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THE HONG KONG
POLYTECHNIC UNIVERSITY

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A thesis submitted in partial satisfaction of the
requirements for the degree of

MASTER OF PHILOSOPHY

Metal-catalyzed Functionalization of Alkynes and
Poly(2,6-dimethyl-1,4-phenylene oxide)

by

Fong Wai Man

Supervisor: Dr. P. Li

31-5-2000



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Abstract of Thesis

Metal-catalyzed Functionalization of Alkynes and Poly(2,6-dimethyl-1,4-phenylene oxide)

Submitted by

Fong Wai Man

for the degree of Master of Philosophy in Chemistry,

at The Hong Kong Polytechnic University

May 2000

Supervisor: Dr. P. Li

The development of new synthetic methods for modification of existing organic compounds and polymers is of scientific and industrial interest. This thesis consists of two parts: 1) A new facile method to selectively oxidize alkynes to the corresponding acetylenic ketones, 2) Chemical modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) to the corresponding PPO with acetoxy pendant group, respectively.

In the first part of thesis, a facile catalytic system using inexpensive metal ions to selectively oxidize alkynes to the corresponding acetylenic ketones under mild conditions will be described. 4-octyne, a model substrate, has been oxidized to the 4-octyn-3-one by using $\text{CuCl}_2/t\text{-BuOOH/O}_2$ in the presence of *t*-butyl

alcohol. Optimal reaction conditions including the variations of metal catalysts, catalyst and oxidant concentrations as well as addition methods have been determined systemically. Moreover, the versatility of this catalytic system on symmetrical, unsymmetrical, terminal and functionalized alkynes has also been studied.

In the second part of the thesis, chemical modification of PPO to the corresponding PPO with acetoxy pendant group by cobalt(III) acetate in a mixture of chloroform and acetic acid under nitrogen was investigated. Reaction variables such as temperature, stirring method, ratio of solvent and cobalt(III) concentration have been examined. Reaction kinetic was also investigated. Chemical structures of the modified PPO were characterized by FTIR, ¹H-NMR, and their physical properties were studied by intrinsic viscosity, GPC and DSC. Finally, the reaction mechanism was proposed which involved an electron transfer reaction and cobalt-induced degradation of PPO.

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List of Abbreviations

<i>Symbol</i>	<i>Description</i>
conc.	concentration
DSC	differential scanning calorimetry
DME	1, 2-dimethoxyethane
FTIR	Fourier transform infrared
GC	gas chromatography
GPC	gel permeation chromatography
GCMS	gas chromatography mass spectroscopy
HOAc	acetic acid
$[\eta]$	intrinsic viscosity
η_{sp}	specific viscosity
NMR	nuclear magnetic resonance
\bar{M}_n	number average molecular weight
\bar{M}_w	weight average molecular weight
PEG-400	poly(ethylene glycol) - 400
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)
PTC	phase transfer catalyst
<i>t</i> -BuOH	<i>tert</i> -butyl alcohol
<i>t</i> -BuOOH	<i>tert</i> -butyl hydroperoxide
TFA	trifluoroacetic acid
T _g	glass transition temperature

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Chapter 1

General Introduction

1.1 Introduction

The controlled partial oxidation of hydrocarbons is the single most important technology for the conversion of oil- and natural gas-based feedstocks to industrial organic chemicals. Traditionally, the production of many fine chemicals has involved oxidations with stoichiometric quantities or large amounts of toxic metal compounds. However, the pressure of increasingly stringent environmental regulation is stimulating the development of catalytic oxidation in the manufacture of fine chemicals. In this thesis, novel synthetic methods for the selective oxidation of organic substrates and polymer will be discussed.

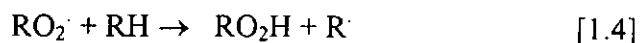
1.2 Liquid phase autoxidation

Autoxidation is a reaction of organic compound with oxygen that proceeds via a free radical chain mechanism⁵⁷. The basic autoxidation scheme contains three processes as follows:

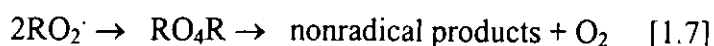
Initiation



Propagation



Termination



Alkylperoxy radicals ($\text{ROO}\cdot$) play a vital role in both propagation and termination processes. Alkylperoxides (RO_2H) are usually the primary products that may be isolated in high yields in some cases. Under an oxygen pressure (100 torr or higher), chain termination proceeds exclusively via the mutual destruction of two alkylperoxy radicals [1.7].

Chain initiation

Chain initiation, accomplished by the addition of initiators such as aliphatic azo compounds or various peroxides (Table 1.1), yields free radicals on the thermal decomposition. In practice, initiators should have substantial rates of decomposition under temperature ranging between 50°C and 150°C .

Chain propagation

The reaction of alkyl radical ($\text{R}\cdot$) and dioxygen is extremely rapid in most diffusion-controlled cases. The rate-determining in autoxidation is the hydrogen transfer from substrate to the alkylperoxy radical [1.4].

The relative reactivities of $\text{RO}\cdot$ and $\text{RO}_2\cdot$ in hydrogen abstraction are shown in Table 1.2. The data indicate that $\text{RO}_2\cdot$ reactivity in hydrogen abstraction is much higher than that of $\text{RO}\cdot$. In addition to its high reactivity, relatively stable and persistent alkylperoxy radicals are very selective and preferentially abstract only the most weakly bound hydrogen.

Table 1.1 Common initiators for autoxidation^a

Initiator name	Structure	Activation energy (kcal mol ⁻¹)	Temp. (°C) for 1 hr half-life
Hydrogen peroxide	HO-OH	48	-
<i>t</i> -Butyl hydroperoxide	<i>t</i> -BuO-OH	42	-
<i>di-t</i> -Butyl peroxide	<i>t</i> -BuO-O- <i>t</i> -Bu	37	150
<i>t</i> -Butyl perbenzoate	<i>t</i> -BuO-OC(O)Ph	34	125
Benzoyl peroxide	PhC(O)O-O(O)CPh	30	95
Acetyl peroxide	CH ₃ COO-OOCCH ₃	30-32	85
Azoisobutylnitrile	(CH ₃) ₂ C(CN)N=N(CN)C(CH ₃) ₂	30	85
<i>t</i> -Butyl hyponitrile	<i>t</i> -BuO-N=N-O- <i>t</i> -Bu	28	60
<i>t</i> -Butyl peroxalate	<i>t</i> -BuO-O ₂ CCO ₂ -O- <i>t</i> -Bu	25.5	40

a. Data taken from [Sheldon and Kochi, 1981]

Table 1.2 Relative reactivity of RO[•] and RO₂[•] in H-atom transfer at 100 °C

Type of C-H bond	RO [•]	RO ₂ [•]
Primary	1.0	1.0
Secondary	10	50
Tertiary	50	1000
Allylic	30	3000

Note: Data taken from [Bamford and Tipper, 1980]

The reactivities of peroxy radicals are strongly dependent on their structure, steric and polar effects. In general, the ability of hydrogen abstraction of primary and secondary peroxy radicals are about three to five times more than the tertiary peroxy radicals. Moreover, peroxy radicals with a strong electron-withdrawing group increase the capacity of α substitution. Acylperoxy radicals, which possess a strong electron-withdrawing carbonyl group, are considerably more reactive than alkylperoxy radicals. For example, the benzoylperoxy radical is 4×10^4 times more reactive than the *tert*-butylperoxy radical toward benzaldehydes.

Chain termination

The chain termination depends on the oxygen concentration. At low oxygen concentration, chain is terminated by reacting with $R\cdot$ only [1.5]. However, at high oxygen concentration, chain is terminated by the reaction of $RO_2\cdot$ [1.6]. In general, it is necessary to take all three termination steps into account.

The chain termination is also affected by the steric effect. The termination rate constants increase following the series tertiary peroxy < secondary peroxy < primary peroxy.

1.3 Metal-catalyzed oxidation

The liquid phase metal-catalyzed oxidation of organic compounds falls into three categories: (1) metal-catalyzed autoxidation; (2) activation of molecular oxygen by metal complexes; (3) direct homolytic oxidation by metal complexes.

1.3.1 Metal-catalyzed autoxidation

Liquid phase free radical autoxidation is a relatively slow reaction. However, the application of metal catalyst accelerates such processes and increases the selectivity of product formation⁵⁶.

The most common pathway for the catalysis of liquid-phase autoxidations is metal-catalyzed homolytic decomposition of alkyl hydroperoxide. In practice, the key role of trace amounts of metal catalysts, such as iron, manganese, cobalt, and copper compounds added to liquid phase systems is to catalyze the decomposition of hydroperoxide species (RO₂H) or, to lesser extent, peroxy species (RO₂R). The metal catalyst can considerably reduce the induction period generally found in the uncatalyzed autoxidation reactions. The two basic steps in decomposition of alkyl hydroperoxides with metal catalyst are shown as follows:

(1) Reduction



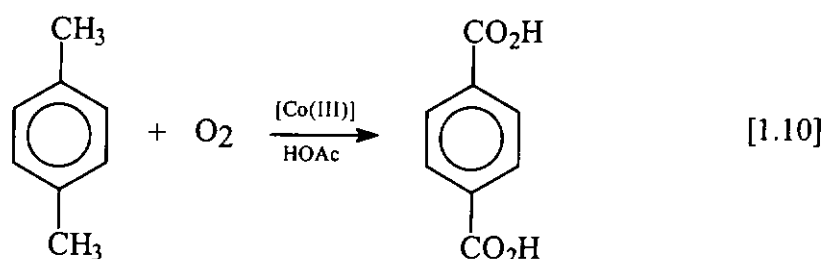
(2) Oxidation



In general, metal complexes catalyze autoxidations by generating chain-initiating radicals via steps [1.8] and [1.9]. The relative rates of these two reactions are roughly correlated with the redox potential of the Mⁿ⁺ / M⁽ⁿ⁻¹⁾⁺ couple.

