**Resorcinol**

Chemistry, Technology and Applications

Raj B. Durairaj

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## Chemistry, Technology and Applications

With 740 Figures

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*This book is dedicated to my father, Sri. R. Bojayan (deceased), and mother, Mrs. B. Chinthamani, for their inspirational wish to see their son succeed in life, and also Lord Sri. Venkateswara of Pittsburgh for his blessings, which gave me the strength, motivation and good excellent health for the successful completion of this book.*

# Preface

In my view, resorcinol is a "wonder chemical" and the chemistry associated with resorcinol is fascinating, challenging and rewarding. Ever since this chemical was synthesized about 150 years ago, the tremendous efforts made on the investigation of resorcinol chemistry produced unique and novel products for various applications. I was quite fortunate to have the opportunity to work on resorcinol chemistry in 1986. During the past 18 years of my R&D experience with resorcinol chemistry, I have admired and been fascinated with this chemistry. Because of this, I had been thinking of writing a true chemistry book on resorcinol so that the scientific community around the world could learn about the uniqueness of this chemical. For a very long time I hesitated to write this book mainly because I doubted whether I could do it.

In April 2003, one of my friends strongly suggested and convinced me that I could write this resorcinol chemistry book. Since then, I have taken this work as a special project for myself. The complete book manuscript planning, formatting and writing was done during the evening and nighttime hours at home, spending on average about six to eight hours per day. I never believed myself that I could finish this monumental task in less than 15 months time, particularly when this was done after my regular office hours.

Resorcinol chemical has a unique molecular structure. It provides the opportunity for chemists, scientists and technologists to explore and develop advanced technologies in the fields of organic, polymer, agricultural and pharmaceutical chemistries with this chemical. In the modern scientific world, a breakthrough technology does not come very often. But with resorcinol chemistry, novel technologies have been developed and reported. Some of the notable technologies developed using the resorcinol chemical are RFL adhesives, Lexan SLX, Zylon fibers, PEN (cyanoarylene ether polymer), UV absorbers, RDP Flame retardant, Penacolite resins (for radial tires), Intal (asthma drug), Osten (osteoporosis), Mikado (herbicide) and Goal (herbicide).

In the scientific community, though remarkable progress has been made in the past with the resorcinol chemistry, a lot of potential still exists for the exploration and development of advanced chemistries and technologies with this chemistry. This reminds me of a quote from the great Tamil Poetess

Avvaiyar who lived thousands of years ago in India: "*What we have learned is like a handful of earth. What we have yet to learn is like the whole world.*" Therefore, by acquiring knowledge in resorcinol chemistry, scientists could expand their skills and explore further in their advanced technologies for humankind. With this in mind, my intention in this book is to outline the advantages of resorcinol chemistry and technology in various applications. The unique feature in this book is that each chapter includes a brief critical review on the subject topic.

Chapter 1 outlines the general structure and physical properties of resorcinol. Chapter 2 gives an account of the current resorcinol manufacturing technologies and also suggests a need for an alternate economical process for the production of resorcinol. In Chap. 3, a general overview of various resorcinolic derivatives is presented. Special compounds based on resorcinol chemical and their industrial applications are briefly detailed in Chap. 4. The RFL technology was developed 50 years ago. Still this chemistry and technology dominates in the adhesion development of various synthetic fibers to rubber compounds. A detailed outline of the chemistry and mechanisms of fibers to rubbers is presented in Chap. 5. For the first time, based on the experimental conditions, a mechanism has been proposed for the bonding of polyester to rubber compound. Resorcinolic resins play a vital role in the bonding of steel tire cords to rubber compounds, which results in the production of high-performance steel-belted radial tires. A bonding mechanism explaining the advantages of resorcinolic resins in the steel cords adhesion improvements is presented in Chap. 6.

Due to meta-substitution, resorcinol provides unexpected and also outstanding properties to polymers synthesized using this chemical. For example, the weatherable thermoplastic polyestercarbonate material developed and sold under the trade names Sollx and Lexan SLX by the General Electric Company showed an outstanding performance of retaining its gloss and color after exposure to sunlight for 10 to 15 years. Similarly, a highly crystalline super-thermoplastic poly (cyanoarylene ether) material was synthesized from resorcinol and sold under the trade name PEN. A resorcinol derivative, namely 4,6-diaminoresorcinol, was used in the production of world's strongest fiber Zylon. Various polymeric materials produced from resorcinol chemistry and their applications are presented in Chap. 7.

