tetroxide in pyridine and benzene yields cis-9,10-dihydrodihydroxyphenanthrene giving 9-phenanthrol by loss of water or diphenyl-o,o'-dialdehyde or treatment with lead tetra acetate.⁴⁸

1.2.3. Rationale and Objectives

Polyurethanes are among the most versatile of polymers. Commercial polyurethanes are nearly always prepared by the reaction of a diisocyanate (or oligoisocyanate) with a diol (polyester or polyether diol). Heat-curing one-component systems are usually based on a combination of hydroxyl terminated prepolymer and blocked isocyanates. Phenol is a common blocking agent. By heating above 150 °C, the blocking agent is removed and the free isocyanate group reacts with the hydroxyl groups to effect cure. The major drawback associated with the masking agent is that a toxic phenol is unavoidably evolved during cure. In two-component systems, two materials must be stored separately and mixed immediately before use. Hence, this system requires a more complicated handling than one-component system.

Our ultimate goal is to develop a versatile, environment-friendly curing chemistry for one-component polyurethane system. This can be achieved by the use of masked-polyol chemistry; based on both the belief that aliphatic polyol can be generated in-situ,

thermally from dihydrophenanthrene-based ketal and its reaction with isocyanate without producing any by-product. Since hydroxyl groups are too reactive to isocyanate groups, they have to be introduced as a latent group. This masked hydroxyl group has to survive the polymerization and remains inactive until being triggered by heat.

In order for this system to be applicable in polymer system, a ketal precursor has to be functionalized and checked for thermal ring-opening, then incorporated in polymer. It is believed that the driving force for thermal ring-opening of the ketal comes from the formation of stable aromatic phenanthrene system. The ring-opening temperature depends on the ring size and electronic nature of the substituent.

Scheme I.17. Masked polyol to reactive polyol.

Ketal precursors, once introduced into a polymer, should generate the hydroxyl groups only when needed at specific temperatures. Polymers containing ketal group can be stored together with oligoisocyanates in the same container, hence eliminating the complication of handling in the two-component system.

I.2.3a. Hypotheses

- 1) Versatile environment-friendly curing chemistry for one-component polyurethane system can be achieved by the use of masked polyol chemistry.
- 2) The use of masked polyol is based on the belief that aliphatic polyol can be generated in-situ, thermally from dihydrophenanthrene-based ketal and its reaction with isocyanate without producing any by-product.
- 3) The deriving force for thermal ring-opening of the ketal is based on the formation of stable aromatic system.
- 4) The ring-opening temperature depends on the ring size and electronic nature of the substituent.

I.2.3b. Objectives

- 1) Synthesis of “Masked Polyol” (dihydrophenanthrene-based ketal).
- 2) Investigation of the influence of ketal ring-size on the ring-opening temperature.
- 3) Synthesis of methyl ether, mesylate and acetate derivatives from dihydrophenanthrene-based ketal and study the effect of substituent on ring-opening temperature.

- 4) Study the effect of different catalysts on the ring-opening of acetate derivative of dihydrophenanthrene-based ketal.
- 5) Study the kinetic of the ring-opening reaction of 7-membered acetate derivative of dihydrophenanthrene-based ketal (model compound) in solution.
- 6) Synthesis of acrylate monomer containing “masked alcohol” moiety.
- 7) Synthesis of copolyacrylate containing “masked alcohol” moiety and study its thermal properties.
- 8) Introduction of a copolymer containing “masked alcohol” moiety into polyurethane system and demonstration of thermal curing with the diisocyanate group of other prepolymers without VOC.

Chapter II

Dihydrophenanthrene-Based Ketal and Derivatives

II.1. Synthesis of Keto-Ketal

Dihydrophenanthrene-based keto-ketal (II-1a) and (II-1b) were synthesized from commercially available penanthrenequinone (I-11) by reacting with 3-equivalents of 1,3-propanediol and 1,4-butanediol respectively. p-Toluenesulfonic acid was used as a catalyst (Scheme II.1). Ketal formation is similar to the hydration reaction. Like water, alcohols are relatively weak nucleophiles that add to ketones only slowly under neutral conditions. Under acidic condition, however, the nucleophilic carbonyl oxygen is protonated and the resultant protonated carbonyl compound is far more reactive than its neutral counterpart. The initial nucleophilic addition of alcohol to the carbonyl group yields hydroxyl ether, but due to the presence of the acid catalyst (p-toluenesulfonic acid), a further reaction occurred. Protonation of the hydroxyl group, followed by an E1-like dehydration, leads to an oxonium ion. Further, the addition of a second hydroxyl group of the diol, followed by deprotonation, yields cyclic ketal.

All the steps of ketal formation are reversible. The equilibrium constant for the addition of alcohol to ketone is about 0.8 M^{-1} .⁴⁹ The comparable value for addition of water is about 0.02 M^{-1} .⁴⁹ The overall equilibrium constant for the formation of ketal is 1.58 M^{-1} .⁴⁹ Since the portion of the equilibrium does not strongly favor the product, the formation of ketal must be carried out in such a way as to drive the reaction to completion. The azeotropic distillation approach was then used so that the water that was released during the protecting reaction of carbonyl group was irreversibly removed from

the system. Toluene was used as an azeotropic solvent. After refluxing for 18 hours, the keto-ketal (II-1a) and (II-1b) were obtained in good yield (Scheme II.1).

Scheme II.1. Synthesis of dihydrophenanthrene-based keto-ketal.

II.1.1. Characterization

II.1.1a. Spectroscopic Characterization of 6-Membered Keto-Ketal (II-1a)

Dihydrophenanthrene-based 6-membered keto-ketal (II-1a) was fully characterized. The IR spectrum showed a ketone carbonyl at 1708 cm^{-1} . There was a disappearance of the other carbonyl narrow spaced small peak at 1662 cm^{-1} , as this peak is usually observed in 1,2-diketons system due to asymmetric absorption. Spectrum also showed four strong bonds for ketal in the region from 1157 to 1000 cm^{-1} . IR spectra for both phenanthrenequinone and keto-ketal (II-1a) are reported in appendix A. The ^1H NMR exhibited a multiplet of doublet at 1.55 ppm, integral area of one with coupling constant ($^2J_{\text{geminal}} = 10.76\text{ Hz}$), ($^3J_{\text{a,a}} = 4.32\text{ Hz}$) and ($^3J_{\text{e,e}} = 1.56\text{ Hz}$) representing equatorial proton (16_e) of the methylene group. The multiplet at 2.25 ppm integral area of one is a triplet of quartet with coupling constant ($^2J_{\text{geminal}} = 10.76\text{ Hz}$), ($^3J_{\text{a,a}} = 10.76\text{ Hz}$)

and ($^3J_{ae} = 5.4$ Hz). This pattern is the characteristic of a hydrogen (16_a) in an axial position of a methylene group with two axial-axial couplings, two axial-equatorial and a geminal coupling. ^1H NMR spectra also exhibited a doublets of quartet at 4.05 ppm, integral area of two with coupling constant ($^2J_{\text{geminal}} = 11.92$ Hz), ($^3J_{ae} = 5.32$ Hz) and ($^3J_{ee} = 1.48$ Hz) representing two equatorial protons (15_e) and (17_e) of the two methylene group attached to oxygen atoms. Another doublets of triplet appeared at 4.50 ppm, integral area of two, with coupling constant ($^2J_{\text{geminal}} = 11.92$ Hz), ($^3J_{aa} = 11.92$ Hz) and ($^3J_{ae} = 2.78$ Hz) representing the other two axial protons (15_a) and (17_a) of the methylene group attached to oxygen atoms. Aromatic protons exhibited a multiplet in the region of 7.37 to 7.40 ppm, integral area of two representing the aromatic protons number 6 and 9. A doublet of triplet appear at 7.44 ppm, integral area of two, with coupling constant ($^3J_{\text{ortho}} = 8.94$ Hz) and ($^4J_{\text{meta}} = 1.64$ Hz) representing the protons number 5 and 10. A doublet of a triplet at 7.62 ppm, integral area of two, with coupling constant ($^3J_{\text{ortho}} = 8.9$ Hz) and ($^4J_{\text{meta}} = 1.44$ Hz) represented proton number 4 and 11. A doublet of quartet at 7.81 and 7.91 ppm integral area of 1 with coupling constant ($^3J_{\text{ortho}} = 8.9$ Hz) and ($^4J_{\text{meta}} = 1.12$ Hz) representing aromatic proton number 12 and 3 respectively. The ^{13}C NMR spectrum displayed peak at 29.73 ppm represent a carbon atom from methylene group, peak intensity was decreased by half as compared to other aliphatic carbon atoms as this methylene group is one time less abundant than the other two chemically equivalent methylene groups. A peak at 65.22 ppm represented the two chemically equivalent carbon atoms from methylene group attached with oxygen atoms. A peak of low intensity at 97.61 ppm represented a carbon atom to which two oxygen atoms are attached. ^{13}C NMR spectrum showed a peak at 196.86 ppm representing the carbonyl group. The

downfield shift of the carbonyl group exhibited the presence of a conjugated system next to the carbonyl group. Spectrum also displayed 12 peaks in the region from 123.14 to 136.89 ppm, each corresponding to the chemically non-equivalent aromatic carbon atoms. Peaks at 130.88, 132.75, 132.14 and 136.89 ppm exhibited the low intensity signals, as these carbon atoms have no directly bonded protons. ^1H and ^{13}C NMR spectra and assignments are reported in Appendix B and C. The HRMS gave the expected mass (266.0124 g/mol). The mass spectrum displayed the $(\text{M} + 1)^+$ peak at $(m/e = 267)$ as well as a peak due to loss of $\text{C}_4\text{H}_6\text{O}_2$ at $(m/e = 180)$.

II.1.1b. Spectroscopic Characterization of 7-Membered Keto-Ketal (II-1b)

Dihydrophenanthrene-based 7-membered keto-ketal (II-1b) was fully characterized spectroscopically. First the IR spectrum showed a ketone carbonyl at 1710 cm^{-1} and the disappearance of the other carboxyl peak of the phenanthrenequinone at 1662 cm^{-1} . Spectrum also showed four strong bonds for ketal in the region from 1150 to 1014 cm^{-1} . IR spectra of both phenanthrenequinone and keto-ketal (II-1b) are shown in Figure II.1.

Figure II.1. IR spectra of phenanthrenequinone and keto-ketal II-1b.

The ^1H NMR spectrum exhibited a multiplet integral area of two at 1.50 and 1.70 ppm corresponding to the two-methylene groups of the ketal, respectively. Another multiplet integral of four in the region of 3.90 to 3.98 ppm represented the other two-methylene groups attached to the oxygen atoms. Aromatic protons had an integral area of eight and exhibited a multiplet in the region of 7.30 and 7.90 ppm. The ^{13}C NMR spectrum displayed peaks of almost equal intensities at 29.73 ppm and 65.22 ppm, representing the two chemically equivalent methylene group without oxygen and other two with oxygen respectively. The downfield shift of the two-methylene group is the result of the electronegative effect of the oxygen atoms. A peak at 196.86 ppm represented a carbonyl group. The downfield shift of the carbonyl group exhibited the presence of conjugated system next to the carbonyl group. In the aliphatic region a peak of low intensity at 97.61 ppm represented a carbon atom to which two oxygen atoms are attached. Since, this carbon has no directly bonded protons; the dipolar relaxation for this carbon is less effective, leading to longer relaxation time. This in turn is responsible for the low intensity of the observed ^{13}C signal for this carbon atom. The ^{13}C spectrum of (II-1b) also displayed 12 peaks in the region from 123.14 to 136.89 ppm, each corresponding to the chemically non-equivalent aromatic carbon atoms. Among the 12 aromatic carbon atoms, 4 carbon atoms at 130.88, 132.75, 135.14, 136.89 ppm exhibited low intensity signals, as these carbon atoms have no directly bonded protons. ^1H and ^{13}C NMR spectra and assignments are reported in Appendix D and E. The HRMS gave the expected mass (280.0131 g/mol). The mass spectrum displayed the $(\text{M} + 1)^+$ peak at $(m/e = 281)$ as well as a peak due to loss of $\text{C}_5\text{H}_8\text{O}_2$ at $(m/e = 180)$.

II.2. Reduction of Keto-Ketal to Hydroxyl-Ketal

Reduction of keto-ketal (II-1a) and (II-1b) was carried out in methanol by sodium borohydride at room temperature. In order to avoid any increase of solution temperature, sodium borohydride was added in small portions and the solution was stirred. After 45 minutes of continuous stirring, hydroxyl-ketals (II-2a) and (II-2b) were obtained in high yields (Scheme II.2).

Scheme II.2. Reduction of keto-ketal to hydroxyl-ketal.

II.2.1. Characterization

II.2.1a. Spectroscopic Characterization of 6-Membered Hydroxyl-Ketal (II-2a)

Dihydrophenanthrene-based 6-membered hydroxyl-ketal (II-2a) was fully characterized by spectroscopic means. The IR spectrum showed the disappearance of a carbonyl peak and the appearance of a broad O-H stretching vibration at 3489 cm^{-1} . IR spectra of both keto-ketal (II-1a) and hydroxyl-ketal (II-2a) are shown in Figure II.2.

Figure II.2. IR spectra of keto-ketal II-1a and hydroxyl-ketal II-2a.

The ^1H NMR exhibited a multiplet at 1.71 ppm, integral area of one. This multiplet is actually a doublet of multiplet, originating from equatorial proton of the methylene group (No. 16) with coupling constant ($^2J_{\text{geminal}} = 10.82$ Hz), while the other equatorial-axial and equatorial-equatorial coupling constant are unresolved. Another multiplet at 2.10 ppm, integral area of one, represented the axial proton of the methylene group (No. 16). This multiplet is a multiplet of triplet with a geminal, two axial-axial, and two axial-equatorial coupling, but only the two coupling constant were resolved from that multiplet, and these are ($^2J_{\text{geminal}} = 10.82$ Hz) and ($^3J_{\text{a,a}} = 4.2$ Hz). A sharp singlet at 2.35 ppm, integral area of one, represented the hydroxyl proton (H_A). ^1H NMR spectrum also exhibited the influences of the chiral center resulted by the reduction of carbonyl group in (II-1a) on the other two methylene groups attached to the oxygen atoms. These methylene protons become diastereotopic and hence become magnetically non-equivalent and

exhibited a multiplet at 3.85 ppm integral area of one, a multiplet at 4.05 ppm integral area of two, and another multiplet at 4.20 ppm, integral area of one, because of complexity with respect to the multiplet coupling constant being unresolved. ^1H NMR spectrum of (II-2a) clearly exhibited a sharp singlet at 5.18 ppm. This characteristic peak appeared from the benzylic proton (H_B). Aromatic protons had an integral area of five and three and exhibit a multiplet in the region 7.30 to 7.50 ppm and 7.80 to 7.90 ppm for five and three aromatic protons respectively. ^1H NMR spectrum and assignment are shown in Figure II.3. The ^{13}C NMR spectrum exhibited the expected seventeen peaks corresponding to the seventeen chemically non-equivalent carbon atoms of hydroxyl ketal (II-2a). ^{13}C NMR spectrum also clearly exhibited the disappearance of carbonyl peak and appearance of new peak in the aliphatic region at 68.21 ppm. This characteristic peak appeared from the benzylic carbon. Finally, the mass spectrum displayed the expected molecular ion peak at ($m/e = 268$).