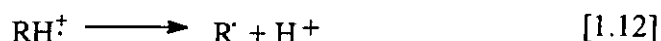
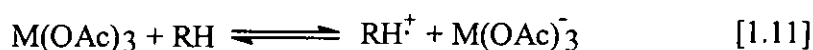
1.3.2 Direct homolytic oxidation by metal complexes

Catalytic oxidations described in previous section involve the interaction of metal catalyst with either dioxygen or alkyl hydroperoxide. There is another class of catalytic oxidation that involves a direct attack on the substrate by the metal complex⁵⁵. An example of industrially important oxidation of *p*-xylene to terephthalic acid with a cobalt catalyst is shown in equation [1.10].

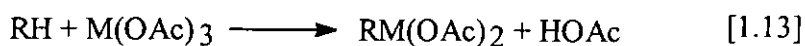


The direct interaction of strong metal oxidants with organic substrates can lead to the production of radical intermediates in two ways. Both processes are depicted below for the reaction of a metal triacetate with hydrocarbon RH.

Electron transfer



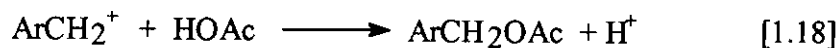
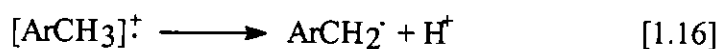
Electrophilic substitution



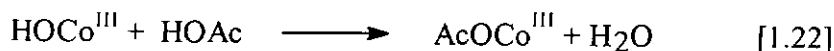
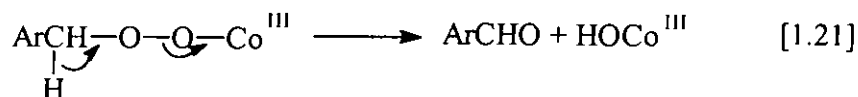
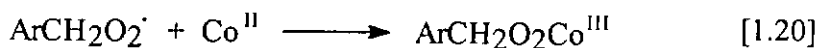
The net result in both cases is an one-electron reduction of the metal oxidant with concomitant formation of the substrate radical (R[·]). The ease of electron transfer oxidation of hydrocarbons to produce the cation-radical (RH^{·+}) is related to the ionization potential.

Electrophilic substitution is expected to be parallel to electron transfer, and there is little distinction between these two processes based on structure-reactivity relationships alone. Moreover, they probably compete with each other in a number of situations, and the dominant pathway with a particular oxidant may vary with change in substrate.

The oxidation of alkybenzenes at relatively low temperature (90-110°C) and oxygen pressure (0.2-1 bar) can be achieved in acetic acid in the presence of relatively high concentration (~0.1 M) of cobaltic acetate. The generally accepted mechanisms are shown as below:



The formation of benzyl acetate is derived from the subsequent reaction of the benzyl radical with cobaltic acetate. If the reaction is carried out under autoxidizing conditions, the benzyl radical is trapped by dioxygen, and aromatic aldehydes are the primary products, formed by the reaction between radicals with cobalt(II). The reaction scheme is shown as follows:



Chapter 2

Synthesis of Conjugated Acetylenic Ketones by Oxidation of Alkynes with *tert*-Butyl Hydroperoxide

2.1 Introduction

Selective catalytic oxidation of organic molecules plays an important role in chemical industry. Ordinary methods of oxidation require the use of stoichiometric quantities or a large amount of toxic metal compounds. Based on the economical and environmental considerations, such approaches have become increasingly unacceptable. Thus, it is highly desirable to develop selective catalytic oxidation systems, using inexpensive metal catalysts under mild conditions.

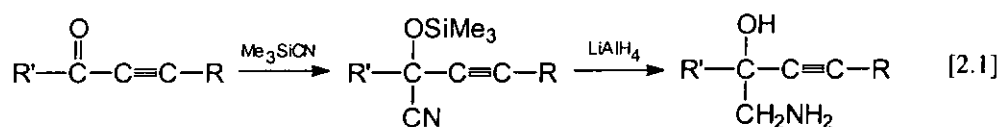
This part of the thesis is focused on the development of a simple, inexpensive catalytic system for selective oxidation of alkynes to the corresponding α , β -conjugated acetylenic ketones.

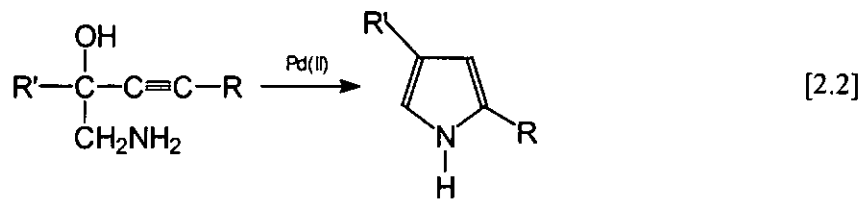
2.1.1 Importances of α , β -conjugated acetylenic ketones

The highly reactive α , β -conjugated acetylenic ketones are very useful precursors and intermediates for the synthesis of a variety of heterocyclic compounds^{16,60}, anticancer agents²⁹, nucleosides⁵⁸, pyroazole derivatives²¹, β -keto 1,3-dithianes⁴⁸, chiral pheromones^{36,61}. Belows are some specific examples.

2.1.1.1 Preparation of heterocyclic compounds

Pyrrrole derivatives were obtained from 1-amino-3-alkyn-2-ols which were produced from reaction between α , β -conjugated acetylenic ketones with Me_3SiCN , and then LiAlH_4 ⁶⁰. The reaction scheme is shown in [2.1] & [2.2]:





2.1.1.2 Preparation of anti-cancer agent

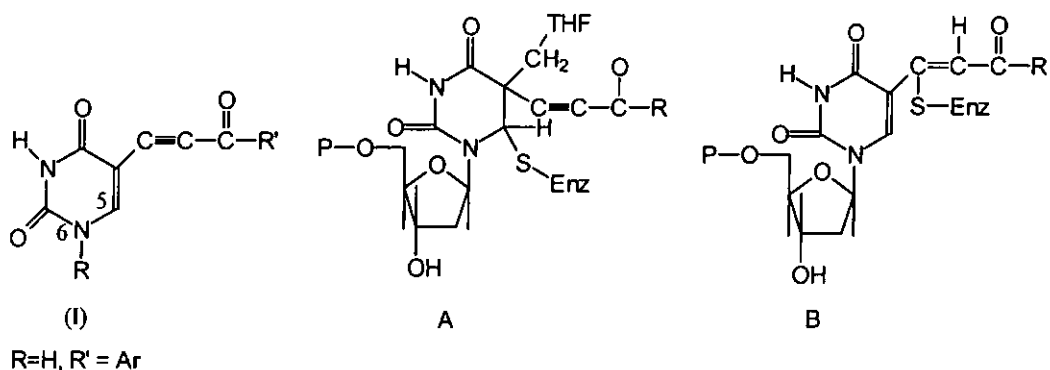
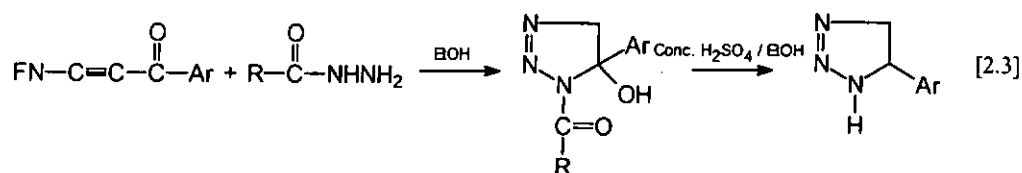


Fig. 2.1 Structures of β -(uracil-5-yl)- α,β -acetylenic ketone and its derivatives

A number of β -(uracil-5-yl)- α,β -acetylenic ketones, e.g., 5-(acylethynyl)uracils (5-AUEs, I), show activity against tumor cell lines and also act as inhibitors of thymidylate synthase enzyme²⁹. The stereoelectronic characteristics of the C-5 substituent are expected to facilitate the attack of thiol group from the cysteine moiety of the enzyme thymidylate synthase (TS), a critical enzyme needed for cellular multiplication. The C-6 position of the uracil ring tightens enzyme inhibitor complexes (A and B). Thus, these compounds are expected to act as effective inhibitors of the TS enzyme and to have antitumor properties.