A very detailed chemistry and an overview of various resorcinol based UV-absorber compounds and their industrial applications are discussed in Chap. 8. The advantages of resorcinol-derived phosphate ester compounds as flame retardants in the advanced thermoplastic polymers such as the PC, PPO, PC/ABS and PPO/HIPS are also outlined in Chap. 8. In pharmaceutical applications, resorcinol chemistry offers numerous possibilities for developing drug compounds to treat and cure various human illnesses and diseases. In Chap. 9, current activities on resorcinol-based drug chemistries and their developments are discussed. For photoresist applications, resorcinol-

based sensitizer compounds offer several advantages and are discussed in Chap. 10.

Throughout the book, wherever possible, procedures for the preparation of compounds and derivatives from resorcinol have been provided. I would like to point out that this book contains information on the chemistry pertaining only to the reactions of resorcinol at the 2, 4 and 6 positions and the two hydroxyl groups. I have written this book with the hope that it may provide enough and suitable information to scientists and professional communities to obtain more knowledge and generate new ideas about this chemistry. I strongly believe that my book will be of value to chemists, researchers, students, professors and other scientific people working in the universities, colleges, industrial and scientific R&D labs around the world.

In the preparation of this manuscript, I made every effort to avoid any mistakes. But, for some reason, if there are any errors or incorrect citations in this book, I accept sole responsibility and personally apologize.

*Raj B. Durairaj, Ph.D.*

**Acknowledgement** The first and most important person I have to thank and express my gratitude is my wife Latha Durairaj. Her patience, understanding, support and encouragement at all stages of preparation of this manuscript in the evening and nighttime hours at home for 15 months were invaluable. Without my wife's support, I could not have achieved my success in this personal book project. I also have to express my deepest thanks to my children, Mohanraj (son) and Umadevi (daughter) for their enthusiastic support, tolerance and love in spite of my preoccupation with the manuscript preparation at home. It is also equally important to acknowledge and thank my friend Dr. G. Rathinakumar and his family members for their extraordinary help giving me the peace of mind necessary for the planning and completion of this book.

My special thanks to Dr. Lalit Chordia, CEO and president, Thar Technologies, who was instrumental in first convincing me that I could write this chemistry book. I am very deeply indebted and grateful to my supervisor Mr. Thomas K. Volek, vice president of Technology, for his outstanding support and for reviewing the complete manuscript and providing constructive and positive comments. I appreciate and acknowledge the help of Ms. Nancy Manion and Prof. C.T. Vijayakumar, Ph.D for their partial review of this manuscript.

It is always nice to recognize people who are instrumental and responsible for a person's success. In this respect, I would like to thank Prof. Frank D. Blum (University of Missouri-Rolla), Prof. M.T. Shaw (University of Connecticut), Prof. G. Ramamurthy (Retd), and Prof. T.S. Venkatraman (Drexel University) for their motivational advice, help and guidance at different stages in my life.

My special and sincere thanks to Mrs. Dhanalakshmi Rathinakumar, who reviewed the entire manuscript for spelling, typos and grammar during her

vacation in Pittsburgh, USA. Also, I would like to acknowledge the moral support and encouragement received from my family members and friends in USA and India during the preparation of this manuscript.

Finally, it is my obligation and duty to sincerely thank all of the Research and Development, and Analytical Department scientists and staff at Indspec Chemical Corporation's Harmarville R&D Center for their appreciation, kindness and wonderful support of my "dream come true" endeavor of publishing this resorcinol chemistry book for the scientific community around the world.

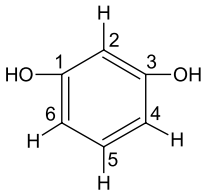
# Contents

# 1 Resorcinol Structure and Physical Properties

## 1.1 Introduction

Resorcinol has been widely known as a versatile chemical compound utilized extensively in the development of advanced chemistries and technologies to benefit humans and other living things. Resorcinol is one of the most remarkable chemicals known in organic chemistry, helping scientists, technologists and researchers around the world to research and develop modern technologies in the diversified fields of chemistry. Due to its unique structure, resorcinol is providing fascinating chemistries and technologies that not many chemicals known in organic chemistry can do. A tremendous amount of exciting and most rewarding chemistries have been developed using resorcinol over the past 125 to 150 years and this trend will be expected to continue in the future.

Resorcinol is a white crystalline dihydric phenol having a faint, characteristic aromatic odor, and with a sweetish bitter taste. This compound is also known as resorcin, meta-dihydroxybenzene, 1, 3-dihdroxybenzene, 1,3-benzenediol and 3-hydroxyphenol. Structurally, the chemical resorcinol can be represented as follows (Figure 1.1).