Figure II.3. ^1H NMR spectrum (400 MHz, CDCl_3) of hydroxyl-ketal II-2a.

II.2.1b. Spectroscopic Characterization of 7-Membered Hydroxyl-Ketal (II-2b)

Hydroxyl-ketal (II-2b) was characterized and the spectroscopic data agreed well with the expected values. The IR spectrum showed the presence of hydroxyl group by showing the broad O-H stretching vibration at 3489 cm^{-1} and the disappearance of carbonyl peak. The IR spectra of both keto-ketal (II-1b) and hydroxyl-ketal (II-2b) are shown in Figure II.4.

Figure II.4. IR spectra of keto-ketal II-1b and hydroxyl-ketal II-2b.

The ^1H NMR exhibited a multiplet at 1.65 and 1.82 ppm, integral area of four corresponding to the two methylene groups. The multiplet at 3.51 to 3.72 and 3.99 ppm with integral area of two represented the other two-methylene groups attached to the oxygen atom respectively. ^1H NMR spectrum also exhibited a characteristic doublet at 4.70 ppm, integral area of one with coupling constant ($^3J_{\text{H,H}} = 3.34\text{ Hz}$) from the benzylic proton (H_B). This doublet was the result of the three bond H.H couplings between the

proton (H_B). This doublet was the result of the three bond H.H couplings between the benzylic proton and the proton of the hydroxyl group. Similar effect was also exhibited by another doublet at 2.34 ppm, integral area of one with coupling constant ($^3J_{H,H} = 3.38$ Hz) from the hydroxyl proton (H_A). Eight aromatic protons displayed a multiplet in the region 7.30 to 7.50 and 7.70 to 7.90 ppm with integral area of eight. 1H NMR spectrum and assignment are shown in Figure II.5.

Figure II.5. 1H NMR spectrum (200 MHz, $CDCl_3$) of hydroxyl-ketal II-2b.

The ^{13}C NMR spectrum of (II-2b) displayed the expected eighteen peaks representing the eighteen chemically non-equivalent carbon atoms of hydroxyl-ketal (II-2b). Characteristic peak from benzylic carbon atom appeared at 71.86 ppm. The mass spectrum gave the expected molecular ion peak at ($m/e = 282$).

II.3. Derivatives Synthesis from Dihydrophenanthrene-Based Hydroxyl-Ketals

Methyl ether, mesylate, and acetate derivatives of the hydroxyl-ketal (II-2a) and (II-2b) were prepared to study the substituent effect on the ring-opening temperature. The methyl ethers (II-3a) and (II-3b) were prepared at room temperature by reacting hydroxyl ketals (II-2a) and (II-2b) with dimethylsulfate under phase transfer condition ($\text{NaOH-H}_2\text{O/CH}_2\text{Cl}_2$ -benzyltriethylammonium chloride). The mesylates (II-4a) and (II-4b) were prepared at room temperature by reacting hydroxyl-ketal (II-2a) and (II-2b) with methanesulfonyl chloride in pyridine, and acetate derivatives (II-5a) and (II-5b) by reacting with acetyl chloride. All the derivatives were prepared in 30 minutes and were obtained in high yields (Scheme II.3).

Scheme II.3. Derivatives synthesis from hydroxyl ketal II-2a and II-2b.

II.3.1. Characterization

II.3.1a. Spectroscopic Characterization of Methyl Ether Derivatives (II-3a) and (II-3b)

Methyl ether derivative (II-3a) and (II-3b) were fully characterized and the spectroscopic data agreed well with the expected values. IR spectra showed the disappearance of O-H stretching vibration both in (II-3a) and (II-3b). The ^1H NMR spectra exhibited a sharp singlet, with integral area of three, at 3.30 and 3.20 ppm corresponding to the methyl group in (II-3a) and (II-3b) respectively. Intact of ketal ring was evident by the appearance of a singlet integral area of one at 4.85 and 4.40 ppm

attributed to the benzylic protons in (II-3a) and (II-3b) respectively. All methylene and aromatic protons appeared at the expected position in accordance with the starting material hydroxyl-ketal (II-2a) and (II-2b) respectively. The ^{13}C NMR spectrum displayed eighteen and nineteen peaks for eighteen and nineteen chemically non-equivalent carbon atoms for methyl ether (II-3a) and (II-3b) respectively. Characteristic peak for methyl group appeared at 64.1 ppm and 65.1 ppm for (II-3a) and (II-3b) respectively. All the other carbon peaks appeared at their expected positions in accordance with the hydroxyl-ketal (II-2a) and (II-2b) respectively. Finally the mass spectrum displayed molecular ion peak at ($m/e = 282$ and 296) for (II-3a) and (II-3b) respectively. Mass spectrum also displayed a peak due to loss of CH_3 at ($m/e = 267$ and 281) for (II-3a) and (II-3b) respectively.

II.3.1b. Spectroscopic Characterization of Mesylate Derivative (II-4a) and (II-4b)

Mesylate derivative (II-4a) and (II-4b) were spectroscopically characterized. IR spectra showed the disappearance of O-H stretching vibration both in (II-4a) and (II-4b). The ^1H NMR spectra exhibited a sharp singlet with integral area of three at 2.80 and 2.99 ppm, showing the presence of methyl group in (II-4a) and (II-4b) respectively. The intact of ketal ring was again evident by the appearance of a sharp singlet integral area of one at 6.22 and 6.30 ppm attributed to the benzylic protons in (II-4a) and (II-4b) respectively. In comparison to methyl ether derivatives, the down field shift of the benzylic proton was the result of the magnetic anisotropy, caused by the presence of π electron system in SO_2 -group. Due to this effect benzylic proton became de-shielded and hence has resonance at higher field than expected. All methylene and aromatic protons are appeared at the

expected position in accordance with the starting material hydroxyl-ketal (II-2a) and (II-2b) respectively. The ^{13}C NMR spectra displayed eighteen and nineteen peaks for eighteen and nineteen chemically non-equivalent carbon atoms from mesylate (II-4a) and (II-4b) respectively. Characteristic peak for methyl group appeared at 20.60 and 21.22 ppm respectively for (II-4a) and (II-4b). All other carbon atoms peaks appeared at their expected positions in accordance with the hydroxyl-ketal (II-2a) and (II-2b) respectively. The mass spectra gave the molecular ion peak at ($m/e = 346$ and 360) for (II-4a) and (II-4b) respectively. Mass spectra also exhibited a peak due to loss of SO_2CH_3 at ($m/e = 267$ and 281) for (II-4a) and (II-4b) respectively.

II.3.1c. Spectroscopic Characterization of Acetate Derivatives (II-5a) and (II-5b)

Acetate derivatives (II-5a) and (II-5b) were spectroscopically characterized and the data agreed well with the expected values. IR spectrum confirmed the disappearance of O-H stretching and the presence of carbonyl peak at 1728 cm^{-1} due to ester linkage both in (II-5a) and (II-5b) respectively. Comparative IR spectra of (II-5b) and starting material hydroxyl-ketal (II-2b) are shown in the Figure II.6

Figure II.6. IR spectra of hydroxyl-ketal II-2b and acetate derivative II-5b.

The ^1H NMR spectrum exhibited a singlet with integral area three at 1.91 ppm corresponding to the methyl group attached to the carbonyl group both in (II-5a) and (II-5b). Benzylic proton again exhibited the influence of magnetic anisotropy caused by the carbonyl group and appeared in the down field at 6.7 and 6.1 ppm both in (II-5a) and (II-5b) respectively. The presence of benzylic proton again confirmed the intact of ketal ring. All methylene and aromatic protons are appeared at the expected positions in accordance with the starting material hydroxyl-ketal (II-2a) and (II-2b) respectively. The ^{13}C NMR spectra displayed nineteen and twenty peaks for nineteen and twenty chemically non-equivalent carbon atoms from acetate derivative (II-5a) and (II-5b) respectively. Characteristic peak for carbonyl group appeared at 171.0 and 170.4 ppm in (II-5a) and (II-5b) respectively. This slightly up-field shift as compared to keto-ketal (II-1a) and (II-1b) representing the non-conjugated system next to the carbonyl group. Another characteristic peak for methyl group attached to carbonyl group appeared at 20.50 and 21.50 ppm in (II-5a) and (II-5b) respectively. ^1H and ^{13}C NMR spectra and assignments for compound (II-5b) are shown in Figures II.7 and II.8 respectively, whereas the spectra for compound (II-5a) are reported in appendix F and G.

Figure II.7. ^1H NMR spectrum (400 MHz, CDCl_3) of II-5b.

Figure II.8. ^{13}C NMR spectrum (100 MHz, CDCl_3) of II-5b.

The mass spectrum gave the expected molecular ion peak at ($m/e = 310$ and 324) for (II-5a) and (II-5b), with relative intensities 45.2 and 46.1% respectively. Mass spectra also exhibited a peak due to loss of OCCH_3 at ($m/e = 267$ and 281) for (II-5a) and (II-5b) respectively. The compounds (II-5a) and (II-5b) were also characterized by UV-vis. The UV-vis spectra of both compounds displayed a maximum absorption peak at 274 nm Figure II.9. The highest peak at 274 nm comes from the absorption of benzene ring. Among the three electronic transitions that usually take place in benzene, the secondary band at 255 nm is shifted to a longer wavelength 274 nm as it often happens in polycyclic aromatic compounds.⁵⁰

Figure II.9. UV-vis spectrum (2.34×10^{-5} mmol/L, chloroform) of II-5b.

II.4. Thermal Aromatization (Ring-opening)

Dihydrophenanthrene ketal and their derivatives undergo thermal rearrangement, and due to the ketal ring-opening, phenanthrene alcohols are obtained. This is achieved by heating hydroxyl-ketal and their derivatives in different sealed Pyrex glass tube under nitrogen in pre-maintained temperature oil bath for 30 min. (Scheme II.4). The reaction was monitored by the disappearance of benzylic proton in the ^1H NMR spectra of the hydroxyl-ketal and their derivatives. Starting compounds, required temperature, and ring-opened products are reported in Table II.1. All ring-opened products were isolated in good yield.

Scheme II.4. Ring-opening reaction of dihydrophenanthrene ketal.

Table II.1. Starting compounds required temperatures and ring-opened products

Starting Compounds		R'	Δ (°C)	Ring-Opened Products
II-2a	OH	200	II-6a
	II-3a	OCH ₃	200	II-7a	
	II-4a	OSO ₂ CH ₃	110	II-8a	
	II-5a	OCOCH ₃	210	II-9a
II-2b	OH	160	II-6b
	II-3b	OCH ₃	190	II-7b	
	II-4b	OSO ₂ CH ₃	110	II-8b	
	II-5b	OCOCH ₃	200	II-9b	

II.4.1. Characterization

II.4.1a. Spectroscopic Characterization of Ring-opened Products (II-6a) and (II-6b)

Thermal aromatization (Ring-opening) of the hydroxyl-ketal (II-2a) and (II-2b) obtained the hydroxyl-ketal ring-opened products (II-6a) and (II-6b) respectively. The products (II-6a) and (II-6b) were fully characterized by spectroscopic means. The IR spectrum showed strong O-H stretching vibration from 3200 to 3600 cm⁻¹ both in (II-6a) and (II-6b) respectively. The ¹H NMR spectrum of (II-6a) exhibited a quintet for methylene group at 2.11 ppm, integral area of two with coupling constant (³J_{vicinal} = 5.48 Hz). This quintet is the characteristic of a linear chain in which the vicinal inter-proton coupling constant (³J) are same for every successive pair of carbon atoms. The intensities of the four lines are (1:4:6:4:1), confirm that they raised from proton in a linear chain

with four neighboring protons. Two triplets appeared at 4.14 and 4.28 ppm, integral area of two and with coupling constant ($^3J_{\text{vicinal}} = 5.56$ and 5.36 Hz) representing the methylene group attached to oxygen and hydroxyl group, respectively. The ^1H NMR spectrum of (II-6a) also clearly exhibited the disappearance of benzylic proton singlet at 5.18 ppm. Aromatic protons of compound (II-6a) exhibited a multiplet in the region of 7.50 to 7.60 ppm, integral area of four, a doublet of doublet at 8.00 ppm, integral area of one with coupling constant ($^3J_{\text{ortho}} = 8.12$ Hz) and ($^4J_{\text{meta}} = 0.88$ Hz) a multiplet at 8.30 ppm integral area one and another multiplet at 8.60 ppm integral area two represented total eight aromatic protons.

The ^{13}C NMR spectrum of compound (II-6a) displayed 17 peaks, each corresponding to the chemically non-equivalent carbon atoms. ^{13}C NMR spectrum also exhibited the disappearance of the two aliphatic carbon atoms at 68.21 and 97.58 ppm, as these carbon atoms become aromatic after the ring-opening and hence appeared in the aromatic region from 121 to 142 ppm with other 12 aromatic carbon atoms. The mass spectrum of compound (II-6a) gave the molecular ion peak at ($m/e = 268$) with relative intensity 32.5%. The extended aliphatic region of ^1H NMR spectrum for compound (II-6a) is shown in Figure II.10. Whereas the complete and comparative ^1H NMR spectra of compounds (II-6a), (II-2a) and assignments are shown in Figure II.11.

Figure II.10. ^1H NMR (400 MHz, CDCl_3) extended aliphatic region of II-6a.

Figure II.11. ¹H NMR (400 MHz, CDCl₃) spectra of II-2a (top) and II-6a (below).

The ^1H NMR spectrum of (II-6b) exhibited a broad singlet peak at 1.70 ppm integral area of one, represented the proton of the hydroxyl group of the aliphatic chain. A multiplet appeared at 2.00 ppm integral area of four, corresponding to the two-methylene groups. This multiplet is actually the overlapped result of two quintets, resulted from two methylene group in a linear chain with four neighboring protons with coupling constant ($^3J_{\text{vicinal}} = 6.04$ Hz). Another broad peak appears at 3.50 ppm, representing the proton of the hydroxyl group attached to the aromatic ring. Two triplets appeared at 3.90 and 4.10 ppm, integral area of two, and with coupling constant ($^3J_{\text{vicinal}} = 5.70$ and 5.66 Hz) represented the two-methylene group attached to oxygen and hydroxyl group respectively. Aromatic protons of the compound (II-6b) exhibited the same pattern like compound (II-6a), that is eight protons exhibited multiplet with integral area of (4:1:1:2) from 7.50 to 8.60 ppm. ^1H NMR spectrum of (II-6b) also showed the disappearance of the benzylic proton peak. The ^{13}C NMR spectrum of (II-6b) displayed 18 peaks for 18 chemically non-equivalent carbon atoms. ^{13}C NMR spectrum of (II-6b) also exhibited the disappearance of two aliphatic carbon atoms at 71.86 and 97.61 ppm as these carbons become aromatic, after the ring-opening and hence appeared in the aromatic region that was evident by the appearance of 14 peaks in the region 121 to 143 ppm. The mass spectrum gave the molecular ion peak at ($m/e = 282$) with relative intensity 31.5%. Comparative ^1H NMR spectra of compounds (II-6b), (II-2b) and assignments are shown in Figure II.12, whereas the ^{13}C NMR spectrum of compound (II-6b) and assignments are shown in Figure II.13.