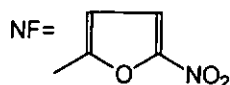
2.1.1.3 Preparation of pyroazole derivatives

Pyroazole derivatives are reported to possess various biological activities such as analgesic, anti-inflammatory, antipyretic, amoebicidal, trichomoacidal, antibacterial, antimicrobial and hypoglycemic. Reactions between nitrofuryl-substituted α , β -conjugated acetylenic ketones with different aroyl- and aryloxyacetyl hydrazines gave hydroxypyrazolines which could further be converted to nitrofuryl pyrazoles²¹. The reaction scheme is shown as follows [2.3]:



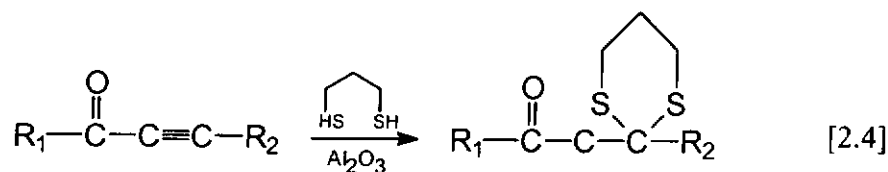
Ar = phenyl, p-Tolyl

R = phenyl, p-chlorophenyl, o-hydroxyphenyl, 2-Naphthylloxymethyl



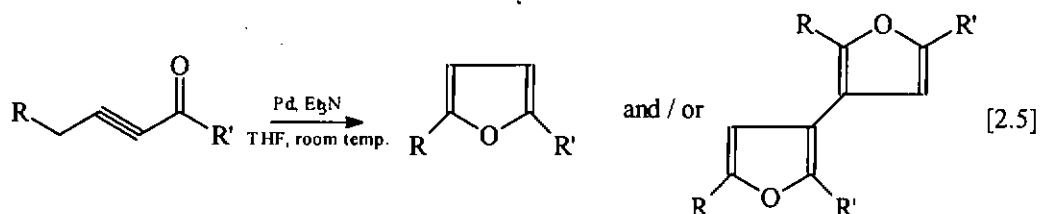
2.1.1.4 Preparation of β -keto 1,3-dithianes

β -keto 1,3-dithianes was produced by double Michael addition of 1,3-propanedithiol to α , β -acetylenic ketones on the surface of alumina⁴⁸. β -keto 1,3-dithianes are versatile synthetic intermediates. For example, 1,3-dithiane substituent may, if desired, be hydrolyzed to a carbonyl group or converted into a methyl group by reductive disulfurization. The general scheme of reaction is shown below [2.4]:



2.1.1.5 Preparation of substituted furans

Alkyl, aryl or hetero aryl substituted furans were prepared by transformation of α , β -acetylenic ketones with palladium catalyst under mild condition in a good yield⁶⁵. The reaction is shown in equation [2.5].



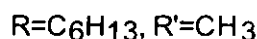
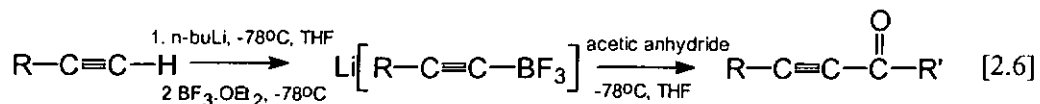
2.1.2 Synthetic methods in preparing α , β -conjugated acetylenic ketones

Since α , β -conjugated acetylenic ketones are very important intermediates for various synthetic strategies, a considerable attention has been received in preparing these compounds. The common synthetic methods are categorized into three types as described in the following sections.

2.1.2.1 Acylation of metal ($\text{Li}^{5,65,66}$, $\text{Sn}^{18,30,33}$, $\text{Mn}^{15,18}$, Zn^{39} , Mg^{27} , $\text{Cu}^{40,45,66}$, $\text{Ag}^{4,11,12}$) acetylides with an activated carboxylic acid derivative

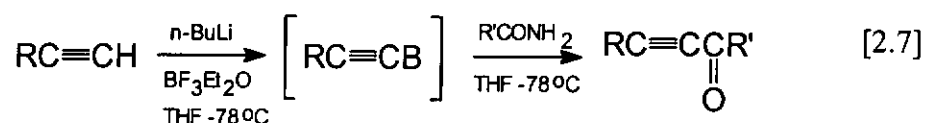
(1) Lithium

The α , β -acetylenic ketones were produced by acylation of lithium acetylide with acid anhydride⁵ as shown in equation [2.6]:



Mole ratio of 1-octyne : acetic anhydride : n-butyllithium : boron trifluoride etherate was 1 : 1.5 : 1 : 1, and the reaction was carried out at -78°C for 1 hour, giving 72% yield of 3-decyn-2-one.

Similar reaction with amides⁶⁵ was studied as shown below [2.7]:

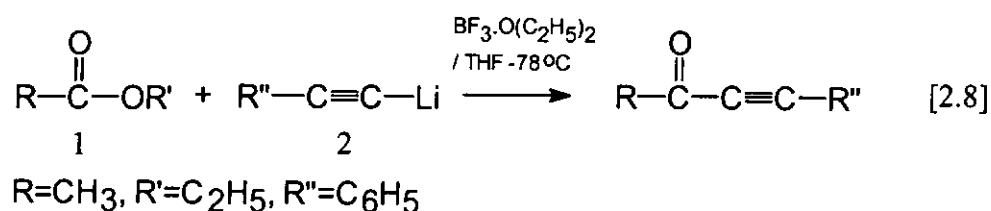


R=Ph, R'= Ph

For example, when phenylacetylene (PhC≡CH) was treated with PhCONH₂ according to above reaction for 50 minutes, PhC≡C-COPh was obtained in 83% yield.

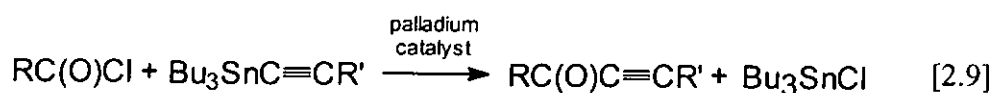
Reaction with esters was also reported as demonstrated in equation [2.8]⁶⁶.

The yield of CH₃COC≡C-C₆H₅ was 82% after 30-minute reaction.



(2) Stannanes

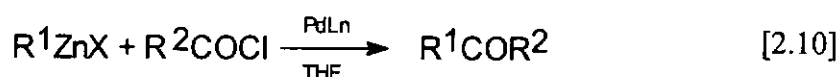
The reaction consisted of the synthesis of a variety of (1-alkynyl)tributystannanes and reacted with acyl chloride to produce α, β-acetylenic ketones [2.9]³³. Mole ratio of RCOCl : stannane : palladium catalyst was 1 : 1 : (1.8x10⁻²). The reaction was carried out at 84°C for 2 hours, resulting in 55% yield.



R=CH₃, R'=Ph

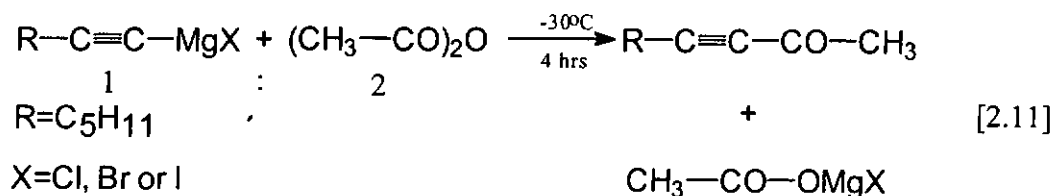
(3) Zinc

Organozincs with acyl chlorides were catalyzed by palladium-phosphine complexes to produce α , β -acetylenic ketones [2.10]³⁹. The reaction was carried out at 25°C in less than 6 hours using 5 mol% of Pd-phosphine complex, giving PhCOMe in 80% yield.



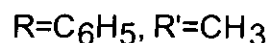
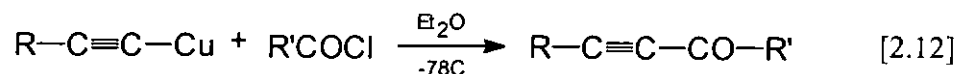
(4) Magnesium (Grignard reagents)

A number of compounds have been reported to react with Grignard reagents to form ketones. Reaction of Grignard reagents with acetic anhydride formed acetylenic ketones as shown in equation [2.11]²⁷.

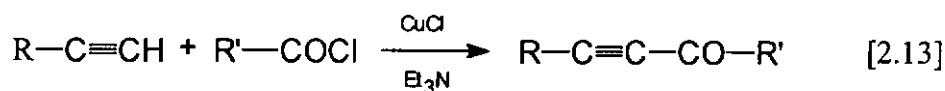


(5) Copper

Reaction of organocopper with acyl chlorides was conducted at -78°C for more than 1 hour, giving 72% yield of $C_6H_5C\equiv CCOCH_3$ [2.12]⁴⁶.



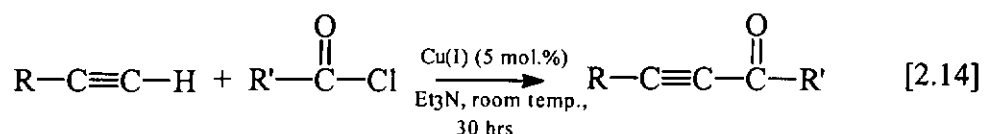
Copper(I) chloride was also used as an active catalysts for acylation of *n*-isoalkyl- and cycloalkenylacetylenes with acyl chlorides [2.13].



R=n-Bu, R'=t-Bu

For example, when pivaloyl chloride (0.2 mol), CuCl (0.02 mol), Et₃N (0.2 mol) and acetylene (0.2 mol) reacted at 50°C for 10 hours, n-BuC≡C-CO-t-Bu was obtained in 80% yield.

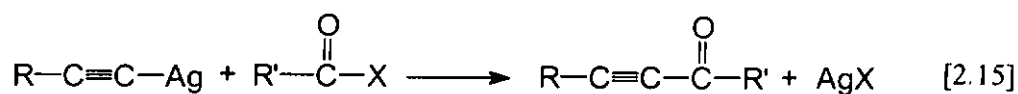
Kundu et al reported the reaction of terminal alkynes with acyl halides in the presence of catalytic amount of copper (I) salts to synthesize α, β-acetylenic ketones [2.14]²⁹.