Emperical Formula : $C_6H_6O_2$
Molecular Weight : 110. 11
CAS Registry Number : 108 - 46 - 3

**Figure 1.1.**

As can be seen, the resorcinol molecule has two hydroxyl groups in the aromatic ring structure, and they are located at their meta-positions with respect to each hydroxyl group. The high reactivity of resorcinol is primarily associated with the location of these two hydroxyl groups in the benzene ring.

As far as the reactivity of resorcinol is concerned, the hydrogen atoms adjacent to the hydroxyl groups, namely at carbon atoms 2,4 and 6, are particularly reactive. The hydrogen atom located at the 5-position of the resorcinol molecule is basically non-reactive, and therefore does not take part in any chemical reactions under normal reaction conditions. Also, the carbon atoms present at the 4 and 6 positions may be designated as "beta or $\beta$", the carbon atom at the 2-position may be designated as "gamma or $\gamma$", and the 5-position carbon atom as "alpha or $\alpha$".

## 1.2 Crystalline Structure and Polymorphism

Resorcinol exists in two crystalline forms, the $\alpha$-form and the $\beta$-form, as evidenced from X-ray diffraction measurements [1–3]. $\alpha$-Resorcinol can be obtained through recrystallization from alcohol or benzene or spontaneous transformation from $\beta$-resorcinol below 71 °C. The $\alpha$-form ordinarily obtained by recrystallization is stable up to about 71 °C under normal pressure conditions. This $\alpha$-resorcinol is converted to the $\beta$-form at about 74 °C, and $\beta$-resorcinol is stable up to the melting point.

$\beta$-Resorcinol could be obtained through recrystallization of the melt, through sublimation or by heating above the transformation point. The heat of transition from $\alpha$- to $\beta$-resorcinol was determined to be $(220 \pm 5)$ cal/mol [2].

The melting point for $\alpha$-resorcinol is 108 °C, and for $\beta$-resorcinol is 110.5 °C. Resorcinol in the $\beta$-form is somewhat more dense (density $= 1.327$) than the $\alpha$-form (density $= 1.28$), which suggests hydrogen bonding between oriented molecules in the crystal lattice [4]. Both $\alpha$- and $\beta$-resorcinol crystallize to produce orthorhombic hemimorphic crystals.

Infrared and Raman spectroscopic studies have been carried out on $\alpha$-resorcinol crystals at high pressure, and also at low temperature conditions [5,6]. The $\alpha$-resorcinol crystals behaved like hydrogen bonded phenolic polymer, exhibiting pyroelectric and piezoelectric properties [2,3,5]. The equilibrium $\alpha\beta$ transition temperature, $T_{\alpha\beta}$, between the $\alpha$-crystalline phase and $\beta$-crystalline phase has been determined [7]. From this study, it was concluded that the $\alpha\beta$ transition would be induced by drastic breakdown of the hydrogen bonds accompanied by redistribution of protons between the covalent structure and ionic structure associated with the transition.

## 1.3 Tautomeric Form of Resorcinol

Resorcinol can exist in two tautomeric forms, namely a "keto" and an "enol" form (Figure 1.2).

Organic compounds exhibiting the "keto" and "enol" structure can show reactions characteristics of these two structures. Resorcinol shows some of the

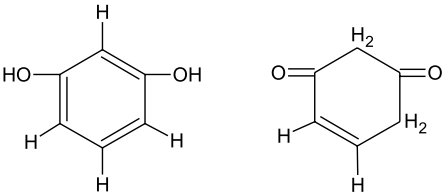



**Figure 1.2.**

reactions of the ketonic form, but the equilibrium seems to be more in favor of the completely enolic form [8].

## 1.4 Physical Properties of Resorcinol

### 1.4.1 Vapor Pressure Data

Resorcinol melts at 108.8 °C and tends to volatilize. This compound has the tendency to sublime at its melting point. Vapor pressure data obtained for resorcinol are presented in Table 1.1 [4, 9, 10].

**Table 1.1.** Vapor pressure data for resorcinol

| Vapor pressure (mm Hg) | Temperature (°C) |
|---|---|
| 1 | 108.4 |
| 3 | 130 |
| 5 | 138 |
| 8.5 | 150 |
| 10 | 152.3 |
| 20 | 168 |
| 23.5 | 170 |
| 40 | 185.3 |
| 53 | 190 |
| 60 | 195.8 |
| 100 | 209.8 |
| 200 | 230.8 |
| 400 | 253.4 |
| 760 | 276.5 |

Data from [4, 9, 10]

This data can be used to separate resorcinol from a mixture of organic compounds, and also to purify resorcinol.