Figure II.12. ^1H NMR (200 MHz, CDCl_3) spectra of II-2b (top) and II-6b (below).

Figure II.13. ^{13}C NMR (100 MHz, CDCl_3) of compound II-6b.

II.4.1b. Spectroscopic Characterization of Ring-opened Products (II-7a) and (II-7b)

The methyl ether derivative ring-opened products (II-7a) and (II-7b) were fully characterized spectroscopically and the spectroscopic data agreed well with the expected values. The IR spectra of both compound (II-7a) and (II-7b) showed the characteristic O-H stretching vibrations at 3479 cm^{-1} and confirmed the ring opening. Comparative IR spectra of compound (II-3a) and ring-opened product (II-7a) are shown in Figure II.14.

Figure II.14. IR spectra of II-3a (top) and II-7a (below)

The ^1H NMR spectrum exhibited a broad singlet at 1.31 and 1.32 ppm, integral area of one represented proton from the hydroxyl group attached to the aliphatic chain both in compound (II-7a) and (II-7b). The ring opening was also evident by the disappearance of the benzylic proton peak in the ^1H NMR spectra of both (II-7a) and (II-7b) methoxy protons showed a sharp singlet at 4.1 ppm integral area of three both in (II-

7a) and (II-7b). All the other methylene and aromatic protons are appeared at the expected position with similar pattern and similar coupling constant in accordance with the ring-opened product (II-6a) and (II-6b), respectively as were explained previously. The ^{13}C NMR spectra of compound (II-7a) and (II-7b) displayed eighteen and nineteen peaks for eighteen and nineteen chemically-non-equivalent carbon atoms respectively, and are in accordance with compound (II-6a) and (II-6b), with an extra aliphatic carbon for methoxy group at 64.1 and 74.1 ppm respectively. The mass spectra gave the molecular ion peak at ($m/e = 282$ and 296) with relative intensity 35.6 and 31.5% for compound (II-7a) and (II-7b) respectively.

II.4.1c. Spectroscopic Characterization of Ring-opened Products (II-8a) and (II-8b)

Mesylate derivative ring-opened products (II-8a) and (II-8b) were characterized and IR spectra showed the presence of hydroxyl group due to O-H stretching vibration from 3200 to 3600 cm^{-1} . The ^1H NMR spectra exhibited a broad singlet at 1.50 ppm for hydroxyl-proton both in (II-8a) and (II-8b) respectively. Ring-opening was evident by the disappearance of the benzylic proton peak in the ^1H NMR spectra of both (II-8a) and (II-8b). ^1H NMR spectra of both (II-8a) and (II-8b) exhibited a sharp singlet integral area of three at 2.40 ppm for methyl group attached to SO_2 group. All other methylene and aromatic protons appeared at the expected position with similar pattern and similar coupling constant in accordance with the ring-opened product (II-6a) and (II-6b) respectively, as were explained previously. The ^{13}C NMR again displayed eighteen and nineteen peaks for eighteen and nineteen chemically non-equivalent carbon atoms, respectively. Aliphatic region shows only 4 and 5 carbons respectively, as the other 2

aliphatic carbon appeared in the aromatic region, after being aromatic due to ring opening. The mass spectra gave a molecular ion peak at ($m/e = 346$ and 360) with relative intensity 33.2 and 37.4% for compound (II-8a) and (II-8b) respectively.

II.4.1d. Spectroscopic Characterization of Ring-opened Products (II-9a) and (II-9b)

Acetate derivative ring-opened product (II-9a) and (II-9b) were characterized spectroscopically and spectroscopic data agreed well with the expected values. The presence of hydroxyl group, due to ring-opening were evident in the IR spectra by O-H stretching vibration at 3458 cm^{-1} both in (II-9a) and (II-9b) respectively. The IR spectra also exhibited a strong carbonyl peak at 1755 cm^{-1} . As compared to the non-ring opened product (II-5a) and (II-5b), carbonyl vibration is shifted to higher frequencies. This exhibited the involving of the single bonded oxygen of the ester in conjugation with the aryl substituent. Apparently, the conjugation interferes with possible resonance with the carbonyl group, leading to an increase in the absorption frequency of carbonyl band. The IR spectra of both compounds (II-5b) and (II-9b) are shown in Figure II.15.

Figure II.15. IR spectra of II-5b (top) and II-9b (below).

The ^1H NMR exhibited a broad singlet at 1.60 ppm integral area of one, represented the hydroxyl proton both in (II-9a) and (II-9b). A sharp singlet appeared at 2.54 and 2.53 ppm integral area of three represented the methyl group attached to carbonyl group both in (II-9a) and (II-9b) respectively. The ring opening was confirmed by the disappearance of the benzylic proton peak from the ^1H NMR spectra of both compound (II-9a) and (II-9b) respectively. Ring opening was also confirmed by the appearance of quintet and triplet from the methylene group. This quintet and triplet appeared in a similar pattern, and with similar coupling constant in accordance with the ring-opened product (II-6a) and (II-6b), respectively as were explained previously. Aromatic protons again exhibited a multiple at 7.65 to 7.70, 7.85, 8.25 and 8.70 ppm with integral area of (4:1:1:2) respectively. Comparative ^1H NMR spectra and assignment of compound (II-5b) and its ring-opened product (II-9b) are shown in Figure II.16.

The ^{13}C NMR spectra of compound (II-9a) and (II-9b) displayed nineteen and twenty peaks for nineteen and twenty chemically non-equivalent carbon atoms. ^{13}C NMR spectra also showed the disappearance of two aliphatic carbon atoms peaks at 71.86 and 98.93 ppm, as these carbon atoms become aromatic after the ring opening and hence appeared in the aromatic region with the other 12 aromatic carbon atoms. A peak at 168.8 ppm represented a carbonyl group both in (II-9a) and (II-9b), respectively. The ^{13}C NMR spectra of compound (II-5b) and the ring-opened product (II-9b) are shown in Figure II.17.

Figure II.16. ^1H NMR (400 MHz, CDCl_3) spectra of II-5b (top) and II-9b (below).

Figure II.17. ^{13}C NMR (100 MHz, CDCl_3) spectra of II-5b (top) and II-9b (below).

The mass spectra gave a molecular ion peak at ($m/e = 310$ and 324) with relative intensity 50.5 and 46.5% for compound (II-9a) and (II-9b) respectively. The compounds (II-9a) and (II-9b) were also characterized by UV-vis. The UV-vis spectra of both compounds displayed a maximum absorption at 257 nm and another absorption at 301 nm. This smaller peak arises from the carbonyl group absorption conjugated with the aromatic ring Figure II.18.

Figure II.18. UV-vis spectrum (2.34×10^{-5} mmol/mL, chloroform) of II-9b.

II.5. Thermal Properties

II.5.1. Ring-opening Temperature

The thermal stability and the ring-opening of keto-ketal (II-1a), (II-1b) hydroxyl-ketal (II-2a), (II-2b) and their derivatives (II-3a), (II-3b), (II-4a), (II-4b), (II-5a), (II-5b), were examined. The weight loss data were obtained from Seiko TG/DTA 220 with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The system was permanently purged with N_2 (flow rate: $200\text{ mL}/\text{min}$). A Seiko DSC 220 instrument was operated from room temperature to $230\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and purged with N_2 (flow rate: $100\text{ mL}/\text{min}$). The instrument temperature and sensitivity were calibrated with indium and tin. 5 mg samples were used to obtain the DSC

traces. The first scan showed only a melting endotherm at 122 °C and 141 °C and no sign of ring opening (exotherm) was observed both in the case of keto-ketals (II-1a) and (II-1b), respectively. The hydroxyl-ketal (II-2a), (II-2b) and their derivatives (II-3a), (II-3b), (II-4a), (II-4b), (II-5a) and (II-5b) showed a melting endotherm and an exotherm due to the ring-opening. The temperature at which the exothermic peak reached its maximum ($T_{\max}$) and the onset temperature (T_{onset}) were directly taken from the graph Figure II.19. The onset temperature was recorded at the intersection of the tangents of the baseline and of the peak. Melting point temperature (T_m), ring-opening temperature at the maximum height of exotherm ($T_{\max}$), and onset ring-opening temperature (T_{onset}) are reported in Table II.2.

Figure II.19. DSC trace of II-2b with a heating rate of 10 °C/min showing (T_m) of a melting endotherm, ($T_{\max}$) and (T_{onset}) of a ring-opening exothermic peak.

Table II.2. Ring-opening and melting temperatures of hydroxyl-ketal and derivatives.

R (CH ₂) ₃	R (CH ₂) ₃	R (CH ₂) ₃	R (CH ₂) ₃	R (CH ₂) ₄	R (CH ₂) ₄	R (CH ₂) ₄	R (CH ₂) ₄
R'	OH	OCH ₃	OSO ₂ CH ₃	OCOCH ₃	OH	OCH ₃	OSO ₂ CH ₃	OCOCH ₃
T _m °C	150	162	103	137	119	104	77	147
T _{max} °C	182	198	107	205	161	187	105	189
T _{onset} °C	164	178	104	182	149	159	100	165

II.5.2. Ketal Size Effect

Dihydrophenanthrene-based hydroxyl-ketals (II-2a), (II-2b) and their derivatives undergo thermal ring-opening. The formation of stable aromatic phenanthrene was the driving force for the thermal rearrangement of cyclic ketals. The DSC results indicate that 7-membered ketal (II-2b) underwent ring-opening at a relatively lower temperature of 149 °C compared to 6-membered ketal (II-2a) at 164 °C. In order to understand the effect of the ketal size on the ring-opening temperature, first one has to consider some stereo-chemical features of heterocyclic analogs of cycloalkane.⁵¹ For the purpose of elaborating conformational principles, the discussion will focus on six-membered ring.

The most stable conformation of cyclo-hexane is the chair. Electron diffraction studies in the gas phase reveal a slight flattening of the chair compared with the geometry obtained when using tetrahedral molecular models.⁵² The torsion angles are 55.9°, compared with 60° for the "ideal" chair conformation, and the axial C-H bonds are not perfectly parallel, but are oriented outward by about 7°. The C-C bonds are 1.528 Å, the C-H bonds are

1.119 Å, and C-C-C angles are 111.05° .⁵² The more obvious changes that occur on introduction of the heteroatom into six or seven-membered ring have to do with bond length and angles. The carbon-oxygen bond length becomes 1.43 Å, which is shorter than the carbon-carbon bond length 1.53 Å. The normal valence angles are somewhat smaller than tetrahedral at oxygen, and this produces angle strain. The six-membered heterocyclic rings resemble the chair conformation of cyclohexane but are modified so as to accommodate the bond length and bond angle characteristics of the heteroatom. The rings are all somewhat more puckered than cyclohexane because of the shorter C-O bond distance. Heterocyclic 6-membered-ring (e.g. 1,3-dioxane) showed in Figure II.20 has larger conformational free energy than in cyclo-hexane ring. The shorter bonds lead to stronger repulsive interaction with the axial hydrogens, which approach each other too closely and hence is responsible for producing steric strain. As ring size increases, there are progressively more conformations that need to be considered. For cycloheptane, four conformations have been calculated to be particularly stable.⁵³ Amongst the four the twist-chair is the most stable⁵⁴ (e.g. 1,3-dioxepane) shown in Figure II.20.

Figure II.20. Stable conformation of 6 and 7 membered heterocyclic ring.

The replacement of carbon by oxygen produces changes in several structural parameters, and consequently affects the conformation features. The shorter C-O bond distance leads to strong repulsive interaction and twisted-chair conformation responsible for producing more angle strain as compared to 6-member chair type conformation. The comparison of strain energies of cyclohexane (1.4 kcal/mol)⁵⁵ and for cycloheptane (7.6 kcal/mol)⁵⁵ shows that 6-membered ring is nearly strain free but 7-membered ring has some strain as molecular geometry requires greater distortion from optimal bond angle. Due to the increased ground state energy resulting from angle strain, reactions that lead to ring-opening often proceed much more readily than do similar reactions in unstrained system. This is the basic reason that 7-membered ketal (II-2b) underwent ring-opening at relatively lower temperature than the 6-membered ketal (II-2a).

II.5.3. Substituent Effect

Methyl ether, mesylate and acetate derivatives of the dihydrophenanthrene-based hydroxyl-ketals (II-2a) and (II-2b) were prepared to study the substituent effect on the ring-opening temperature. The methyl ethers (II-3a) and (II-3b) underwent clean ring-opening reaction and showed ring-opening onset temperature at 178 °C and 159 °C respectively as can be seen in Table II.2. Both mesylate derivatives (II-4a) and (II-4b) rearranged at relatively lower temperatures of 105 °C and 100 °C respectively Table II.2. Ring-opening temperatures of hydroxyl-ketals (II-2a), (II-2b) and methyl ether derivatives (II-3a) and (II-3b) were found to be higher as compared to mesylate derivatives (II-4a) and (II-4b). The results indicate that the presence of an electron-withdrawing group, such as sulfonate, facilitates the thermal aromatization and hence the ring-opening reaction, further proving that the thermal

aromatization is the driving force for the conversion of dihydrophenanthrene-based ketals to phenanthrene-based alcohols.

The DSC traces of acetate derivatives (II-5a) and (II-5b) showed an exotherm onset temperature at 182 °C and 165 °C respectively in Table II.2, implying ring-opening of cyclic ketal. The ring-opening temperatures of acetates (II-5a) and (II-5b) were found to be higher than expected based on electron withdrawing effect of acetate group. In all the cases of methyl ether, mesylate and acetate derivatives, 7-membered ketals under went ring-opening at relatively lower temperatures than 6-membered ketals.

II.5.4. Catalysis

Acetate derivatives of dihydrophenanthrene-based ketals (II-5a) and (II-5b) were selected as a model compounds and the effect of different catalysts on the ring-opening temperature was investigated and the results are summarized in Table II.3.

Table II.3. Catalyst effect on ring-opening temperature of II-5a and II-5b.