A typical example is shown as follows: to a mixture of dimethyl propargyl alcohol (2.5 mmol) and cuprous iodide (5 mol. %, 0.125 mmol) in triethylamine, acyl chloride (3.12 mmol) was added. The mixture was stirred at room temperature for 30 hours under argon atmosphere. The product yield ranged between 44%-83%.

(6) Silver

Reaction of silver acetylides and acyl chloride was carried out for 5 hours under reflux, giving 3-octyn-2-one in 42% yield [2.15]¹².

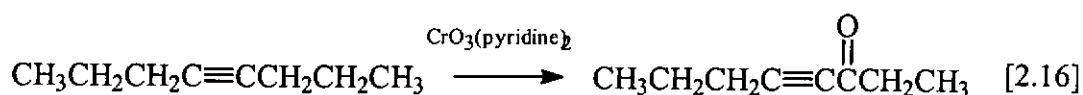


R=1-hexyne, R'=acetyl chloride, X=bromide

The use of metal acylation method to produce α , β -acetylenic ketones is limited in the sense that it requires multiple-step reactions. Some reactions is also carried out at a very low temperature, which is difficult to handle.

2.1.2.2 Selective oxidation of alkynes

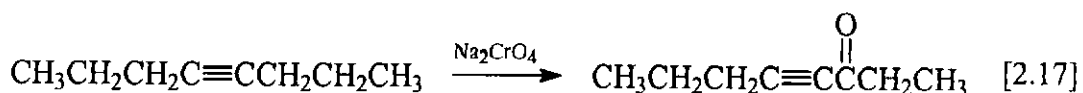
Shaw and Sherry reported the use of chromium trioxide-pyridine complex or sodium chromate in oxidation of alkynes⁵³ [2.16].



For example, 4-octyne (0.015 mol) was oxidized with $\text{CrO}_3(\text{pyridine})_2$ (0.225 mol) at room temperature for 24 hours, giving 4-octyn-3-one in 42% yield.

This method was disadvantageous as it had to use a large amount of toxic catalyst and yet generated a low yield of product.

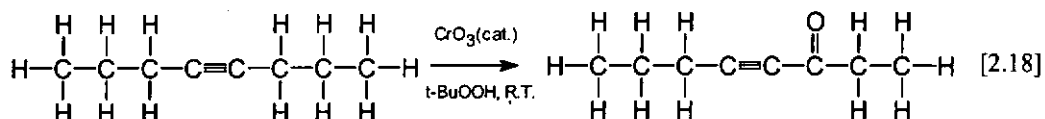
Oxidation of alkynes with sodium chromate was also studied [2.17].



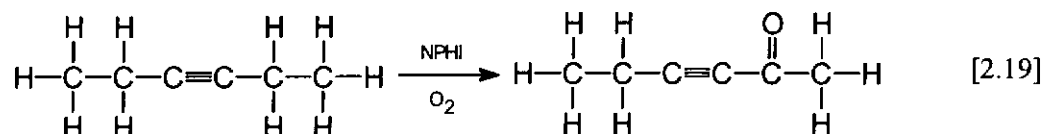
For example, 4-octyne (0.069 mol) was treated with anhydrous Na_2CrO_4 (0.120 mol) at 40-45°C for 2 days, giving 4-octyn-3-one in 19% yield. This system required 48 hours to oxidize 4-octyne to 4-octyn-3-one at 40-45°C with only 19% yield.

Muzart and Piva reported an improved oxidation system using *t*-BuOOH (2 equiv.) with catalytic amounts of CrO_3 (0.05 equiv.)³⁸. For example, 4-octyne was oxidized to 4-octyn-3-one in 28% yield after 70 hours at room temperature [2.18].

Although the amount of CrO_3 was greatly reduced in the presence of $t\text{-BuOOH}$, long reaction time and low yield were still the major drawbacks.

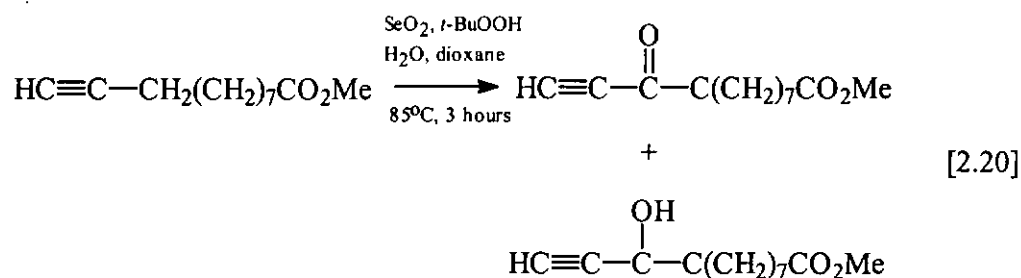


Ishii and coworkers recently reported that using N-hydroxyphthalimide (NPHI) combined with $\text{Co}(\text{acac})_2$ or $\text{Cu}(\text{acac})_2$ could oxidize various alkynes to the corresponding conjugated acetylenic ketones⁴⁹. For example, oxidation of 4-octyne with NPHI and $\text{Co}(\text{acac})_2$ in acetonitrile under oxygen at 50°C for 6 hours gave 85% conversion to 4-octyne-3-one with 72% selectivity. Some by-products such as acetylenic alcohol, acetylenic diketone and a cleaved product, butanoic acid, were also produced. Besides the formation of these by-products, the reaction needs to use relatively expensive N-hydroxyphthalimide (NPHI).



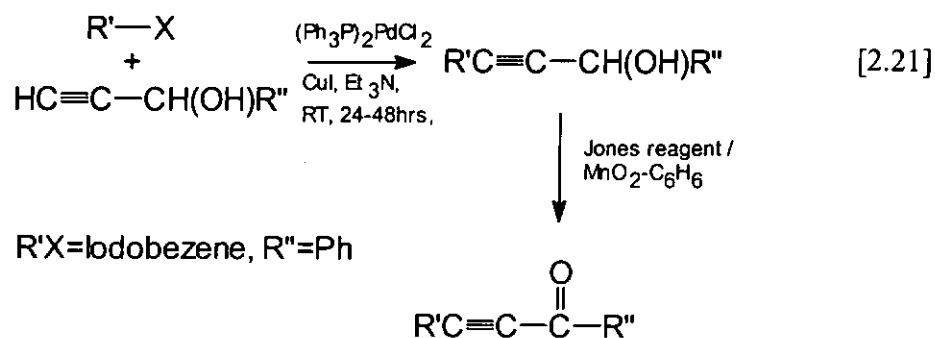
(Conditions: 3-hexyne (2mmol), $\text{Cu}(\text{acac})_2$ (0.05 mole%), NPHI (0.05 mole%), at 50°C for 6 hours).

(4) Oxidation of acetylenic fatty esters with selenium dioxide and t -butyl hydroperoxide have also been reported as illustrated in equation [2.20]²³.

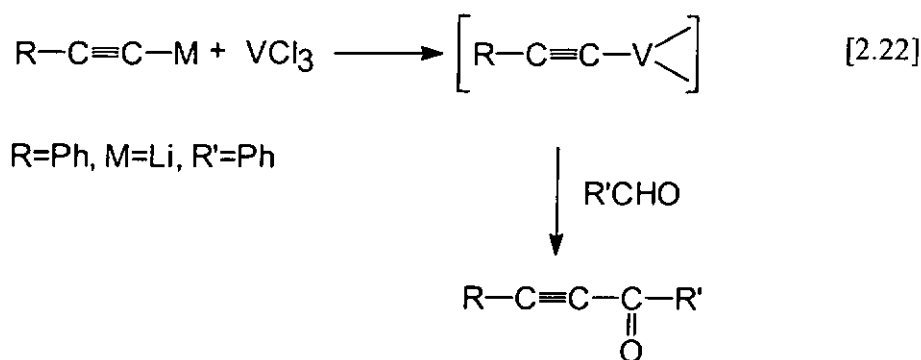


2.1.2.3 Miscellaneous methods

(1) Palladium-copper catalyzed reaction of aryl halides with terminal acetylenic alcohol was carried out at room temperature for 48 hours, followed by oxidation with Jones reagent [2.21]²⁹. When R'=R''=Ph, PhC≡CCOPh was obtained in 79% yield. However, multiple steps of reactions and long reaction time were required to synthesize this product.



(2) Oxidative nucleophilic addition of vanadium acetylides with aldehyde²⁰

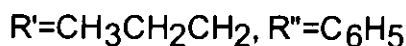
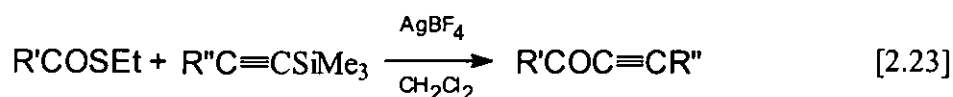


The reaction was carried out for 5 hours under reflux and the yield of Ph-C≡C-CO-Ph was 66% [2.22].

Vanadium acetylides were generated in CH₂Cl₂ at -78°C by treatment of vanadium trichloride with 1 equiv. of acetylenic Grignard or lithium compound. Then the product reacted with aldehydes to form corresponding α, β-acetylenic ketones.

This approach requires multiple steps synthesis, giving a moderate yield.