### 1.4.2
### Melt Viscosity Data

Molten resorcinol viscosities measured at elevated temperatures are shown in Figure 1.3 [11].

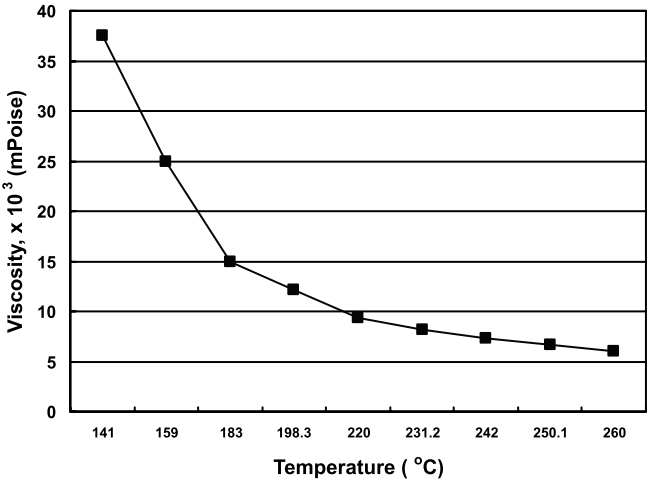



**Figure 1.3.** Viscosity of resorcinol as a function of temperature

### 1.4.3
### Solubility of Resorcinol in Solvents

Resorcinol is highly soluble in water. The density of water solutions of resorcinol appears to increase approximately proportionally to the resorcinol concentration [12]. The solubility of resorcinol in water at various temperatures is plotted and shown in Figure 1.4 [13].

Resorcinol solubility in solvents may vary widely due to the presence of $\alpha$- and $\beta$-phases [12]. Solubility data of resorcinol in different organic solvents is presented in Table 1.2 [4, 13–15].

### 1.4.4
### Weight Loss of Resorcinol

The percent weight loss temperature of resorcinol determined from thermogravimetric analysis (TGA) is shown in Table 1.3 [4, 8].

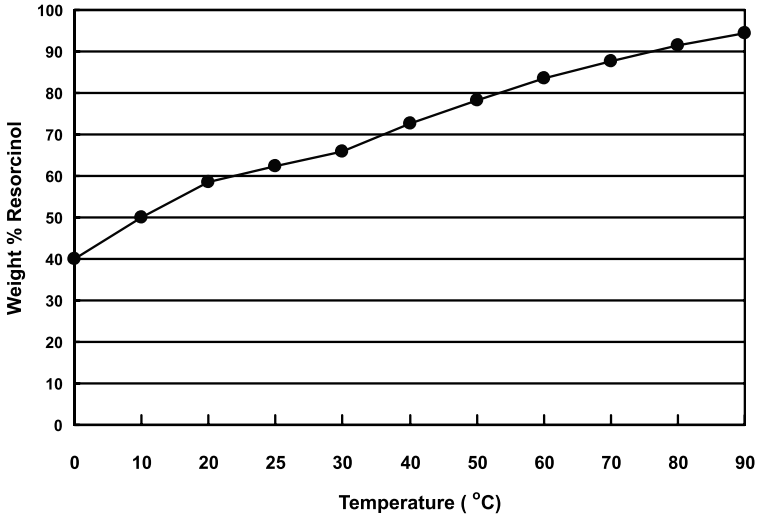



**Figure 1.4.** Solubility of resorcinol in water at various temperatures

**Table 1.2.** Solubility of resorcinol in various solvents

| Solvent | Solubility (Weight percent) at 20 °C | 60 °C |
|---|---|---|
| Water | 58.4 | 83.5 |
| Ethanol | 61 | 73.2 |
| Acetone | 66.9 | 75.1 |
| Benzene | 2.2 | 14.1 |
| Chloroform | NA | 1.2 |
| Carbon tetrachloride | NA | 0.3 |
| Nitrobenzene | 6 | 6.8 |

Resorcinol is also soluble in liquid ammonia, liquid sulfur dioxide, liquid hydrogen sulfide and pyridine
Data from [4, 13–15]

**Table 1.3.** Resorcinol volatility determination by TGA methods

| Temperature (°C) | Weight loss (%) |
|---|---|
| 50 | $< 0$ |
| 100 | $< 0.1$ |
| 150 | 5 |
| 200 | 55 |
| 250 | 100 |

Heating rate at 20 °C/min under nitrogen
Data from [4, 9]

### 1.4.5
### Spectral Data of Resorcinol

$^{13}$C-NMR spectrum and the chemical shift data obtained from the $^{1}$H and $^{13}$C-NMR spectra are shown in Figure 1.5 and Table 1.4 [16].