Catalysts
	$T_{RO(onset)}\text{ }^{\circ}\text{C}$	$T_{RO(max)}\text{ }^{\circ}\text{C}$	$T_{RO(onset)}\text{ }^{\circ}\text{C}$	$T_{RO(max)}\text{ }^{\circ}\text{C}$
No catalyst	182	205	165	189
AlCl_3	181	202	75	83
SnCl_2	184	204	110	128
$\text{Cr(III)Acetylacetonate}$	182	202	139	178
Silica gel	182	205	166	185
Molecular Sieve (3Å)	182	205	166	189
DABCO	182	205	165	189
DBTDL	179	200	151	165

Effects of the different catalysts were found to be more prominent in 7-membered acetate derivative (II-5b), compared to 6-membered acetate (II-5a) as expected. The 7-membered ketal ring has more strain than 6-membered. That is, after the formation of complex between the metal of Lewis acid and the etheric oxygen, the etheric group becomes the better leaving group than in 6-membered ring. This is evident by the DSC results,

compound (II-5b) underwent ring-opening at 83 °C when AlCl_3 was used, but the same catalyst was almost ineffective in compound (II-5a).

II.5.5. Kinetic Studies

From practical point of view, it is useful to consider the kinetics of the ring-opening of acetate derivative of dihydrophenanthrene-based ketal (II-5b), this compound was selected as a model compound. The kinetic parameters are useful for the determination of the time for the reaction to take place at a given temperature. On the basis of the results of the solubility of compound (II-5b) in different solvents, kinetic study was done in DMAc. Solubility results are summarized in Table II.4.

Table II.4. Solubility of model compound II-5b.

Solvent	Solubility
m-Xylene	++++
N,N-Dimethylacetamide (DMAc)	++++
Decahydronaphthalene	+/-
2-Methoxy ethyl ether	++

The activation energy for the ring-opening reaction was determined by finding the rate of ring-opening reaction at different constant temperatures: 100 °C, 120 °C, 140 °C and 160 °C for different intervals of time. It was found that the reaction went to 50% ring-opening at 160 °C in 10 minutes, 40% at 140 °C in 90 minutes, 17% at 120 °C in 150 minutes and 14% at 100 °C in 300 minutes. Data for rate of reaction at 160 °C, 140 °C, 120 °C and 100 °C are reported in Table II.5, II.6, II.7 and II.8, whereas the UV-vis spectra for ring-

opening trends with respect to different interval of time and the graphs to determine rate constant (K) are reported in Figure II.21, II.22, II.23 and II.24 respectively. Data for finding activation energy are reported in Table II.9, whereas the graph in Figure II.25 and the activation energy after two trials are reported in Table II.10.

Table II.5. Kinetic data at 160 °C.

Initial concentration $[A_0] = 9.3104 \times 10^{-2}$ mol/L; Absorbance at zero time $A_0 = 0.06281$.

Concentration of reactant after time "t" $[A] = [A_0] - [X]$

Serial #	Time (min)	Absorbance at λ 301 nm	[Product] _t [X]	[Reactant] _t [A] = [A ₀] - [X]	$\ln[A_0]/[A]$	% Conversion
1	1	0.09924	8.0208×10^{-3}	8.5083×10^{-2}	0.09008	8.60
2	2	0.11834	1.2226×10^{-2}	8.0878×10^{-2}	0.14077	13.13
3	3	0.16973	2.3540×10^{-2}	6.9564×10^{-2}	0.29146	25.28
4	8	0.26683	4.4919×10^{-2}	4.8185×10^{-2}	0.65860	48.24

Figure II.21. Ring opening trends and graph for rate of reaction at 160 °C.

Table II.6. Kinetic data at 140 °C.

Initial concentration $[A_0] = 9.3104 \times 10^{-2}$ mol/L; Absorbance at zero time $A_0 = 0.06281$.

Concentration of reactant after time "t" $[A] = [A_0] - [X]$

Serial #	Time (min)	Absorbance at λ 301 nm	[Product] _t [X]	[Reactant] _t [A] = [A ₀] - [X]	$\ln[A_0]/[A]$	% Conversion
1	25	0.12225	1.3087×10^{-2}	8.0017×10^{-2}	0.15147	14.05
2	35	0.15787	2.0929×10^{-2}	7.2175×10^{-2}	0.25462	22.47
3	50	0.17771	2.5295×10^{-2}	6.7809×10^{-2}	0.31702	27.16
4	80	0.19908	3.0002×10^{-2}	6.3102×10^{-2}	0.38896	32.22
5	90	0.21135	3.2704×10^{-2}	6.0400×10^{-2}	0.43272	35.12

Figure II.22. Ring opening trends and graph for rate of reaction at 140 °C.

Table II.7. Kinetic data at 120 °C.

Initial concentration $[A_0] = 9.3104 \times 10^{-2}$ mol/L; Absorbance at zero time $A_0 = 0.06281$.

Concentration of reactant after time "t" $[A] = [A_0] - [X]$

Serial #	Time (min)	Absorbance at λ 301 nm	[Product] _t [X]	[Reactant] _t [A] = [A ₀] - [X]	ln[A ₀]/[A]	% Conversion
1	60	0.07785	3.3113×10^{-3}	8.9793×10^{-2}	0.03621	3.55
2	90	0.10430	9.1349×10^{-3}	8.3969×10^{-2}	0.10326	9.81
3	150	0.10816	9.9848×10^{-3}	8.3119×10^{-2}	0.11344	10.72
4	180	0.12884	1.4537×10^{-2}	7.8566×10^{-2}	0.16971	15.61

Figure II.23. Ring opening trends and graph for rate of reaction at 120 °C.

Table II.8. Kinetic data at 100 °C.

Initial concentration $[A_0] = 9.3104 \times 10^{-2}$ mol/L; Absorbance at zero time $A_0 = 0.06281$.

Concentration of reactant after time "t" $[A] = [A_0] - [X]$

Serial #	Time (min)	Absorbance at λ 301 nm	[Product] _t [X]	[Reactant] _t [A] = [A ₀] - [X]	$\ln[A_0]/[A]$	% Conversion
1	30	0.06280	0	9.3104×10^{-2}	0	0
2	90	0.07099	1.8032×10^{-3}	9.1300×10^{-2}	0.01956	1.93
3	180	0.09613	7.3383×10^{-3}	8.5765×10^{-2}	0.08210	7.88
4	300	0.10771	9.8879×10^{-3}	8.3210×10^{-2}	0.11227	10.62

Figure II.24. Ring opening trends and graph for rate of reaction at 100 °C.

Table II.9. Data for activation energy.

Serial #	T(°C)	1/T(K)	K (min ⁻¹)	ln K
1	160	2.33×10^{-3}	0.0821	-2.49981
2	140	2.42×10^{-3}	0.0038	-5.57275
3	120	2.54×10^{-3}	0.0009	-7.01311
4	100	2.68×10^{-3}	0.0004	-7.82404

Figure II.25 Graphs representing the activation energies of model compound II-5b (Left -> The activation energy "A" by using rate constant K at 160 °C, 140 °C, 120 °C and 100 °C). (Right -> The activation energy "B" by using rate constant K at 160 °C, 140 °C and 120 °C).

Table II.10. Activation energies of model compound II-5b

Activation Energy	KJ/mol	kcal/mol
A ^a	119.15	28.37
B ^b	174.42	41.53
C ^c	125.85	29.97
D ^d	182.05	43.35

^a Measured by 1st trial (using rate constant “K” at 160 °C, 140 °C, 120 °C and 100 °C).

^b Measured by 1st trial (using rate constant “K” at 160 °C, 140 °C and 120 °C).

^c Measured by 2nd trial (using rate constant “K” at 160 °C, 140 °C, 120 °C and 100 °C).

^d Measured by 2nd trial (using rate constant “K” at 160 °C, 140 °C and 120 °C).

The activation energy graphs show that the ring-opening reaction of the model compound (II-5b) is a first-order reaction with activation energy 43.35 kcal/mol.

Chapter III

Monomer Containing Dihydrophenanthrene Ketal “Masked Alcohol” Moiety

III.1. Synthesis of Acrylate Monomer

A novel acrylate monomer containing dihydrophenanthrene ketal moiety “masked alcohol” was synthesized by reacting dihydrophenanthrene-based 7-membered hydroxyl-ketal (II-2b) with acryloyl chloride. The compound (II-2b) was selected because of its lower ring-opening temperature compared to the 6-membered hydroxyl-ketal (II-2a). In order to avoid ring-opening, the esterification reaction was carried out below 0 °C in dry THF. Triethylamine was used to capture the formed hydrogen chloride during the esterification process. The product was purified by column chromatography using methylene chloride: hexane (8:2 v/v) ratio, and was obtained as a white solid with 65% yield. (Scheme III. 1).

Scheme III.1. Synthesis of acrylate monomer III-1.

III.2. Characterization

The structure of monomer (III-1) was verified by spectroscopic means. The IR spectrum showed the disappearance of the O-H peak. The carbonyl group peak appeared at 1722 cm^{-1} . The ester vibration is shifted to lower frequencies due to conjugation of the carbonyl with the double bond of the vinyl group. IR spectrum also exhibited vinyl C=C stretch at 1618 cm^{-1} , aromatic CH stretch 3095 cm^{-1} , alkyl CH stretch 2946 cm^{-1} and five strong bands for ketal C-O stretch from 1263 to 1084 cm^{-1} . IR spectra of both compound (II-2b) and monomer (III-1) are shown in Figure III.1.

Figure III.1. IR spectra of monomer III-1 with hydroxyl-ketal II-2b

The ^1H and ^{13}C NMR spectra and assignments are shown in Figures III.2 and III.3. The ^1H NMR spectrum showed the presence of three vinylic protons in addition to the peaks from the starting material dihydrophenanthrene-based 7-membered hydroxyl-ketal (II-2b). The three vinyl proton spectrum is some what typical of a compound with

three hydrogen atoms substituted on a double bond. Each proton has a chemical shift and a coupling constant different from those of each of the other protons. The spectrum shown in Figure III.2 is some how unexplained for the acrylate part concerning the splitting. Each hydrogen should have to split into doublet of doublets, but only a doublet was observed at 5.77 ppm with coupling constant ($^3J_{\text{cis}} = 10.04$ Hz), whereas geminal coupling constant was unresolved representing the chemical shift of vinyl proton (H_{21B}). A broad triplet appeared at 5.96 ppm with coupling constant ($^3J_{\text{cis}} = 10.04$ Hz) and ($^3J_{\text{trans}} = 15.84$ Hz), which represented the proton (H_{20C}) cis to proton (H_{21B}) and trans to proton (H_{21A}). Spectrum also exhibited a doublet at 6.22 ppm with coupling constant ($^2J_{\text{geminal}} = 3.24$ Hz), which represented the proton (H_{21A}) trans to proton (H_{20C}) but trans coupling constant was unresolved due to overlapping with the singlet from proton (H_D) at 6.18 ppm. If this spectrum is compared with the proton spectrum of methacrylate (MA),⁵⁶ the chemical shift of each significant proton matches well (see Table III.1). However, the multiplicity of each signal looks different. The slight downfield shift of proton (H_{21A}) resulted due to conjugated ketone-alkene system.

Table III.1. Proton chemical shift in ppm of monomer III.1 and methacrylate (MA).

Proton	III-1	MA
A	6.22	6.38
B	5.77	5.78
C	5.96	6.00

Figure III.3. ^{13}C NMR (100 MHz, CDCl_3) spectra and assignments of acrylate monomer III-1(below). Extended aromatic region (top).

The ^1H NMR spectrum exhibited two multiplets at 1.63 and 1.79 ppm integral area of two, which represented the methylene carbon (No.16) and (No.17), respectively, where none of the coupling constant was resolved. A broad singlet, broad triplet, broad doublet, and another broad singlet integral area of one, respectively represented four methylene protons from carbon (No. 15) and carbon (No.18) at 3.38, 3.62, 3.86 and 4.10 ppm respectively. Aromatic protons showed a doublet of triplet at 7.30 and 7.39 ppm with coupling constant ($^3J_{\text{ortho}} = 7.45 \text{ Hz}$) and ($^4J_{\text{meta}} = 1.12 \text{ Hz}$), which represented protons (H_5), (H_{10}), (H_4) and (H_{11}) respectively. A doublet of quartet is originated from proton (H_3), at 7.46 ppm with coupling constant ($^3J_{\text{ortho}} = 7.45 \text{ Hz}$, $^4J_{\text{meta}} = 1.44 \text{ Hz}$ and $^5J_{\text{para}} = 0.88 \text{ Hz}$). The downfield shift of the proton (H_3) was the result of magnetic anisotropy effect of the carbonyl group. Other three protons (H_6), (H_9) and (H_{12}) appeared at 7.84 ppm as a multiplet.

The ^{13}C NMR spectrum displayed the expected twenty one peaks for twenty one chemically non-equivalent carbon atoms. The carbon (C_{19}) from the ester carbonyl group is assigned at 166.93 ppm. The two vinyl carbon atoms (C_{20}), and (C_{21}) are displayed in the lower field region of alkene (128.34 and 131.14 ppm) due to the conjugated ketone-alkene system. All other carbon atoms appeared at the expected position, in accordance with the model compound (II-5b) Figure II. 10.

The HRMS confirmed the exact mass (336.1301 g/mol). Mass spectrum clearly showed the fragment peak due to loss of COCHCH_2 at ($m/e = 281$) and another fragment peak due to loss of $\text{C}_8\text{H}_{11}\text{O}_3$ at ($m/e = 181$).

The UV-vis absorption spectrum of monomer (III-1) displayed a maximum absorption peak at 274 nm Figure III.4. This absorption peak is similar to the model compound (II-5b) and appeared from the polycyclic aromatic ring that is from dihydrophenanthrene-based ketal moiety.

Figure III.4. UV-vis spectrum (2.34×10^{-5} mmol/mL, chloroform) of monomer III-1.

III.3. Thermal Property

Thermal stability and the ring-opening of monomer (III-1) were examined. The onset decomposition temperature for 5% weight loss was found to be 220 °C. The DSC scan was run up to 220 °C and purged with N₂ (Flow rate: 100 mL/min). The first scan showed a melting endotherm at 128 °C and an exothermic peak due to ring-opening at 158 °C, where as the onset ring-opening temperature was found to be 139 °C. The DSC trace of monomer (III-1) is shown in Figure III.5.

Figure III.5. DSC trace of monomer III-1 with heating rate $10\ ^\circ\text{C}/\text{min}$. Showing T_m , T_{max} and T_{onset} of an exothermic peak.

Chapter IV

Polyacrylate Containing "Masked Alcohol" Moiety and Curing

IV.1. Free Radical Polymerization.

The match of monomer (III-1) and MMA of the smaller methyl ester group favor the formation of copolymers. Copolymers were prepared by radical polymerization using AIBN as a radical initiator. A THF solution of monomer (III-1), MMA and AIBN (0.1% weight) was first deoxygenated with nitrogen, placed in a sealed vessel, and heated at 60 °C for 24 hours. The resulting polymer was precipitated in methanol as a white fibrous solid. The remaining unreacted monomer and oligomers were removed by successive precipitation in methanol, and monitored by GPC (Scheme IV.1).