(3) Reactions of 1-alkynyltrimethylsilanes with acid chlorides in the presence of lewis acid^{24,61}, or with thiol ester²⁶

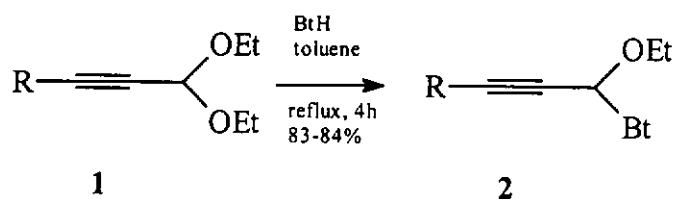


The mole ratio of silyacetylene : thiol ester : AgBF₄ was 1 : 1.2 : 2.2. The reaction was carried out at room temperature for 10 minutes. The yield of CH₃CH₂CH₂COC≡CC₆H₅ was 88% [2.23].

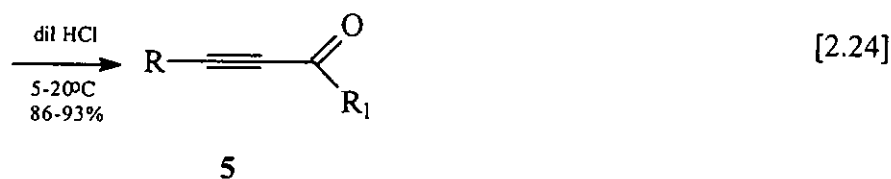
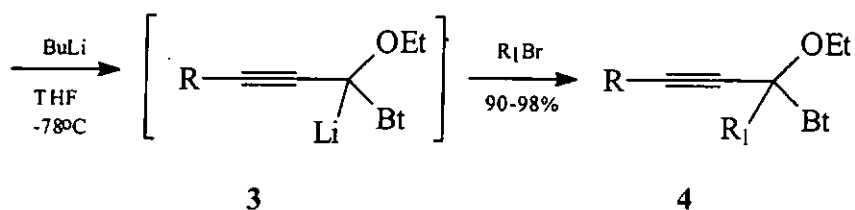
(4) From *i*-(benzotriazol-1-yl)propargyl ethyl ether²⁵

The reaction scheme is shown in equation [2.24]:

The reaction also requires several steps synthesis and a low temperature for the use of n-butyllithium.



1, 2, 3 a R=Ph, b R=n-C₆H₁₃



4, 5 a R=Ph, R₁=Et

Bt = benzotriazole

b R=Ph, R₁=3-Mo-Bu

c R=Ph, R₁=PhCH₂

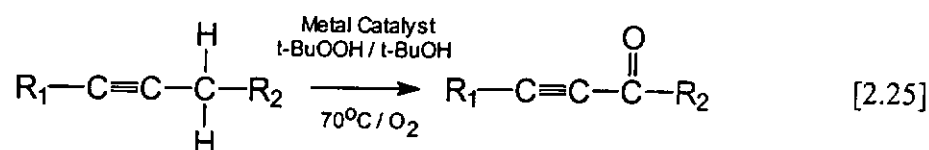
d R=Ph, R₁=n-C₁₀H₂₃

e R=n-C₆H₁₃, R₁=Et

In conclusion, most of the synthetic methods for preparing α , β -conjugated acetylenic ketones mentioned above suffer from drawbacks as multiple-step synthesis, difficulties in handling the reaction, and the use of expensive and toxic metal catalysts. Therefore it is necessary to develop new oxidative system using inexpensive and readily available transition metal catalysts for the catalytic oxidation of alkynes. These catalysts, together with a simple, inexpensive and environmental friendly oxidant such as oxygen, would make a desirable industrial process.

2.2 Objective

This project aims to study a homogenous catalytic oxidation of various alkynes to their α , β -conjugated acetylenic ketones catalyzed by readily available and inexpensive transition metal compounds with *t*-butyl hydroperoxide as an oxidant [2.25]. The oxidation system is highly selective for acetylenic monoketones without over-oxidation to acetylenic diketones or cleavage products.



Reaction parameters were systematically studied, using 4-octyne as a model substrate. They include effects of i) metal catalyst; ii) catalyst concentration; iii) oxidant concentration; and iv) oxidant addition methods. Versatility of the catalytic system on other alkynes was also investigated under the optimal conditions discovered.

2.3 Experimental section

2.3.1 Instruments

¹H nuclear magnetic resonance spectra were recorded on a Bruker DPX400 spectrometer. FTIR spectra were recorded on a Nicolet, Magna-IR 750 spectrometer. Gas chromatographic-mass spectral determinations were made on Hewlett Parkard 5972 series mass selective detector equipped with Hewlett Parkard 5890 series II gas chromatography with HP-5MS column. Gas chromatography analyses were carried out on a Hewlett Parkard 5890 series II with HP-FFAP column equipped with flame ionization detectors.

2.3.2 Chemicals

Metal catalysts such as cobalt (II) chloride anhydrous (Aldrich), cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) (Ajax Chemicals), cobalt bromide (Aldrich), cobalt (III) acetylacetonate [$\text{Co}(\text{acac})_3$] (Aldrich), copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Reidel-de Haen), cobalt (II) acetate tetrahydrate [$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$] (Riedel-de Haen), manganese (II) chloride hexahydrate ($\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$) (Peking Chemicals), Iron (II) chloride hydrate ($\text{FeCl}_2 \cdot n\text{H}_2\text{O}$) (Peking Chemicals), and chromium (III) chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) (Acros Chemicals) were all used as received. All alkynes were purchased from Aldrich Chemicals. *Tert*-Butyl hydroperoxide (*t*-BuOOH, 70%) was purchased from Arcos Chemicals, while *tert*-butyl alcohol (*t*-BuOH) was supplied by Mallinkrodt Chemicals. Oxygen gas was obtained from Hong Kong Oxygen. All other chemicals were reagent grade and used without further purification.

2.3.3 General procedures:

2.3.3.1 Effect of metal catalyst on the oxidation of 4-octyne

Metal catalyst (0.18mmol) dissolved in 14.5 mL of *t*-BuOH was stirred at 70°C under oxygen for 15 mins. 4-octyne (0.5g, 4.5mmol) with a known weight of *t*-butylbenzene (internal standard) were then charged to the reaction flask. *t*-Butyl hydroperoxide (70%) (0.5mL 3.15mmol) pre-mixed with 5.5 mL of *t*-BuOH, was added stepwise into the reaction flask every hour for 4 times (1.5mL x 4 times). After 24-hour reaction, 1mL of reaction mixture was withdrawn from the flask and passed through a small aluminum oxide column, followed by GC analysis. The conversion was then calculated based on the internal standard.

2.3.3.2 Effect of CuCl₂·2H₂O concentration on the oxidation of 4-octyne

Different concentrations of CuCl₂·2H₂O dissolved in 14.5 mL of *t*-BuOH was stirred at 70°C under oxygen for 15 mins. 4-Octyne (0.5g, 4.5mmol) with a known weight of *t*-butylbenzene (about the weight of substrate) were added into the reaction flask, followed by addition of a mixture of *t*-butyl hydroperoxide (70%) (0.5 mL, 3.15mmol) and *t*-BuOH (5.5ml) in hourly interval (1.5 mL x 4 times). The reaction was allowed to react for 24 hours.

2.3.3.3 Effect of concentration of *t*-butyl hydroperoxide on the oxidation of 4-octyne

CuCl₂·2H₂O (31mg, 0.18mmol) dissolved in 14.5 mL of *t*-BuOH was stirred at 70°C under oxygen for 15 mins. 4-Octyne (0.5g, 4.5mmol) and a known weight of *t*-butylbenzene (about the weight of substrate) were added into the reaction flask. Different concentrations of *t*-butyl hydroperoxide made up with *t*-BuOH to 6 mL were added stepwise in hourly interval (1.5 mL x 4 times) and the reaction was stopped after 24 hours.

2.3.3.4 Effect of addition methods of *t*-butyl hydroperoxide on the oxidation of 4-octyne

CuCl₂·2H₂O (31mg, 0.18mmol) dissolved in 14.5 mL of *t*-BuOH was stirred at 70°C under oxygen for 15 mins. 4-Octyne (0.5g, 4.5mmol) and a known weight of *t*-butylbenzene (about the weight of substrate) were added into the reaction flask. *t*-Butyl hydroperoxide (70%) (1.23mL, 9mmol) mixed with 4.8mL of *t*-BuOH was added into the reaction flask in three ways: (a) Batch addition: all *t*-BuOOH solution was added at once at the beginning of reaction; (b) Continuous addition: *t*-BuOOH solution was added dropwise to the reaction mixture (2 hours). (c) Stepwise addition: *t*-BuOOH was charged hourly in four portions. The reactions were all stopped after 24 hours and the conversion as well as selectivity were determined by GC.

2.3.3.5 Kinetic study of the oxidation of 4-octyne

CuCl₂·2H₂O (31mg, 0.18mmol) dissolved in 14.5mL of *t*-BuOH was stirred at 70°C under oxygen for 15 mins. 4-Octyne (0.5g, 4.5mmol) and a known weight of *t*-butylbenzene (about the weight of substrate) were added into the reaction flask, followed by addition of a mixture of *t*-butyl hydroperoxide (70%) (1.23mL, 9mmol) and 4.8mL *t*-BuOH. During the reaction, 0.5 mL of sample was withdrawn at different time intervals and was analyzed by GC.

2.3.3.6 Oxidation of various alkynes using *t*-BuOOH/CuCl₂·2H₂O system under O₂

CuCl₂·2H₂O (31mg, 0.18mmol) dissolved in 14.5 mL *t*-BuOH was stirred at 70°C under oxygen for 15 mins. Different substrates (4.5mmol) and a known weight of *t*-butylbenzene (about the weight of substrate) were added into the reaction flask. *t*-Butyl hydroperoxide (70%) (1.23 mL, 9mmol) was pre-mixed with 4.8 mL of *t*-BuOH, and the mixture was added to the reaction flask by the

stepwise method. During the reaction, 1 mL of sample was withdrawn and passed through a mini-column containing aluminum oxide in order to remove the catalyst. The purified sample was analyzed by GC to determine the conversion using *t*-butylbenzene as the internal standard.