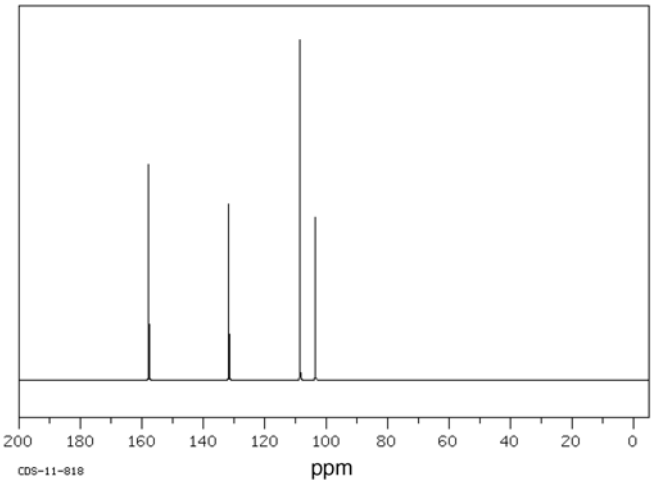
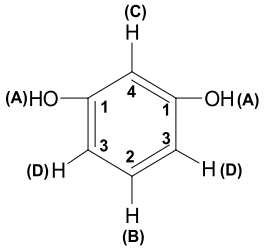



**Figure 1.5.** $^{13}$C-NMR spectrum of resorcinol recorded in $D_2O$ [16]

**Table 1.4.** $^{1}$H and $^{13}$C NMR chemical shift data for resorcinol




$^{1}$NMR (1) $^{13}$C NMR (2)

| Assign | Shift (ppm) | Assign | Shift (ppm) |
|---|---|---|---|
| A | 9.15 | 1 | 157.73 |
| B | 6.929 | 2 | 131.65 |
| C | 6.22 | 3 | 108.52 |
| D | 6.21 | 4 | 103.55 |

(1) 400 MHz in DMSO-$D_6$
(2) 25.16 MHz in $D_2O$
Data from [16]

## 1.5 General Properties of Resorcinol

Resorcinol is triboluminescent, and therefore its crystal can emit light when struck or ground together [4, 17]. The needle-like crystals of resorcinol can become pink on exposure to light and air, or by contact with iron. Resorcinol is hygroscopic, and also has the tendency to pick up moisture when exposed to humid atmosphere. The presence of moisture in resorcinol can reduce the

**Table 1.5.** General physical properties of resorcinol

| Property | Value |
|---|---|
| Freezing point (°C) | 110 |
| Melting point (°C) | 108.8 |
| Boiling point (°C, at 760 mm Hg) | 281.4 |
| Density (g/cm$^3$) | |
| Solid at 20 °C | 1.292 |
| Molten at 150 °C | 1.151 |
| $\alpha$-phase at 20 °C | 1.278 ** |
| $\beta$-phase at 20 °C | 1.327 ** |
| Flash point (°C) | |
| Tag open cup | 168 |
| Tag closed cup | 127 |
| Specific gravity (15 °C/4 °C) | 1.272 |
| Dipole moment (benzene) | 207 D |
| Auto ignition temperature (°C) | 608 |
| Deflagration index (Kst, Bar. m/s) | 134 |
| Heat capacity at 298 °K (J/mol) | 131 |
| Heat of combustion (cal/g) | 6200 |
| Heat of crystallization (kcal/mol) | 5.09 |
| pH (10% aqueous) | 4.5 |
| Dissociation constants (water) | |
| Ionization constant (25 °C) | $K_1 = 1.55 \times 10^{-10}$ |
| Activity constants (30 °C) | $K_1 = 7.11 \times 10^{-10}$ |
| | $K_2 = 4.78 \times 10^{-12}$ |
| Heat of sublimation (kcal/mol) | |
| Vapor temperature = 56.5 °C | 22.8 |
| Vapor temperature = 10 – 50 °C | 21.7 |
| Distribution between solvents at 20 °C | |
| K [benzene/water] | 0.0073 |
| K [dichloroethane/water] | 0.0318 |
| K [ether/water] | 4.67 |
| K [ether/dichloroethane] | 146 |

** Data from [1–3]
Data from [4, 9]