Scheme IV.1. Copolymerization of monomer III-1 with MMA.

Three different molar ratio between monomer (III-1) and MMA were experimented. The molar composition of the two monomers in the copolymer was determined by UV-vis calibration of monomer (III-1) at 274 nm Figure IV.1 and Table IV.1.

Figure IV.1. UV-vis calibration curve ($\lambda_{\text{max}} = 274 \text{ nm}$, chloroform, 22 °C) of monomer III-1.

Table IV.I. Composition of copolymers (molar percentage).

Copolymers	X in feed ^a	X in polymer ^b
IV-1	0.050	0.045
IV-2	0.100	0.071
IV-3	0.150	0.069

^a mole fraction of monomer III-1 in feed.

^b mole fraction of monomer III-1 in copolymers is determined by UV-vis calibration of monomer III-1.

Due to the difference in the reactivity of the monomers, the composition of the copolymer is different from that of the feed mixture.⁵⁷ Indeed a decrease of monomer (III-1) content in copolymers is observed relative to the reaction mixture. This effect occurred more specifically when the monomer (III-1) content in the feed mixture is high. The reactivity ratio r_1 and r_2 characterize the reactivity of monomers. These parameters measure the relative preference that the polymer radical $A^\bullet$ and $B^\bullet$ have for the two monomers A and B. When $r_1 < 1$, the polymer radical $A^\bullet$ reacts more preferentially with the monomer B, as opposed to the monomer A. Conversely when $r_1 > 1$, the polymer radical $A^\bullet$ reacts more preferentially with the monomer A, as opposed to monomer B. As stated above the content of copolymers (IV-1), (IV-2), and (IV-3) are richer in MMA and poorer in monomer (III-1) compared to the feed mixture composition. Therefore, MMA is the most reactive monomer. MMA is more reactive than monomer (III-1) toward both propagation species. The radical from MMA preferentially adds monomer MMA instead of monomer (III-1) $r_{\text{MMA}} > 1$ and the radical from monomer (III-1) preferentially adds monomer MMA than monomer (III-1) $r_{\text{monomer III-1}} < 1$.⁵⁸

IV.2. Polymer Characterization.

NMR analysis has been done with copolymer (IV-1). The ^1H and ^{13}C NMR spectra were not always well resolved and broad lines were displayed. However some of the peaks were assigned. ^1H and ^{13}C NMR spectra are shown in Figures IV.2 and IV.3 respectively.

Figure IV.2. ^1H NMR spectrum (400 MHz, CDCl_3) of copolymer IV-1.

Figure IV.3. ^{13}C NMR spectrum (100 MHz, CDCl_3) of copolymer IV-1.

The ^1H NMR spectrum proved the incorporation of monomer (III-1) into copolymer. Despite the overlap of most peaks corresponding to monomer (III-1) with MMA, the characteristic benzylic proton peak at 5.95 ppm was clearly identified. The transformation of monomer (III-1) into copolymer is also seen by the disappearance of three vinylic protons ($\text{H}_{20\text{C}}$), ($\text{H}_{21\text{A}}$) and ($\text{H}_{21\text{B}}$) peaks from the double bond (vinylic region) and the presence of new peaks in the alkyl region at 1.03 and 1.56 ppm for methylene and methine proton respectively. The ^{13}C NMR spectrum also confirmed the chemical transformation of carbon atom (C_{20}), (C_{21}) and showed peaks in the alkyl region for them. Carbon atom (C_{20}) appeared downfield at 54.22 ppm, may be due to anisotropy effect of the carbonyl group next to it, whereas carbon atom (C_{21}) signal is shifted to higher field at 18.71 ppm, as the double bond reacted to give a carbon-carbon single bond. The ^{13}C NMR spectrum displayed two peaks for carbon atom (C_B) and (C_{19}) at 177.81 and 178.11 ppm, which represented the ester carbonyl group from MMA and monomer (III-1) respectively. It is interesting to notice that the signal intensities for monomer (III-1) are smaller than for MMA. However, this was expected as the composition of copolymer (IV-1) is 4.5% of monomer (III-1).

The IR spectra of copolymers (IV-1), (IV-2), and (IV-3) indicated the presence of the ester carbonyl group by showing carbonyl stretching at 1734 cm^{-1} . It could be seen that the carbonyl group stretching is shifted back to usual frequency 1734 cm^{-1} as the carbonyl group is no longer in conjugation with the double bond. IR spectra of (IV-1), (IV-2), and (IV-3) do not show any O-H stretching vibration, which indicates that ketal ring has survived the polymerization and remained intact Figure IV.4.

Figure IV.4. IR spectrum of copolymer IV-1.

IV.3. Thermal Properties

Thermogravimetry is widely used for assessing the thermal stability of polymeric materials. However, the conclusion drawn with regards to stability is only relevant with the context of the weight loss of the sample. There are reactions that can take place on heating a polymer and which alter drastically the physical properties of the material without an observed change in weight.⁵⁹

Thermal stability of the copolymers (IV-1), (IV-2), and (IV-3) were assessed by thermogravimetric analysis (TGA) in nitrogen. The onset temperature for 5% weight loss for these polymers ranged from 216 °C to 220 °C Table IV.2.

Table IV.2. Thermal properties of copolymers

Copolymers	Monomer III-I content	T_d^a (°C)	T_g^b (°C)	T_{max} (°C)	T_g (°C) 2 nd Scan
PMMA	0	222	NA	NA	NA
IV-1	0.045	220	107	165	126
IV-2	0.071	218	109	165	128
IV-3	0.069	216	111	165	129

^a Measured by TG at 10 °C/min, under a nitrogen flow of 200 mL/min.

^b Measured by DSC at 10 °C/min, under nitrogen flow of 100 mL/min.

The DSC of polymer (IV-1) showed two types of transition temperatures Figure IV.5. The glass transition (T_g), and an exothermic peak (T_{max}) due to ring-opening of the ketal unit. The 2nd run DSC, however, showed only (T_g) and no exothermic peak due to ring-opening was observed which meant an irreversible ring-opening process.

Figure IV.5 DSC traces of copolymer IV-1 with a heating rate of 10 °C/min under nitrogen flow rate 100 mL/min.

IV.4. Copolymethacrylate Containing Isocyanate Group

In order to establish a one component polyurethane system in two polymer system, a copolymer containing isocyanate group was synthesized. For that purpose, MMA was copolymerized with commercially available new dual functional monomer 2-isocyanatoethyl methacrylate (2-IEMA). A THF solution of MMA (90% weight), 2-IEMA (10% weight) and AIBN (0.1% weight) was deoxygenated with nitrogen, placed in sealed vessel and heated at 60 °C for 24 hours. The resultant polymer (IV-4) was precipitated out in methanol. The gummy polymer was separated from the unreactive monomer by successive re-precipitation from methanol (Scheme IV.2).

Scheme IV.2. Copolymerization of MMA with 2-IEMA.

IV.5. Characterization

The copolymer (IV-4) was fully characterized by spectroscopic means. The IR showed strong absorption at 1731 cm^{-1} corresponding to the ester carbonyl group and another absorption at 2274 cm^{-1} corresponding to the isocyanate group. NMR spectra were not well resolved and broad lines were displayed, however, some of the chemical shifts were resolved. In ^1H NMR spectrum, there is a distinction between (H_6) and (H_D) while the others were unresolved. The ^{13}C NMR spectrum displayed twelve peaks for twelve chemically non-equivalent carbons. In ^{13}C NMR spectrum, two peaks are displayed for (C_B)/(C_4), (C_D)/(C_6) and (C_E)/(C_7). The characteristics peaks from the isocyanate group (C_1) appeared at 168.72 ppm along with the other 2 carbonyl peaks representing the ester carbonyl group from MMA and 2-IEMA, i.e. (C_4) and (C_B) at 176 and 177 ppm respectively. ^1H and ^{13}C NMR spectra of copolymer (IV-4) are shown in figures IV.6 and IV.7 respectively.

Figure IV.6. ^1H NMR spectrum (400 MHz, CDCl_3) of copolymer IV-4

Figure IV.7. ^{13}C NMR spectrum (100 MHz, CDCl_3) of copolymer IV-4

IV.6. Curing of Copolymer Containing “Masked Alcohol” Moiety

O. Bayer first prepared polyurethanes in 1937. Their commercial importance was realized in early 1950's with polyurethane elastomers and foams. Since then, the applications of polyurethanes have been extended to fibers, surface coatings, elastomers, adhesives and sealants. Today, because of the known structure-property relationship and the large variety of starting materials, polyurethane may be tailored for specific applications. Urethane is not usually the major functional group present in polyurethane. Essentially, any polymer containing urethane groups will be referred to as polyurethane. The chemical compositions of polyurethanes include a large variety of functional groups such as ester, ether, amide, and urea.

Polyurethanes are conventionally prepared from a diol and a diisocyanate. Since alcohol reacts with isocyanate at room temperature, they must be kept separate. These two monomers are mixed in equimolar amount just before curing. Recently, much effort has been directed towards the development of an one-component heat-curing polyurethane. Some of such polyurethanes exist in which the isocyanate is masked. The diisocyanate is first reacted with phenol or an oxime to form the corresponding urethane which is chemically inert to alcohol. Upon heating, the masking agent is liberated and the resulting isocyanate could then react with an alcohol to produce a urethane. The disadvantage of these masking agents is that during cure, toxic phenol and oxime are liberated. There is a need for the development of a one component heat-curing system which does not liberate any volatile organic compounds during the curing process.

It has been shown in the previous section (chapter II) that dihydrophenanthrene-based ketal thermally undergoes ring-opening between 100 °C and 200 °C, and generates

an aliphatic alcohol without producing any by-products. It has also been shown in Figure IV.4 that masked alcohol moiety survives the copolymerization and remain intact, since the formation of aliphatic alcohol occurs without producing any by-product, that give an additional advantage, as the properties of material would not be impaired by the presence of gas or other small trapped products.

A copolymer containing dihydrophenanthrene-based ketal (masked alcohol) moiety could be used to thermally cure with an isocyanate prepolymer or other copolymer containing the reactive isocyanate group. If satisfactory, this one-component polyurethane would be a VOC-free curing system.

IV.7. Polymer Curing

Films set I for curing experiments were prepared by blending copolymer (IV-1) with diisocyanate prepolymer (Desmodur from Bayer) in equimolar amount just before curing. Another set II of films were prepared by blending copolymer (IV-1) with copolymer (IV-4) in equimolar amount. The mixtures were placed on glass plates. Films were dried at 80 °C for 24 hours in the vacuum oven under nitrogen. One of the films was used for IR analysis before curing. After heating at 100 °C, 120 °C, 140 °C and 160 °C in an oven for different interval of times (1 to 4 hours), the glass plates were taken out from the oven and allowed to cool to room temperature. The polymer film was then peeled off for characterization.

The polymer films which were heated below 140 °C did not show any change, but those heated for (2 to 4 hours) at 140 °C and 160 °C were found to be insoluble in organic solvents. The insolubility of the polymer film indicated the crosslinking due to reaction between in-situ thermally generated hydroxyl group and the isocyanate group of prepolymer (Desmodur from Bayer) or copolymer (IV-4) (Scheme IV.3).

Scheme IV.3. One-component polyurethane without VOC

The IR spectrum of the film was obtained by analyzing the surface of the film. The IR spectrum showed the disappearance of isocyanate peak at 2273 cm^{-1} and the formation of a new peak due to urethane at 1690 cm^{-1} . The film set II (copoly IV-1 + copoly IV-4) gives the same result except that the urethane peak appeared at 1632 cm^{-1} and the OH stretching vibration at 3445 cm^{-1} due to the unconsummated or unreacted hydroxyl group generated in-situ during cure. The IR spectra of films set I and set II are shown in Figures IV.8 and IV.9 respectively.

Figure IV.8. IR spectrum of film set I

Figure IV.9. IR spectrum of film set II

Conclusion

The main objective of this thesis was to synthesize "Masked Polyol" and its application in polymer curing.

The "Masked Alcohol" was successfully synthesized by reacting commercially available phenanthrenequinone with 1,3-propanediol and 1,4-butanediol in high yield. The influence of ketal ring-size on the ring-opening temperature was investigated and the results indicated that the 7-membered ketal underwent ring-opening at relatively lower temperatures than the 6-membered ketal. The influence of substituent effect on the ring-opening temperature was investigated by synthesizing the methy ether, mesylate and acetate derivatives from dihydrophenanthrene-based 6 and 7-membered ketals. Experimental results indicate that ether and mesylate derivatives underwent clean ring-opening reactions to the phenanthrene alcohol as compared to acetate. Mesylate derivatives of both 6- and 7-membered ketal underwent ring-opening reactions at relatively lower temperature i.e. 100 °C than the methyl ether 200 °C and acetate 189 °C

The effect of different catalysts on both, 6 and 7-membered acetate derivative of dihydrophenanthrene-based ketal was investigated. None of the Lewis acid catalyst showed effect on the ring-opening of the 6-membered ketal. However, the 7-membered acetate derivative was highly influenced by AlCl_3 (due to more strain in 7-membered ketal ring) and underwent ring-opening at 83 °C, which is 106 °C less compared to ring-opening 189 °C without catalyst.

Kinetic of the ring-opening reaction for 7-membered acetate derivative was also studied in solution using DMAc, and it was found that the ring-opening reaction is a first order with activation energy 43.35 kcal/mol.

A novel heat-curing one-component polyurethane system was demonstrated based on finding that dihydrophenanthrene-based ketal thermally generated an aliphatic alcohol in-situ upon heating from 100 °C to 200 °C. A copolymer containing dihydrophenanthrene-based ketal "Masked Alcohol" moiety was introduced into polyurethane system and successfully thermally cured with reactive isocyanate group of other copolymer upon heating at 140 °C and 160 °C from more than 2 to 4 hours, and a cured material was obtained. The crosslinking was evident by the insolubility of the cured material in all the common organic solvents, and the appearance of urethane peak at 1690 cm^{-1} in the IR spectrum of the cured material.