At the end of the reaction, solvent was first removed by a rotary evaporator. The residue was then dissolved in 30 mL of diethyl ether and washed with 30 mL brine for 3 times in a separating funnel. The brine was then extracted with 30 mL diethyl ether for 2 times. The diethyl ether layer was dried with excess amounts of anhydrous calcium chloride and filtered. The solvent was subsequently removed by a rotary evaporator, and the crude product was further isolated using thick TLC plates. Both the crude and purified products were analyzed by GC, GCMS, FTIR and ¹H-NMR data are summarized in Table 2.1.

2.3.4 Characterization of products

Table 2.1 Data of products characterization

Substrate	Products	Eluent	M ⁺	FTIR (cm ⁻¹)	¹ H-NMR
4-ocytne	4-ocytyn-3-one	C ₆ H ₁₄ : CH ₃ CO OC ₂ H ₅ = 3 : 1	124, 109, 95, 67, 55	2213, 1714, 1681	δ2.52(qt, 2H), δ2.31(t, 2H), δ1.55(sextet, 2H), δ1.11(t, 3H), δ0.99(t, 3H)
3-hexyne	3-hexyn-2-one	C ₆ H ₁₄ : CH ₃ CO OC ₂ H ₅ = 2 : 1	96, 82, 67	2211, 1715, 1624	-
5-decyne	5-decyn-4-one	CH ₂ Cl ₂ : C ₆ H ₁₂ = 4 : 1	152, 137, 123, 109, 81	2212, 1714, 1672	δ2.50(t, 2H), δ2.37(t, 2H), δ1.66(m, 6H), δ0.94(t, 6H)
3-heptyne	3-heptyn-2-one	-	110, 95, 67	2235, 1716	-
	3-heptyn-5-one		110, 81, 53		
4-nonyne	4-nonyn-3-one	-	123, 109, 81	2238, 1716	-
	4-nonyn-6-one		137, 123, 95, 67		
2-decyne	2-decyn-4-one	CH ₂ Cl ₂ : C ₆ H ₁₂ = 4 : 1	137, 123, 109, 95, 82	2219, 1671	δ2.51(t, 2H), δ2.01(s, 3H), δ1.58(m, 8H), δ0.88(t, 3H)
1-ocytne	1-octyn-3-one	C ₆ H ₁₄ : CH ₃ CO OC ₂ H ₅ = 3 : 1	123, 109, 95, 81, 68, 53	2237, 1693	δ2.35(t, 2H), δ1.59(quintet, 2H), δ3.61(m, 4H), δ0.90(t, 3H)

Substrate	Products	Eluent	M ⁺	FTIR (cm ⁻¹)	¹ H-NMR
1-phenyl-1-pentyne	1-phenyl-1-pentyn-3-one	CH ₂ Cl ₂ : C ₆ H ₁₂ = 4 : 1	158, 129, 101, 77	2202, 1700, 1670	δ7.68(m, 5H), δ2.67(t, 2H), δ1.79(q, 2H), δ1.01(t, 3H)
Cis-cyclooctene	2-Cis-cyclooten-1-one	C ₆ H ₁₄ : CH ₃ CO · OC ₂ H ₅ = 2 : 1	124, 83, 67, 55	1715, 1651	-
3-hexyn-2,5-diol	2-hydroxy-3-hexyn-5-one	C ₆ H ₁₄ : CH ₃ CO OC ₂ H ₅ = 3 : 2	112, 97, 69	3412, 2253, 2223, 1713, 1679, 1229	δ4.68(qt, 1H), δ2.35(s, 3H), δ1.61(s, -OH), δ1.47(d, 3H)

2.4 Results and discussions

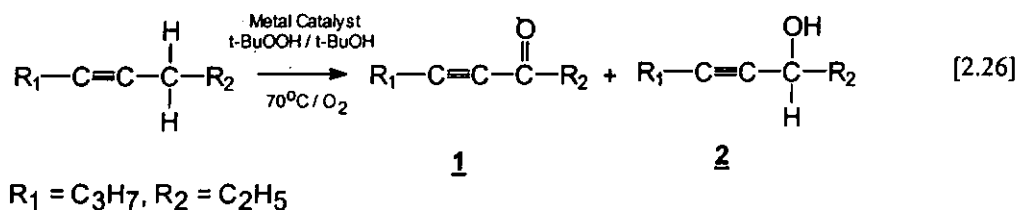
In bulk chemical manufacture, the preferred choice of oxidant is usually molecular oxygen. Although peroxide is more expensive than molecular oxygen, it is often used in fine chemical production for its simplicity of operation.

Besides the price and simplicity of handling, the two important factors that influence the economics are the nature of coproduct and the percentage of available oxygen. The former is important in an environmental context and the latter directly influences the volume yield.

In this catalytic system, *tert*-butyl hydroperoxide (*t*-BuOOH) was used as an oxidant due to following advantages⁵⁴, such as:

- It has a high thermal stability in dilute organic solutions.
- It is less sensitive to contamination by metals.
- In contrast to H₂O₂ and peracetic acid, it is unreactive to most organic compounds in the absence of metal catalysts. This is a key factor in determining selectivity.
- It is readily soluble in hydrocarbon solvents.
- Oxidations are carried out under essentially neutral conditions.
- Processes are much less subject to corrosion problems than those employing peracids.
- The coproduct, *tert*-butanol, has a relatively low boiling point and is readily removed by distillation.

4-Octyne was chosen as a model substrate, and it was allowed to react with *t*-BuOOH catalyzed by a transition metal compound under oxygen. The reaction scheme is shown as belows [2.26]:



2.4.1 Effect of metal catalyst on the oxidation of 4-octyne

Two products were usually observed during the reaction. The major and minor products were 4-octyn-3-one (**1**) and 4-octyn-3-ol (**2**), respectively. Based on the GC analysis, product (**2**) could be converted to product (**1**) under prolonged reaction time. In order to obtain the optimal reaction conditions for this oxidation, various reaction parameters were investigated systematically.

Transition metal catalysts such as Co, Cr, Cu, Fe and Mn complexes were studied as shown in Table 2.2. These metal catalysts had a discrete effect on both conversion and selectivity. In general, catalysts promoted the rate of oxidation as compared to the oxidation in the absence of catalyst. When Co, Cu and Mn complexes were used, near complete conversion could be achieved after 24 hours. However, Cr and Fe gave relatively lower conversion.

Regarding the selectivity, 4-octyn-3-one (**1**) was found to be the major product for all the catalysts studied, but 4-octyn-3-ol (**2**) was the major one in the absence of catalyst. Among them, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was selected because of its high

conversion of 4-octyne and selectivity. Furthermore, it was readily available and inexpensive.

Table 2.2 Effect of metal catalysts on the oxidation of 4-octyne^a

Metal catalysts	Weight of catalyst (mmol)	Conversion ^b (%)	Product distribution ^c (%)		
			<u>1</u>	<u>2</u>	Unknown
Without catalyst	Nil	56%	17%	80%	3%
Co(acac) ₃	0.18	89%	96%	2%	2%
CoBr ₂	0.18	89%	92%	4%	4%
CoCl ₂	0.18	88%	96%	2%	2%
CoCl ₂ .6H ₂ O	0.18	91%	97%	1%	2%
Co(OAc) ₂ .4H ₂ O	0.18	89%	92%	5%	3%
CrCl ₃ .6H ₂ O	0.18	81%	95%	2%	3%
CuCl ₂ .2H ₂ O	0.18	91%	97%	1%	2%
FeCl ₂ .nH ₂ O	0.18	83%	72%	23%	5%
MnCl ₂ .6H ₂ O	0.18	96%	68%	31%	1%

^aReaction conditions: mole ratio of metal catalyst : 4-octyne : *t*-BuOOH = 1 : 25 : 17.5. Reaction was carried out at 70°C for 24 hrs under O₂.

^bConversion was determined based on the internal standard, *t*-butylbenzene.

^cProduct distribution was determined by GC.

2.4.2 Effect of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentration on the oxidation of 4-octyne

The effect of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentration on the oxidation of 4-octyne with respect to the conversion and selectivity was studied by varying the mole ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to 4-octyne from 1 : 10 to 1 : 200, and the results are shown in Table 2.3.

Table 2.3 Effect of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentration on the oxidation of 4-octyne^a

Mole ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to 4-octyne	Weight of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (mg)	Conversion ^b (%)	Product distribution ^c (%)		
			1	2	unknown
1 : 10	76	94%	97%	1%	2%
1 : 25	31	91%	97%	1%	2%
1 : 50	15.5	90%	88%	10%	2%
1 : 75	10.2	92%	77%	21%	2%
1 : 100	8	90%	78%	20%	2%
1 : 200	4	88%	68%	29%	3%
Without $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Nil	56%	17%	80%	3%

^aReaction conditions: mole ratio of 4-octyne : *t*-BuOOH = 1 : 0.7. Reaction was carried out at 70°C for 24 hrs under O_2 .

^bConversion was determined based on the internal standard, *t*-butylbenzene.

^cProduct distribution was determined by GC.