Experimental Section

Material

Phenanthrenequinone (95%), 1,3-propanediol (99%), 1,4-butanediol (99%), toluene (99.5%), sodium borohydride (90%, 10–40 mesh), acryloyl chloride (99%), triethylamine (98%), 2,2'-azobisisobutyronitrile (recrystallized from ethanol), methanesulfonyl chloride (98%), benzyltriethylammonium chloride (99%), dimethyl sulfate (98%), dichlorobenzene (99%), acetyl chloride (98.5%), pyridine (99% dry before use), anhydrous MgSO_4 (99%), decahydronaphthalene (98%), dimethyl ethyl ether (99%), anhydrous N,N-dimethylacetamide (99%), *m*-xylene (99%), anhydrous aluminium chloride (99.99%), chromium (III) acetyl acetate (97%), molecular sieves (3 Å, beads, 3–8 mesh), dibutyltin dilurate (95%), 1,4-diaza[2,2,2]bicyclooctane (98%) were purchased from Aldrich Chemical Co. and were used as received. Anhydrous ethyl ether purchased from Caledon, *p*-toluenesulphonic acid (98%) from BDH, silica gel 0.063–0.200 mm mesh from EM Science, methylene chloride (99.5%) purchased from Anachemia were used as received. Methyl methacrylate (95%) 2-isocyanatoethyl methacrylate (98%), were purchased from Aldrich and were distilled at 20 mm Hg at room temperature. These were then passed through a column packed with De-hibiter-200 (from Polyscience). Desmodur N-3300 (diisocyanate prepolymer 21.5% wt./NCO) was provided by Bayer Co. THF from BDH was dried over sodium metal and distilled prior to use. Other organic solvents were reagent grade, unless otherwise stated, and were purchased from Aldrich and used as received. Chloroform was spectrograde, when used for GPC and UV-vis analysis.

Characterisation

The ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument and results are reported in ppm from tetramethylsilane on the δ scale. The coupling constants were assigned by assuming the spectra obtained to be first order. Infrared measurements were performed on a Bomem-FTIR Michelson series instrument with a resolution of 4 cm^{-1} . The spectra were recorded after two scans. Low-resolution mass spectra were obtained on a DuPont 21-492B spectrometer. The apparent molecular weights of the polymers were determined by gel permeation chromatography using chloroform at ambient temperature at the flow rate of 1.0 mL/min . on a Perkin-Elmer LC-250 GPC. Molecular calculations were based on novel polyacrylate standards containing dihydrophenanthrene-based ketal (masked alcohol) units. Presence of dihydrophenanthrene-based ketal (masked alcohol) units in copolymers were detected by UV-vis spectra on a Varian Cary 3 spectrometer using 1 cm quartz cells. Other UV-vis spectra were obtained by using the same instrument. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. The model compound and polymer samples were analysed using thermal analysis techniques: thermogravimetry (TG) and differential scanning calorimetry (DSC). Weight loss data were obtained from Seiko TG/DTA 220 with a heating rate of $10\text{ }^\circ\text{C/min}$. The system was permanently purged with N_2 (flow rate: 200 mL/min). Ring-opening temperatures were obtained from Seiko DSC 220 with a heating fate of $10\text{ }^\circ\text{C/min}$. The system was purged with N_2 (flow rate: 100 mL/min), both in normal and in oscillation mode. The temperature of both instruments was calibrated using indium and tin.

Dihydrophenanthrene-based 6-membered keto-ketal (II-1a)

Phenanthrenequinone (20.800 g, 0.100 mol), 1,3-propanediol (22.800 g, 0.300 mol), *p*-toluenesulfonic acid (0.800 g) and toluene (240 mL) were placed in a 500 mL round-bottomed flask fitted with a Dean-Stark trap (for removing water produced during the reaction). The reaction mixture was refluxed for 18 hours until only a very small amount of starting material showed on TLC (Hexane: Acetone 9:1 v/v). Solvent (toluene) was evaporated from the reaction mixture by rotary evaporator at 80 °C to afford the crude solid, which was washed with a minimum volume (20 mL) of methanol and dissolved in 35 mL of toluene. Undissolved impurities were separated by suction filtration. The solvent (toluene) from the filtrate was removed again by rotary evaporator at 80 °C, yielding a light green solid. The isolated solid was then dissolved in 20 mL of methylene chloride in a 150 mL beaker and 60 mL of methanol was added to afford pure keto-ketal light green precipitate. The product was suction filtered and washed with 2 x 10 mL of methanol in two portions. After drying in a vacuum oven (100 °C, 20 mm Hg), 20.520 g of pure keto-ketal was finally obtained. Yield (%) 77; m.p. 122 °C; IR (KBr, cm^{-1}) 1708 (C=O); ^1H NMR (400 MHz, CDCl_3) δ 1.55 (md, 1H, $^2J_{\text{geminal}} = 10.76$ Hz, $^3J_{\text{a,a}} = 4.32$ Hz, $^3J_{\text{e,e}} = 1.56$ Hz), 2.25 (tq, 1H, $^2J_{\text{geminal}} = 10.76$ Hz, $^3J_{\text{a,a}} = 10.76$ Hz, $^3J_{\text{e,e}} = 5.40$ Hz), 4.05

(dq, 2H, $^2J_{\text{geminal}} = 11.92$ Hz, $^3J_{\text{a,a}} = 5.32$ Hz, $^3J_{\text{e,e}} = 1.48$ Hz), 4.50 (dt, 2H, $^2J_{\text{geminal}} = 11.92$ Hz, $^3J_{\text{a,a}} = 11.92$ Hz, $^3J_{\text{e,e}} = 2.78$ Hz), 7.37-7.40 (m, 2H), 7.44 (dt, 2H, $^3J_{\text{ortho}} = 8.90$ Hz, $^4J_{\text{meta}} = 1.64$ Hz), 7.62 (dt, 2H, $^3J_{\text{ortho}} = 8.90$ Hz, $^4J_{\text{meta}} = 1.44$ Hz), 7.81 (dq, 1H, $^3J_{\text{ortho}} = 8.90$ Hz, $^4J_{\text{meta}} = 1.12$ Hz), 7.91 (dq, 1H, $^3J_{\text{ortho}} = 8.90$ Hz, $^4J_{\text{meta}} = 1.12$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 29.73, 65.22, 97.61, 123.14, 125.52, 125.82, 127.90, 128.30, 128.60, 128.90, 130.88, 132.75, 134.70, 135.14, 136.89, 196.86; MS (EI, m/e, relative intensity %) 266 (M^+ , 10.2), 222 ($\text{M}^+ - \text{C}_2\text{H}_4\text{O}$, 60.1), 180 ($\text{M}^+ - \text{C}_4\text{H}_6\text{O}_2$, 100), 152 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}_3$, 59.4).

Dihydrophenanthrene-based 7-membered keto-ketal (II-1b)

The same procedure as above was used by mixing phenanthrenequinone (20.800 g, 0.100 mol), 1,4-butanediol (26.401 g, 0.300 mol), *p*-toluenesulfonic acid (0.800 g) in toluene (240 mL). The yield was 22.400 g (80%); m.p. 141 °C; IR (KBr, cm^{-1}) 1710 ($\text{C}=\text{O}$); ^1H NMR (400 MHz, CDCl_3) δ 1.50 (m, 2H), 1.70 (m, 2H), 3.90, 3.98 (m, 4H), 7.30-7.90 (m, 8H aromatic); ^{13}C NMR (100 MHz, CDCl_3) δ 29.73, 65.22, 97.61, 123.14, 125.04, 127.46, 127.82, 128.10, 128.47, 129.80, 130.88, 132.75, 134.24, 135.14, 136.89, 196.86; MS (EI, m/e, relative intensity %) 280 (M^+ , 9.1), 222 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$, 62.4), 180 ($\text{M}^+ - \text{C}_5\text{H}_8\text{O}_2$, 100), 152 ($\text{M}^+ - \text{C}_6\text{H}_8\text{O}_3$, 61.6).

Dihydrophenanthrene-based hydroxyl-ketal (II-2a)

In a 150 mL beaker, keto-ketal II-1a (15.960 g, 0.060 mol) was dissolved in methanol (50 mL). To that solution was added sodium borohydride (2.272 g, 0.060 mol) in small portions. The reaction mixture was stirred at room temperature for 45 min., and then poured into a 200 mL beaker filled with 50 mL of distilled water. The mixture was extracted three times with diethyl ether (3 x 25 mL). The organic layers were dried over magnesium sulfate and filtered. The solvent was evaporated with a rotary evaporator at 60 °C to yield a white solid. The product was dried overnight in a vacuum oven (60 °C, 20 mm Hg) to give 14.630 g of product. Yield (%) 91; m.p. 150 °C; IR (KBr, cm^{-1}) 3489 (O-H); ^1H NMR (400 MHz, CDCl_3) δ 1.71 (m, 1H), 2.10 (m, 1H), 2.35 (s, 1H), 3.85 (m, 1H), 4.05 (m, 2H), 4.20 (m, 1H), 5.18 (s, 1H), 7.30-7.90 (m, 8H aromatic); ^{13}C NMR (100 MHz, CDCl_3) δ 25.43, 60.13, 60.93, 68.21, 97.60, 123.18, 125.18, 127.78, 127.95, 128.21, 128.62, 129.97, 130.95, 133.04, 134.32, 135.25, 136.90; MS (EI, m/e, relative intensity %) 268 (M^+ , 30.1), 210 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$, 20.8), 197 ($\text{M}^+ - \text{C}_4\text{H}_7\text{O}$, 9.2), 181 ($\text{M}^+ - \text{C}_4\text{H}_7\text{O}_2$, 100), 165 ($\text{M}^+ - \text{C}_4\text{H}_7\text{O}_3$, 19.7), 152 ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}_3$, 30.4).

Dihydrophenanthrene-based hydroxyl-ketal (II-2b)

The same procedure as above was used by mixing the keto-ketal II-1b (16.800 g, 0.060 mol) in methanol (50 mL) and sodium borohydride (2.271 g, 0.060 mol) in small portions. The yield was 16.070 g (94.9%); m.p. 119 °C; IR (KBr, cm^{-1}) 3479 (O-H); ^1H NMR (200 MHz, CDCl_3) δ 1.65, 1.82 (m, 4H), 2.34 (d, 1H, $^3J_{\text{H-H}} = 3.38$ Hz), 3.51-3.72 (m, 2H), 3.99 (m, 2H), 4.70 (d, 1H, $^3J_{\text{H-H}} = 3.34$ Hz), 7.30-7.50 (m, 5H, aromatic), 7.70-7.90 (m, 3H, aromatic); ^{13}C NMR (100 MHz, CDCl_3) δ 29.60, 30.41, 63.50, 63.92, 71.86, 97.61, 123.14, 125.04, 127.75, 127.90, 128.10, 128.51, 129.97, 130.89, 132.75, 134.30, 135.20, 136.89; MS (EI, m/e, relative intensity %) 282 (M^+ , 32.0), 210 ($\text{M}^+ - \text{C}_4\text{H}_8\text{O}$, 21.2), 197 ($\text{M}^+ - \text{C}_3\text{H}_9\text{O}$, 10.3), 181 ($\text{M}^+ - \text{C}_3\text{H}_9\text{O}_2$, 100), 165 ($\text{M}^+ - \text{C}_3\text{H}_9\text{O}_3$, 20.2), 152 ($\text{M}^+ - \text{C}_6\text{H}_{10}\text{O}_3$, 31.5).

Methyl ether of dihydrophenanthrene-based ketal (II-3a)

In a 50 mL beaker hydroxyl-ketal II-2a (1.073 g, 0.040 mol) was dissolved in methylene chloride (5 mL) and (1 g/10 mL) NaOH/water. The reaction mixture was stirred vigorously and benzyltriethylammonium chloride (100 mg) was added. To the reaction mixture, a solution of dimethylsulfate (0.760 g, 0.006 mol) was added. The reaction mixture was stirred at room temperature for 30 min. and was monitored by TLC (Hexane: Acetone 9:1 v/v) until no more starting material was left. The mixture was then poured into a 100 mL beaker filled with distilled water (25 mL). The mixture was extracted three times with diethyl ether (3 x 10 mL). The organic layers were dried over magnesium sulfate and filtered. The solvent was removed with a rotary evaporator at 60 °C to yield a brownish-white solid. The product was dried overnight in a vacuum oven (60 °C, 20 mm Hg) to afford 0.914 g of pure product. Yield (%) 81; m.p. 162 °C; ¹H NMR (200 MHz, CDCl₃) δ 1.90, 2.20 (m, 2H), 3.30 (s, 3H), 3.80, 4.00, 4.20 (m, 4H), 4.80 (s, 1H), 7.30-8.00 (m, 8H, aromatic); ¹³C NMR (100 MHz, CDCl₃) δ 30.39, 63.47, 63.86, 64.10, 70.70, 98.12, 123.20, 125.23, 127.80, 127.95, 128.24, 128.64, 129.98, 131.02, 133.60, 134.52, 135.60, 136.90; MS (EI, m/e, relative intensity %) 282 (M⁺, 35.5), 267 (M⁺ - CH₃, 30), 181 (M⁺ - C₅H₉O₂, 100), 152 (M⁺ - C₆H₁₀O₃, 34.4)

Methyl ether of dihydrophenanthrene-based ketal (II-3b)

The same procedure as above was used by mixing hydroxyl-ketal II-2b (1.128 g, 0.004 mol), methylene chloride (5 mL), NaOH/water (1 g/10 mL), benzyltriethylammonium chloride (100 mg) and dimethyl sulfate (0.760 g, 0.006 mol). The yield was 0.923 g (78%); m.p. 104 °C; ^1H NMR (200 MHz, CDCl_3) δ 1.80, 2.00 (m, 4H), 3.20 (s, 3H), 3.60, 3.70, 4.00 (m, 4H), 4.40 (s, 1H), 7.30-7.90 (m, 8H, aromatic); ^{13}C NMR (100 MHz, CDCl_3) δ 29.68, 30.46, 63.50, 63.59, 65.12, 71.32, 97.80, 123.24, 125.12, 127.78, 127.92, 128.00, 128.41, 129.87, 130.88, 132.76, 134.30, 135.28, 136.90; MS (EI, m/e, relative intensity %) 296 (M^+ , 30.2), 281 ($\text{M}^+ - \text{CH}_3$, 29.2), 181 ($\text{M}^+ - \text{C}_6\text{H}_{11}\text{O}_2$, 100), 152 ($\text{M}^+ - \text{C}_7\text{H}_{12}\text{O}_3$, 31.2).

Mesylate of dihydrophenanthrene-based ketal (II-4a)

In a 50 mL beaker, hydroxyl-ketal II-2a (1.610 g, 0.006 mol) was dissolved in freshly distilled pyridine (8 mL). To that solution was added methanesulfonyl chloride (0.920 g, 0.008 mol). The reaction mixture was stirred at room temperature for 30 min. and was monitored by TLC (Hexane: Acetone, 9:1 v/v) until no more starting material was left. The Reaction mixture was poured into a 100 mL beaker filled with distilled water (25 mL). The mixture was extracted three times with diethyl ether (3 x 10 mL). The

organic layers were dried over magnesium sulfate and filtered. The solvent was evaporated with a rotary evaporator at 60 °C to yield a blackish-white solid. The product was dried overnight in a vacuum oven (60 °C, 20 mm Hg) to afford 1.912 g of pure product. Yield (%) 92; m.p. 103 °C; ^1H NMR (200 MHz, CDCl_3) δ 1.80, 2.10 (m, 2H), 2.80 (s, 3H), 3.90, 4.20, 4.40 (m, 4H), 6.20 (s, 1H), 7.30-7.90 (m, 8H, aromatic); ^{13}C NMR (100 MHz, CDCl_3) δ 20.60, 30.10, 63.21, 63.43, 71.20, 97.90, 122.90, 124.87, 127.00, 127.95, 128.21, 128.59, 130.10, 131.22, 133.60, 134.52, 135.60, 136.89; MS (EI, m/e, relative intensity %) 346 (M^+ , 30.2), 331 ($\text{M}^+ - \text{CH}_3$, 25.6), 267 ($\text{M}^+ - \text{SO}_2\text{CH}_3$, 28.5), 181 ($\text{M}^+ - \text{C}_5\text{H}_9\text{O}_4\text{S}$, 100), 152 ($\text{M}^+ - \text{C}_6\text{H}_{10}\text{O}_5\text{S}$, 21.5).

Mesylate of dihydrophenanthrene-based ketal (II-4b)

The same procedure as above was used by mixing hydroxyl-ketal II-2b (1.692 g, 0.006 mol), pyridine (8 mL) and methanesulfonyl chloride (0.921 g, 0.008 mol). The yield was 2.052 g (95%); m.p. 77 °C; ^1H NMR (200 MHz, CDCl_3) δ 1.80, 2.20 (m, 4H), 2.90 (s, 3H), 3.60, 3.70, 4.10 (m, 4H), 6.30 (s, 1H), 7.30-7.90 (m, 8H, aromatic); ^{13}C NMR (100 MHz, CDCl_3) δ 21.22, 29.68, 30.46, 63.50, 63.93, 70.32, 97.80, 123.25, 124.98, 126.78, 127.92, 128.00, 128.52, 129.87, 130.88, 132.76, 134.40, 135.30, 136.89; MS

(EI, m/e, relative intensity %) 360 (M^+ , 38.2), 345 ($M^+ - CH_3$, 28.5), 281 ($M^+ - SO_2CH_3$, 25.5), 181 ($M^+ - C_6H_{11}O_4S$, 100), 152 ($M^+ - C_7H_{12}O_5S$, 23.5).

Acetate derivative of dihydrophenanthrene-based ketal (II-5a)

In a 100 mL beaker, hydroxyl-ketal II-2a (10.720 g, 0.040 mole) was dissolved in freshly distilled pyridine (30 mL). To that solution, was added acetyl chloride in drops (4.710 g, 4.3 mL, 0.060 mol). The reaction mixture was stirred at room temperature for 1 hour and was monitored by TLC (Hexane: Acetone 9:1 v/v) until no more starting material was left. The reaction mixture was then poured into a 150 mL beaker filled with distilled water (50 mL). The mixture was extracted three times with diethyl ether (3 x 25 mL) and the organic layers were washed with distilled water (3 x 25 mL). The organic layers were dried over magnesium sulfate and filtered. The solvent was evaporated with a rotary evaporator at 60 °C to yield a white solid. The product was dried overnight in a vacuum oven (60 °C, 20 mm Hg) to afford 12.152 g of pure product. Yield (%) 98; m.p. 137 °C; IR (KBr, cm^{-1}) 1728 (C=O); 1H NMR (200 MHz, $CDCl_3$) δ 1.55 (m, 1H), 2.15 (m, 1H), 1.91 (s, 3H), 3.78 (m, 1H), 4.15 (m, 2H), 4.35 (m, 1H) 6.75 (s, 1H), 7.25-7.65 (m, 5H, aromatic), 7.85 (m, 3H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.50, 29.06,

62.89, 63.82, 69.55, 98.93, 123.88, 124.27, 127.12, 127.37, 128.19, 129.12, 129.74, 130.75, 132.87, 133.50, 133.65, 134.13, 170.43; MS (EI, m/e, relative intensity %) 310 (M^+ , 45.2), 267 ($M^+ - C_2H_3O$, 37.0), 181 ($M^+ - C_6H_9O_3$, 100), 152 ($M^+ - C_7H_{10}O_4$, 41.3); UV (λ_{max} , nm, $CHCl_3$) 274.

Acetate derivative of dihydrophenanthrene-based ketal (II-5b)

The same procedure as above was used by mixing hydroxyl-ketal II-2b (11.280 g, 0.040 mol), pyridine (30 mL) and acetyl chloride (4.710 g, 4.3 mL, 0.060 mol). The yield was 12.83 g (99%); m.p. 147 °C; IR (KBr, cm^{-1}) 1728 (C=O); 1H NMR (400 MHz, $CDCl_3$) δ 1.62 (m, 2H), 1.79 (m, 2H), 1.91 (s, 3H), 3.35 (m, 1H), 3.60 (m, 1H), 3.85 (m, 1H), 4.08 (m, 1H), 6.10 (s, 1H), 7.25-7.56 (m, 5H, aromatic), 7.85 (m, 3H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.20, 29.00, 29.76, 62.89, 63.83, 71.86, 98.97, 123.88, 124.27, 127.12, 127.37, 128.19, 129.12, 129.74, 130.75, 132.87, 133.50, 133.65, 134.13, 170.43; MS (EI, m/e, relative intensity %) 324 (M^+ , 45.2), 281 ($M^+ - C_2H_3O$, 37.0), 181 ($M^+ - C_7H_{11}O_3$, 100), 152 ($M^+ - C_8H_{11}O_4$, 42.7); UV(λ_{max} , nm, $CHCl_3$) 274.

Acrylate monomer containing dihydrophenanthrene-based ketal (III-1)

In a 150 mL beaker, hydroxyl-ketal II-2b (11.840 g, 0.042 mol) was dissolved in dry THF (25 mL). Triethylamine (13.330 g, 18.4 mL, 0.132 mol) was added in drops and the beaker was placed in an ice-bath to maintain the temperature below 0 °C. To that solution, acryloyl chloride (4.160 g, 5.7 mL, 0.046 mol) was added in drops. The reaction mixture was stirred vigorously below 0 °C for 1 hour and was monitored by TLC (Hexane: Methylene chloride, 9:1 v/v) until no more starting material was left. The reaction mixture was then poured into a 250 mL beaker filled with distilled ice water (100 mL). The mixture was extracted three times with methylene chloride (3 x 25 mL). The organic layers were dried over magnesium sulfate and filtered. The solvent was evaporated with a rotary evaporator at room temperature to yield a greenish-white solid. The product was purified by column chromatography using (Methylene chloride: Hexane, 8:2 v/v). All the elution showing the same one spot on TLC were pooled together and evaporated with a rotary evaporator at room temperature to yield a white solid. The product was dried overnight in a vacuum oven at room temperature under reduced pressure (water pump) to afford 9.170 g of pure product. Yield (%) 65; m.p. 128 °C; IR (KBr, cm^{-1}) 1722 (C=O), 1618 (C=C), 3095 (=C-H); ^1H NMR (400 MHz, CDCl_3) δ 1.63 (m, 2H), 1.79 (m, 2H),

3.38 (bs, 1H) 3.62 (bt, 1H), 3.86 (bd, 1H), 4.10 (bs, 1H), 5.70 (d, 1H, $^3J_{\text{cis H-H}} = 10.04$ Hz), 5.96 (bt, 1H, $^3J_{\text{trans H-H}} = 15.84$ Hz, $^3J_{\text{cis H-H}} = 10.40$ Hz), 6.15 (s, 1H), 6.22 (d, 1H, $^2J_{\text{geminal H-H}} = 3.24$ Hz), 7.30 (dt, 2H $^3J_{\text{ortho H-H}} = 7.45$ Hz, $^4J_{\text{meta H-H}} = 1.12$ Hz), 7.39 (dt, 2H, $^3J_{\text{ortho H-H}} = 7.45$ Hz, $^4J_{\text{meta H-H}} = 1.12$ Hz), 7.46 (dq, 1H, $^3J_{\text{ortho H-H}} = 7.45$ Hz, $^4J_{\text{meta H-H}} = 1.44$ Hz, $^5J_{\text{para H-H}} = 0.88$ Hz), 7.84 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.08, 29.72, 62.93, 63.79, 69.68, 99.01, 123.89, 124.26, 127.13, 127.37, 128.18, 128.34, 129.11, 129.79, 130.80, 131.14, 132.74, 133.52, 133.73, 134.15, 166.93; MS (EI, m/e, relative intensity %) 336 (M^+ , 29.6), 281 ($\text{M}^+ - \text{COCHCH}_2$, 37.0), 264 ($\text{M}^+ - \text{C}_3\text{H}_4\text{O}_2$, 14.6), 181 ($\text{M}^+ - \text{C}_8\text{H}_{11}\text{O}_3$, 100), 165 ($\text{M}^+ - \text{C}_8\text{H}_{11}\text{O}_4$, 27.9), 152 ($\text{M}^+ - \text{C}_9\text{H}_{12}\text{O}_4$, 22.7); UV(λ_{max} , nm, CHCl_3) 274.

UV-vis calibration curve acrylate monomer containing 7-membered Ketal.

(Chloroform, 22 °C, $\lambda_{\text{max}} = 274$ nm; Equation $y = 47.534 x + 0.0172$ $R^2 = 0.9999$).

Concentration (mg/mL)	Absorbance at $\lambda_{\text{max}} = 274$ nm
4.59×10^{-2}	2.2013
3.36×10^{-2}	1.6123
1.83×10^{-2}	0.8802
9.10×10^{-3}	0.4629
1.81×10^{-3}	0.0979

General procedures for thermal aromatization (Ring opening) of 6-membered hydroxyl-ketal and derivatives

Ring-opening of dihydrophenanthrene-based hydroxyl ketal (II-2a)

II-6a

Hydroxyl ketal II-2a (0.500 g) was placed in a Pyrex glass tube. After being sealed under nitrogen, the tube was heated at 200 °C pre-maintained temperature oil bath for 30 minutes. The ring-opened product II-6a was recrystallized from CH₂Cl₂/hexane to give fine white crystals 0.480 g. Yield (%) 96; m.p. 94 °C; IR (KBr, cm⁻¹) 3200-3600 (O-H); ¹H NMR (400 MHz, CDCl₃) δ 2.11 (q, 2H, ³J_{vicinal H-H} = 5.48 Hz), 4.14 (t, 2H, ³J_{vicinal H-H} = 5.56 Hz), 4.28 (t, 2H, ³J_{vicinal H-H} = 5.36 Hz), 7.50-7.60 (m, 4H), 8.00 (dd, 1H, ³J_{ortho H-H} = 8.12 Hz, ⁴J_{meta H-H} = 0.88 Hz), 8.30 (m, 1H), 8.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 29.00, 62.89, 63.92, 121.35, 122.87, 122.93, 126.17, 126.85, 127.01, 127.23, 127.45, 127.95, 128.29, 128.57, 130.05, 135.55, 143.69; MS (EI, m/e, relative intensity %) 268 (M⁺, 32.5), 181 (M⁺ - C₄H₇O₂, 100), 152 (M⁺ - C₃H₆O₃, 20.6);

Ring-opening of methyl ether derivative (II-3a)

II-7a

The same procedure as above was used by taking methyl ether II-3a (0.500 g) and keeping the oil bath temperature at 200 °C. The yield of the product II-7a was 0.490 g (98%); m.p. 75 °C; IR (KBr, cm⁻¹) 3479 (O-H); ¹H NMR (200 MHz, CDCl₃) δ 1.30 (bs, 1H), 2.18 (q, 2H, ³J_{vicinal} H-H = 5.94 Hz), 4.00 (t, 2H, ³J_{vicinal} H-H = 5.94 Hz), 4.10 (s, 3H), 4.40 (t, 2H, ³J_{vicinal} H-H = 5.94 Hz), 7.50-7.60 (m, 4H), 8.20 (m, 2H), 8.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 29.10, 63.47, 63.86, 64.10, 121.33, 122.85, 122.93, 126.14, 126.85, 127.04, 127.25, 127.43, 127.94, 128.30, 128.34, 130.10, 135.56, 143.70; MS (EI, m/e, relative intensity %) 282 (M⁺, 35.6), 181 (M⁺ - C₃H₉O₂, 100), 152 (M⁺ - C₆H₁₀O₃, 21.5);

Ring-opening of mesylate derivative (II-4a)

II-8a

The same procedure as above was used by taking mesylate II-4a (0.500 g) and keeping the oil bath temperature at 110 °C. The yield of the product II-8a was 0.460 g (92%); m.p. 68 °C; IR (KBr, cm^{-1}) 3200-3600 (O-H); ^1H NMR (400 MHz, CDCl_3) δ 1.50 (bs, 1H), 2.10 (q, 2H, $^3J_{\text{vicinal H-H}} = 5.54$ Hz), 2.40 (s, 3H), 3.80 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.54$ Hz), 4.20 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.54$ Hz), 7.60 (m, 4H), 7.80 (m, 1H), 8.10 (m, 1H), 8.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.50, 25.50, 62.30, 74.00, 121.30, 122.80, 122.90, 126.17, 126.85, 127.01, 127.23, 127.45, 127.95, 128.29, 128.57, 130.05, 135.55, 149.69; MS (EI, m/e, relative intensity %) 346 (M^+ , 33.2), 181 ($\text{M}^+ - \text{C}_3\text{H}_9\text{O}_4\text{S}$, 100), 152 ($\text{M}^+ - \text{C}_6\text{H}_{10}\text{O}_5\text{S}$, 20.5);

Ring-opening of acetate derivative (II-5a)

II-9a

The same procedure as above was used by taking acetate II-5a (0.500 g) and keeping the oil bath temperature at 210 °C. The yield of the product II-9a was 0.480 g (96%); m.p. 80 °C; IR (KBr, cm^{-1}) 3458 (O-H), 1755 ($\text{C}=\text{O}$); ^1H NMR (400 MHz, CDCl_3) δ 1.50 (s, 1H), 2.10 (q, 2H, $^3J_{\text{vicinal H-H}} = 5.52$ Hz), 2.54 (s, 3H), 3.80 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.54$ Hz), 4.20 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.54$ Hz), 7.60 (m, 4H), 7.80 (m, 1H), 8.20 (m,

1H), 8.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.00, 29.00, 62.00, 74.10, 121.30, 122.80, 122.90, 126.17, 126.85, 127.01, 127.23, 127.45, 127.95, 128.29, 128.57, 130.05, 135.55, 149.69, 168.80; MS (EI, m/e, relative intensity %) 310 (M^+ , 50.5), 181 (M^+ - $\text{C}_6\text{H}_9\text{O}_3$, 100), 152 (M^+ - $\text{C}_7\text{H}_{10}\text{O}_4$);

General procedures for thermal aromatization (Ring opening) of 7-membered hydroxyl-ketal and derivatives.