It was found that the concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ had little effect on the total conversion of 4-octyne, but it had a remarkable influence on the selectivity. On one hand, when $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentration decreased, the selectivity towards

acetylenic ketone was considerably decreased. On the other hand, when the mole ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to 4-octyne further increased from 1 : 25 to 1 : 10, little effect on both conversion and selectivity was observed. Therefore, the mole ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to 4-octyne equal to 1 : 25 was selected for subsequent studies.

2.4.3 Effect of concentration of *t*-butyl hydroperoxide on the oxidation of 4-octyne

Table 2.4 showed that increasing the *t*-BuOOH concentration led to a slight increase of 4-octyne conversion. Higher *t*-BuOOH concentration also increased the undesired alcohol intermediate (**2**). However, lower *t*-BuOOH concentrations, such as 1 : 0.5, resulted in incomplete reaction within 24 hours.

Table 2.4 Effect of concentration of *t*-butyl hydroperoxide on oxidation of 4-octyne^a

Ratio of 4-Octyne to <i>t</i> -BuOOH	Volume of <i>t</i> -BuOOH (mL)	Conversion ^b (%)	Product distribution ^c (%)		
			1	2	Unknown
1 : 0.5	0.307	62%	95%	0	5%
1 : 0.8	0.500	91%	97%	1%	3%
1 : 1	0.615	92%	96%	2%	2%
1 : 2	1.230	99%	94%	5%	2%
1 : 3	1.850	97%	80%	18%	2%

^aReactions conditions: mole ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: 4-octyne = 1 : 25. Reaction was carried out at 70°C for 24 hrs under O_2 .

^bConversion was determined based on the internal standard, *t*-butylbenzene.

^cProduct distribution was determined by GC.

Although the ratio of 4-octyne to *t*-BuOOH equal to 1 : 0.8 could give over 90% conversion, the ratio of 4-octyne to *t*-BuOOH equal to 1 : 2 was finally selected in order to achieve quantitative conversion.

2.4.4 Effect of addition methods of *t*-butyl hydroperoxide on the oxidation of 4-octyne

Three addition methods of oxidant have been examined and results are shown in Table 2.5.

Table 2.5 Effect of addition method of *t*-butyl hydroperoxide on oxidation of 4-octyne^a

Addition method	Conversion ^b (%)	Product distribution ^c (%)		
		1	2	Unknown
Batch addition ^d	73%	77%	20%	3%
Continuous addition ^e	83%	92%	6%	2%
Stepwise addition ^f	91%	94%	4%	2%

^aConditions: mole ratio of CuCl₂·2H₂O : 4-octyne : *t*-BuOOH = 1 : 25 : 50. Reaction was carried out at 70°C for 24 hrs under O₂.

^bConversion was determined based on the internal standard, *t*-butylbenzene.

^cProduct distribution was determined by GC.

^dBatch addition: all of *t*-BuOOH solution was added into the reaction flask at the beginning of reaction.

^eContinuous addition: *t*-BuOOH was added dropwise to the reaction mixture (2 hours)

^fStepwise addition: *t*-BuOOH was charged hourly in four portions

Interestingly, the stepwise addition method gave the highest conversion of 4-octyne (91%) among the three methods. This might be explained by the fact that

the concentration of *t*-BuOOH was relatively low for the stepwise addition as compared to other addition methods, thus radical termination could be reduced.

2.4.5 Kinetic study of the oxidation of 4-octyne

Figure 2.2 shows the kinetics of the oxidation of 4-octyne using mole ratios of 4-octyne : *t*-BuOOH : CuCl₂·2H₂O = 50 : 25 : 1 at 70 °C under oxygen according to the procedure 2.3.3.5 by the stepwise addition method. The reaction took place rapidly, and reached 90% conversion within 5 hours. When monitoring the product formation by GC, it was noted that two products, 4-octyne-3-one and 4-octyne-3-ol together with a small amount of unidentified products (less than 2%) were formed. Figure 2.3 exhibits the product distribution of the two major products. It was very interesting to discover that the acetylenic ketone was the major product initially. As the reaction proceeded further, the amount of acetylenic alcohol increased while the acetylenic ketone decreased. Prolonged reaction slowly converted all the acetylenic alcohol to the ketone. This suggests that conversion of 4-octyne to a mixture of the corresponding acetylenic alcohol and ketone could be nearly completed within 5 hours. However, a longer reaction time was needed to further convert the acetylenic alcohol to the ketone product.

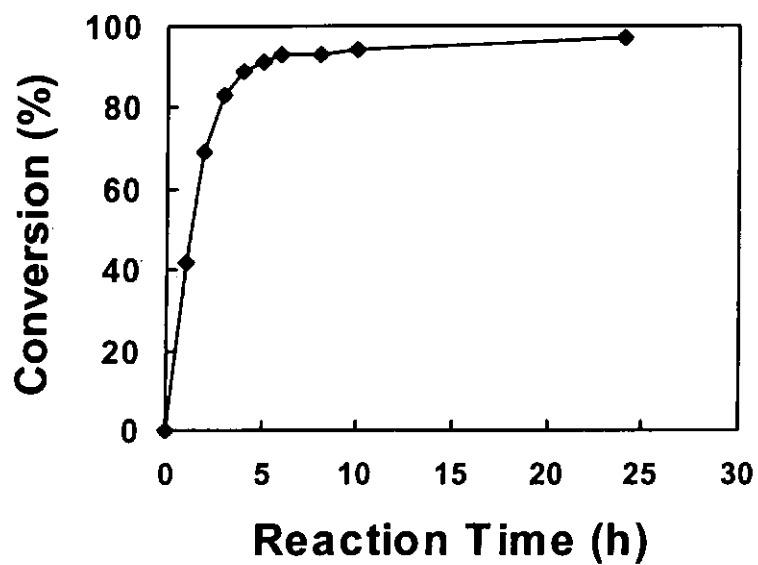


Fig. 2.2 Kinetic study of the oxidation of 4-octyne

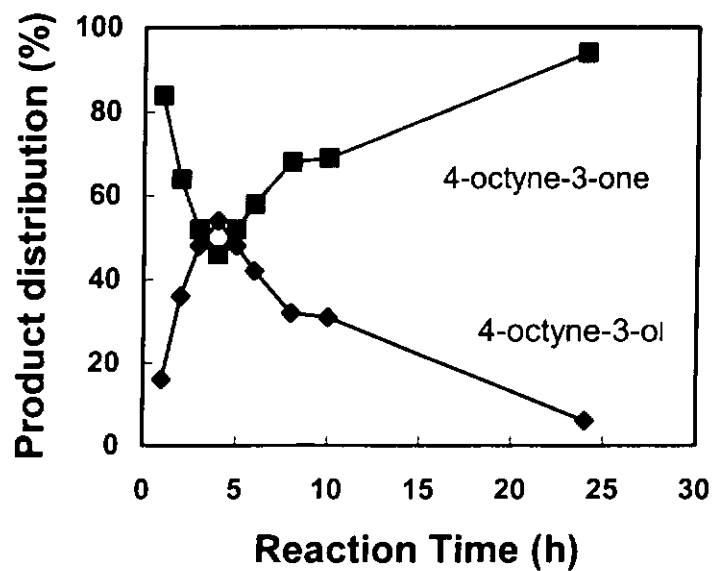


Fig. 2.3 Product distribution during the oxidation of 4-octyne

2.4.6 Oxidation of various alkynes catalyzed by *t*-BOOH/ CuCl₂·2H₂O system under O₂

By using the optimal conditions for the oxidation of 4-octyne (alkyne : CuCl₂·2H₂O : *t*-BuOOH = 25 : 1 : 50), various alkynes were investigated in order to determine the versatility of this catalytic system. The results are summarized in Table 2.6.

For the symmetrical alkynes, such as 3-hexyne, 4-octyne and 5-decyne, near complete conversions to the corresponding acetylenic ketones were obtained under this catalytic system. It seemed that the carbon chain length had little effect on the conversion. For unsymmetrical alkynes, such as 3-heptyne and 4-nonyne, two acetylenic ketones with a similar distribution were identified. Interestingly, when 2-decyne was oxidized, the oxidation occurred preferentially at the internal methylene group. The terminal methyl group did not react at all. These results suggested that the catalytic system could not distinguish the reactivity difference between the two asymmetric internal methylene groups, but could easily discern the variance between the methyl and methylene groups. When 1-octyne was oxidized, much lower conversion was obtained. This result indicated that the presence of alkyl group might increase the stability of acetylenic radical, resulting in a higher rate of oxidation.

It was observed that the reactivity of the alkyne substrates was highly correlated with their electron-richness. Electron donating substitution adjacent to the triple bond enhanced the rate of oxidation. For example, the conversion of 4-octyne, 1-phenyl-1-pentyne and 1-octyne was decreased in descending order. In contrast to the electron donating group, substitution of just one electron-

withdrawing group, e.g. methyl-2-octynoate or 2-octynoic acid, severely reduced the alkyne reactivity. No apparent substrate oxidation was observed after 24 hours.

Oxidation of other substrate was also investigated. For example, cis-cyclooctene could be converted to the corresponding cis-cycloocten-3-one, but the selectivity was much poorer compared with the alkyne substrate. Furthermore, this catalytic system could rapidly convert 3-hexyn-2,5-diol to 3-hexyn-2-ol-5-one in high yield. However, further oxidation to 3-hexyn-2,5-dione was also observed.