Ring-opening of dihydrophenanthrene-based hydroxyl ketal (II-2b)

II-6b

Hydroxyl ketal II-2b (0.500 g) was placed in a Pyrex glass tube. After being sealed under nitrogen, the tube was heated in an oil bath at 160 °C pre-maintained temperature for 30 minutes. The ring-opened product II-6b was recrystallized from CH_2Cl_2 /hexane to give fine white crystals 0.480 g. Yield (%) 96; m.p. 75 °C; IR (KBr, cm^{-1}) 3200-3600 (O-H); ^1H NMR (200 MHz, CDCl_3) δ 1.70 (b, 1H), 2.00 (m, 4H), 3.50 (b, 1H), 3.90 (t, 2H, $^3J_{\text{vicinal H,H}} = 5.70$ Hz), 4.10 (t, 2H, $^3J_{\text{vicinal H,H}} = 5.66$ Hz), 7.50 (m, 4H), 8.00 (dd, 1H, $^3J_{\text{ortho H,H}} = 8.12$ Hz), 8.30 (m, 1H) 8.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.00, 29.60, 62.70, 74.10, 121.30, 122.80, 122.90, 126.10, 126.80, 127.00, 127.20, 127.40, 127.90, 128.20, 128.50, 130.00, 135.50, 143.60; MS (EI, me, relative intensity %) 282 (M^+ , 31.5), 181 (M^+ - $\text{C}_5\text{H}_9\text{O}_2$, 100)

Ring-opening of methyl ether derivative (II-3b)

II-7b

The same procedure as above was used by taking methyl ether II-3b (0.510 g) and keeping the oil bath temperature at 190 °C. The yield of the product II-7b was 0.480 g (96%); m.p. 54 °C; IR (KBr, cm^{-1}) 3478 (O-H); ^1H NMR (200 MHz, CDCl_3) δ 1.32 (s, 1H), 2.11 (q, 2H, $^3J_{\text{vicinal H-H}} = 5.84$ Hz), 2.20 (q, 2H, $^3J_{\text{vicinal H-H}} = 5.84$ Hz), 4.00 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.82$ Hz), 4.10 (s, 3H), 4.41 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.82$ Hz), 7.50-7.70 (m, 4H), 8.20 (m, 2H), 8.61 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.01, 29.60, 62.70, 63.81, 74.10, 121.30, 122.80, 126.10, 126.80, 127.01, 127.21, 127.40, 127.91, 128.21, 128.34, 128.51, 130.30, 135.70, 143.90; MS (EI, m/e, relative intensity %) 296 (M^+ , 31.5), 181 ($\text{M}^+ - \text{C}_6\text{H}_{11}\text{O}_2$, 100), 152 ($\text{M}^+ - \text{C}_7\text{H}_{12}\text{O}_3$, 33.5);

Ring-opening of mesylate derivative (II-4b)

II-8b

The same procedure as above was used by taking mesylate II-4b (0.500 g) and keeping the oil bath temperature at 110 °C. The yield of the product II-8b was 0.451 g (90%); m.p. 52 °C; IR (KBr, cm^{-1}) 3200-3600 (O-H); ^1H NMR (400 MHz, CDCl_3) δ 1.50 (s, 1H), 1.90 (q, 2H, $^3J_{\text{vicinal H-H}} = 5.20$ Hz), 2.10 (q, 2H, $^3J_{\text{vicinal H-H}} = 5.20$ Hz), 2.40 (s, 3H), 3.90 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.30$ Hz), 4.10 (t, 2H, $^3J_{\text{vicinal H-H}} = 5.30$ Hz), 7.48-7.75 (m, 4H), 8.20 (m, 2H), 8.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.50, 27.50, 29.60, 62.60, 74.20, 121.40, 122.90, 126.10, 126.90, 127.20, 127.30, 127.40, 127.90, 128.20, 128.40, 128.50, 130.40, 135.70, 143.90; MS (EI, m/e, relative intensity %) 360 (M^+ , 37.4), 181 ($\text{M}^+ - \text{C}_6\text{H}_{11}\text{O}_4\text{S}$, 100), 152 ($\text{M}^+ - \text{C}_7\text{H}_{12}\text{O}_5\text{S}$, 24.6);

Ring-opening of acetate derivative (II-5b)

II-9b

The same procedure as above was used by taking acetate II-5b (0.510 g) and keeping the oil bath temperature at 200 °C. The yield was 0.461 g (90%); m.p. 67 °C; IR (KBr, cm^{-1}) 3458 (O-H), 1755 (C=O); ^1H NMR (400 MHz, CDCl_3) δ 1.60 (s, 1H), 1.90 (m, 2H), 2.10 (m, 2H), 2.54 (s, 3H), 3.80 (t, 2H, $^3J_{\text{vicinal H-H}} = 6.32$ Hz), 4.20 (t, 2H, $^3J_{\text{vicinal H-H}} = 6.28$ Hz), 7.60-7.70 (m, 4H), 7.85 (m, 1H), 8.25 (m, 1H), 8.70 (m, 2H); ^{13}C NMR

(100 MHz, CDCl_3) δ 20.76, 27.06, 29.65, 62.70, 74.15, 121.35, 122.80, 122.93, 126.17, 126.85, 127.01, 127.23, 127.45, 127.95, 128.29, 128.57, 130.05, 135.55, 143.69, 168.85; MS (EI, m/e, relative intensity %) 324 (M^+ , 46.5), 181 ($\text{M}^+ - \text{C}_7\text{H}_{11}\text{O}_3$, 100), 152 ($\text{M}^+ - \text{C}_8\text{H}_{11}\text{O}_4$, 43.8);

Random copolymerization of acrylate monomer III-1 and MMA

Copolymer IV-1 (feed ratio: 5% monomer III-1)

To a solution of monomer III-1 (0.168 g, 0.500 mmol) in anhydrous THF (5 mL) was added MMA (0.950 g, 9.500 mmol), which had been passed through a short Dehibiter-200 column prior to use to remove the inhibitor, and AIBN (0.008 g, 0.050 mmol). The solution was degassed with nitrogen for 20 minutes and the vessel was sealed. The solution was stirred at 60 °C overnight. The polymer was precipitated out by pouring into a large amount of methanol under vigorous stirring. The solid was purified from the monomers by three successive reprecipitations (re-dissolving the polymer in chloroform and precipitating from methanol). The polymer was dried under vacuum (60 °C, 5 mm

Hg) overnight. The yield was 0.970 g (87%). GPC: $M_w = 6000$, $M_n = 3141$, $M_w/M_n = 1.91$; UV (λ_{max} , nm, $CHCl_3$, 25 °C) 274; IR (KBr, cm^{-1}) 2959 (C-H, aromatic), 2874 (C-H, aliphatic), 1734 (C=O, ester), 1453 (CH_2), 1164 (C-O); 1H NMR (400 MHz, $CDCl_3$) δ 0.86 (bs, 3H), 1.03 (bs, 2H), 1.18 (m, 2H), 1.42 (m, 2H), 1.56 (bs, 1H), 1.82 (bs, 2H), 3.43 (m, 2H), 3.61 (s, 3H), 3.77 (m, 2H), 5.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.45, 18.71, 29.28, 29.84, 44.53, 44.87, 51.82, 52.74, 54.22, 54.42, 69.97, 99.2, 123.87, 124.19, 127.28, 127.99, 128.17, 129.00, 129.77, 130.65, 132.38, 133.56, 133.97, 134.23, 177.81, 178.11.

Copolymer IV-2 (feed ratio: 10% monomer III-1)

The same procedure as above was used by mixing monomer III-1 (0.336 g, 1.000 mmol), anhydrous THF (8 mL), MMA (0.901 g, 9.000 mmol) and AIBN (0.008, 0.050 mmol). The yield was 1.100 g (89%); GPC: $M_w = 8553$, $M_n = 4454$, $M_w/M_n = 1.92$; UV (λ_{max} , nm, $CHCl_3$, 25 °C) 274; IR (KBr, cm^{-1}) 2959 (C-H, aromatic), 2874 (C-H, aliphatic), 1734 (C=O, ester), 1453 (CH_2), 1164 (C-O); 1H NMR (400 MHz, $CDCl_3$) δ 0.86 (bs, 2H), 1.03 (bs, 2H), 1.18 (m, 2H), 1.42 (m, 2H), 1.56 (bs, 1H), 1.82 (bs, 2H), 3.43 (m, 2H), 3.61 (s, 3H), 3.77 (m, 2H), 5.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.45, 18.71, 29.28, 29.84, 44.53, 44.87, 51.82, 52.74, 54.22, 54.42, 69.97, 99.2, 123.87, 124.19, 127.28, 127.99, 128.17, 129.00, 129.77, 130.65, 132.38, 133.56, 133.97, 134.23, 177.81, 178.11.

Copolymer IV-3 (feed ratio: 15% monomer III-1)

The same procedure as above was used by mixing monomer III-1 (0.504 g, 1.500 mmol), anhydrous THF (11 mL), MMA (0.851 g, 8.500 mmol) and AIBN (0.008, 0.050 mmol). The yield was 1.190 g (88%); GPC: $M_w = 7276$, $M_n = 3829$, $M_w/M_n = 1.90$; UV (λ_{max} , nm, $CHCl_3$, 25 °C) 274; IR (KBr, cm^{-1}) 2959 (C-H, aromatic), 2874 (C-H, aliphatic), 1734 (C=O, ester), 1453 (CH_2), 1164 (C-O); 1H NMR (400 MHz, $CDCl_3$) δ 0.86 (bs, 2H), 1.03 (bs, 2H), 1.18 (m, 2H), 1.42 (m, 2H), 1.56 (bs, 1H), 1.82 (bs, 2H), 3.43 (m, 2H), 3.61 (s, 3H), 3.77 (m, 2H), 5.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.45, 18.71, 29.28, 29.84, 44.53, 44.87, 51.82, 52.7, 54.22, 54.42, 69.97, 99.20, 123.87, 124.19, 127.28, 127.99, 128.17, 129.00, 129.77, 130.65, 132.38, 133.56, 133.97, 134.23, 177.81, 178.11.

Random copolymerization of MMA and 2-IEMA

Copolymer IV-4 (feed ratio: 10% 2-IEMA)

To a solution of 2-IEMA (0.122 g, 1.000 mmol) in anhydrous THF (8 mL) was added MMA (0.901 g, 9.000 mmol) and AIBN (0.008, 0.050 mmol). Both MMA and 2-

IEMA were passed through a short De-hibiter-200 column prior to use to remove the inhibitor. The solution was degassed with nitrogen for 20 minutes and the vessel was sealed. The solution was stirred at 60 °C overnight. The polymer was precipitated out by pouring into a large amount of methanol with vigorous stirring. The gummy product was purified from the unreacted monomers by three successive reprecipitations from methanol. The polymer was placed in a dessiccator under reduced pressure (water pump) in the presence of phosphorus pentoxide and was continuously purged with nitrogen. The pump was then turned off and the product was kept in for overnight. The yield was 0.950 g (90%); IR (NaCl, cm^{-1}) 1731 (C=O, ester), 2274 (NCO), 1148 (C-O); ^1H NMR (400 MHz, CDCl_3) δ 1.26 (s, 3H), 1.62 (s, 3H), 1.80 (b, 2H), 2.10 (b, 2H), 4.00 (b, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.64, 18.87, 35.99, 44.60, 44.94, 51.77, 54.16, 54.41, 61.83, 168.72, 176.96, 177.79.

Catalysis

The catalyst, namely silica gel, molecular sieves, dibutyltin dilurate, 1,4-diaza[2,2,2]bicyclooctane, aluminium chloride and chromium(II) acetylacetonate, as mixed separately in 5% wt. Ratio with model compound acetate derivative of dihydrophenanthrene-based ketal (II-5a) and (II-5b). The mixtures were ground by mortar and pestle. The DSC and oscillating DSC were then run with the resulting powder.

Sample preparation for kinetic study of model compound (II-5b) in solution

A stock solution was prepared by dissolving 1.508 g model compound acetate derivative of dihydrophenanthrene-based 7-membered ketal (II-5b) in 50 mL DMAc. 0.5 mL of the stock solution was then introduced in screw cap vials. The vials were then placed in pre-maintained oil baths of constant temperature 100 °C, 120 °C, 140 °C, 160 °C for different intervals of time. 0.1 mL of the reaction mixtures were diluted 2000 times by using spectrograde chloroform. Absorbance was measured from the diluted sample at the λ_{max} (301 nm, 25 °C).

Film preparation for curing experiment

Film Set-I

Films for curing experiments were prepared by blending copolymer (IV-1) and Desmodur N-3300 (diisocyanate prepolymer 21.5% wt. NCO) in a 1:1 ratio. 0.100 g of Desmodur N-3000 was dissolved in chloroform (10 mL) and (0.1 mL, 0.001 g, 2.05×10^{-2} mmol) of this solution was mixed with (0.100 g, 2.05×10^{-2} mmol) of copolymer (IV-1). The content of the mixture was transferred on to a number of glass plates. The glass plates were covered with glass jars constantly purge with nitrogen and kept overnight for drying at room temperature. The films were again dried at 80 °C for 24 hours in the vacuum oven under reduced pressure (water pump). One of the films was used for IR analysis before curing. IR (NaCl, cm^{-1}) 2273 (NCO), 1732 (C=O). After heating at 100 °C, 120 °C, 140 °C and 160 °C in a pre-maintained oven for 4 hours, the films were peeled off the glass plates for characterisation. IR (NaCl, cm^{-1}) 1735 (C=O, ester), 1692 (C=O, urethane).

Film set II:

Films for curing experiments were prepared by blending copolymer (IV-1) and copolymer (IV-4) in a 1:1 ratio. 0.100 g of copolymer (IV-4) was dissolved in 50 mL of chloroform and then (0.480 mg, 0.24 mL, 2.05×10^{-2} mmol) of this solution was mixed with (0.100 g, 2.05×10^{-2} mmol) of copolymer (IV-1). The contents of the mixture was transferred on to a number of glass plates and covered with glass jars. The plates were dried overnight at room temperature with a continuous purging of nitrogen. The films were dried again at 80 °C for 24 hours in the vacuum oven under reduced pressure (water pump). One of the films was used for IR analysis before curing. IR (NaCl, cm^{-1}) 2273 (NCO), 1732 (C=O, ester). After heating at 120 °C, 140 °C and 160 °C in a pre-maintained oven for 4 hours, the films were peeled off the glass plates for characterisation. IR (NaCl, cm^{-1}) 3445 (OH), 1732 (C=O, ester), 1632 (C=O, urethane).

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Appendix A. IR spectra for phenanthrenequinone(top) keto-ketal II-1a (below).

Appendix B. ^1H NMR spectrum (400 MHz, CDCl_3) and assignments of keto-ketal II-1a.

Appendix C. ^{13}C NMR spectrum (100 MHz, CDCl_3) and assignments of keto-ketal II-1a.

Appendix D. ^1H NMR spectrum (400 MHz, CDCl_3) and assignments of keto-ketal II-1b.

Appendix E. ^{13}C NMR spectrum (100 MHz, CDCl_3) and assignments of keto-ketal II-1b.

Appendix F. ^1H NMR spectrum (200 MHz, CDCl_3) and assignments of acetate derivative II-5a.

Appendix G. ^{13}C NMR spectrum (100 MHz, CDCl_3) and assignments of acetate derivative II-5a.