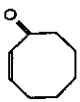
Table 2.6 Oxidation of various alkynes catalyzed by *t*-BuOOH/CuCl₂·2H₂O system under O₂^a

Substrate	Time (hrs)	Products	Conversion ^b (%)	Yield ^b (%)
CH ₃ CH ₂ C≡CCH ₂ CH ₃ 3-hexyne	24	CH ₃ C(O)C≡CCH ₂ CH ₃	91	81
CH ₃ (CH ₂) ₂ C≡C(CH ₂) ₂ CH ₃ 4-octyne	24	CH ₃ CH ₂ C(O)C≡C(CH ₂) ₂ CH ₃	99	94
CH ₃ (CH ₂) ₃ C≡C(CH ₂) ₃ CH ₃ 5-decyne	24	CH ₃ (CH ₂) ₂ C(O)C≡C(CH ₂) ₃ CH ₃	95	86
CH ₃ CH ₂ C≡CCH ₂ CH ₂ CH ₃ 3-heptyne	24	CH ₃ C(O)C≡CCH ₂ CH ₂ CH ₃	100	55
		CH ₃ CH ₂ C≡C(O)CH ₂ CH ₃		45
CH ₃ (CH ₂) ₂ C≡C(CH ₂) ₃ CH ₃ 4-nonyne	24	CH ₃ CH ₂ C(O)C≡C(CH ₂) ₃ CH ₃	89	45
		CH ₃ (CH ₂) ₂ C≡C(O)(CH ₂) ₂ CH ₃		43

Continued

Substrate	Time (hrs)	Products	Conversion ^b (%)	Yield ^b (%)
$\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_6\text{CH}_3$ 2-decyne	24	$\text{CH}_3\text{C}\equiv\text{CC}(\text{O})(\text{CH}_2)_5\text{CH}_3$	84	73
$\text{HC}\equiv\text{C}(\text{CH}_2)_5\text{CH}_3$ 1-octyne	24	$\text{HC}\equiv\text{CC}(\text{O})(\text{CH}_2)_4\text{CH}_3$	61	41
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}(\text{CH}_2)_2\text{CH}_3$ 1-phenyl-1-pentyne	24	$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}(\text{O})\text{CH}_2\text{CH}_3$	78	70
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{-C}\equiv\text{C}\text{COOCH}_3$ Methyl-2-octynoate	24	No reaction	-	-
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{-C}\equiv\text{C-COOH}$ 2-Octynoic acid	24	No reaction	-	-

Continued

Substrate	Time (hrs)	Products	Conversion ^b (%)	Yield ^b (%)
	24		97	62
cis-cyclooctene				
CH ₃ CH(OH)C≡CCH(OH)CH ₃	10	CH ₃ C(O)C≡CCH(OH)CH ₃	100	82
3-hexyn-2,5-diol		CH ₃ C(O)C≡C(O)CH ₃		18

^aReaction conditions: mole ratio of CuCl₂·2H₂O : substrate : t-BuOOH = 1 : 25 : 50. Reaction was carried out at 70°C under O₂.

^bConversion and product yield were determined by GC based on the internal standard, *t*-butylbenzene. The major by-product was acetylenic alcohol.

2.4.7 Proposed mechanism

Copper-catalyzed oxidation of alkynes is proposed to follow a radical mechanistic pathway as shown in Fig. 2.4. Copper (II) ions first decompose the *t*-butyl hydroperoxide into *t*-butyl peroxide (*t*-BuO[•]) and peroxy (*t*-BuOO[•]) radicals. These radicals then abstract the methylene hydrogen adjunct on the triple bond to give an acetylenic radical. In the presence of oxygen, the acetylenic radical can react with the oxygen to form an acetylenic peroxy radical, which may undergo reaction by one of two pathways: i) further abstract the methylene hydrogen from the substrate, giving an acetylenic hydroperoxide intermediate, or ii) interact with Cu⁺ ions, then re-arrange to form a conjugated acetylenic ketone directly. This second reaction may dominate at the beginning of reaction, thus the conjugated acetylenic ketone is formed as the major product. The acetylenic peroxide is rapidly decomposed to an acetylenic alcohol, which can be further oxidized to the corresponding ketone via the abstraction of the hydrogen adjunct to the alcohol. The rate of conversion of acetylenic alcohol to ketone was found to depend upon the stability of the acetylenic alcohol radical. For example, the conversion of 1-octyn-3-ol to the ketone product (Fig. 2.5) was much slower than that of the 1-phenyl-1-pentyn-3-ol (Fig. 2.6). This might be due to the phenyl group of 1-phenyl-1-pentyn-3-ol that could stabilize the acetylenic alcohol radical better than the hydrogen of 1-octyn-3-ol.

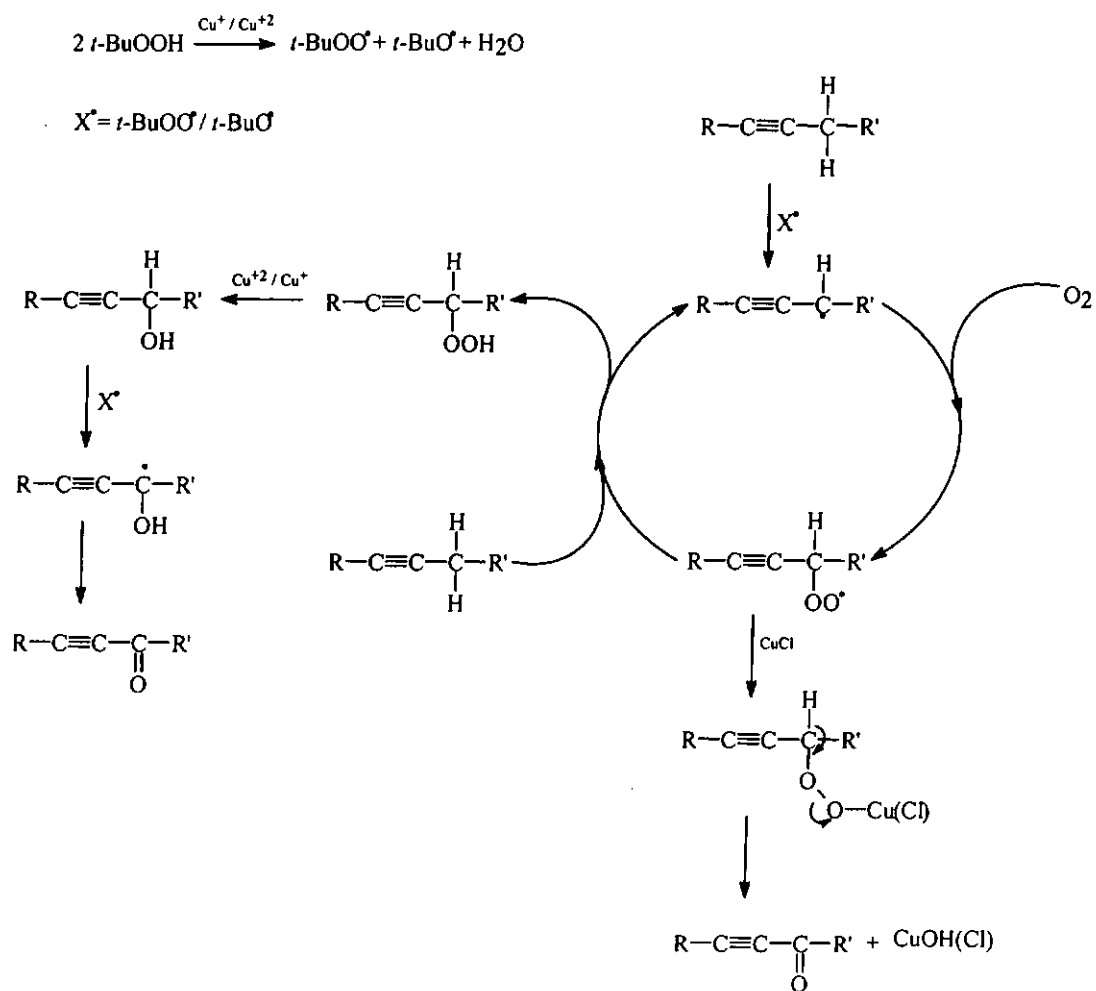


Fig. 2.4 Proposed mechanism of oxidation of alkyne by *t*-BuOOH catalyzed with Cu^{2+}

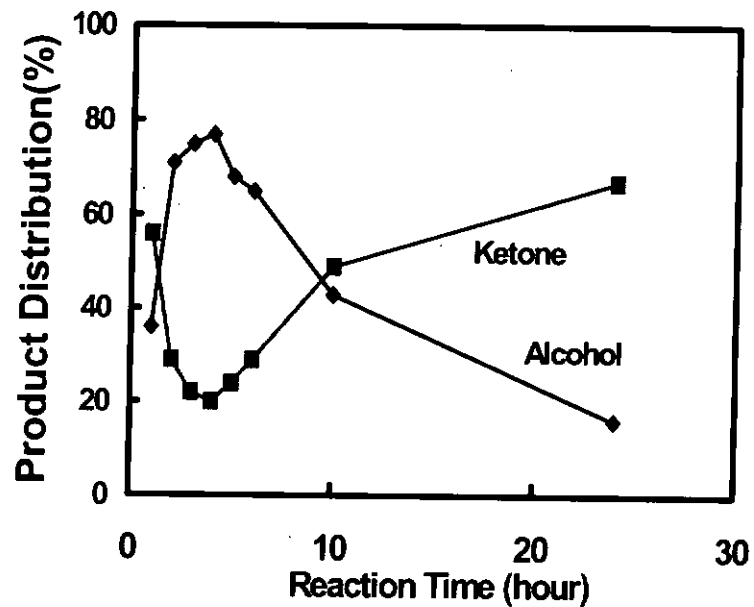


Figure 2.5 Product distribution during the oxidation of 1-octyne

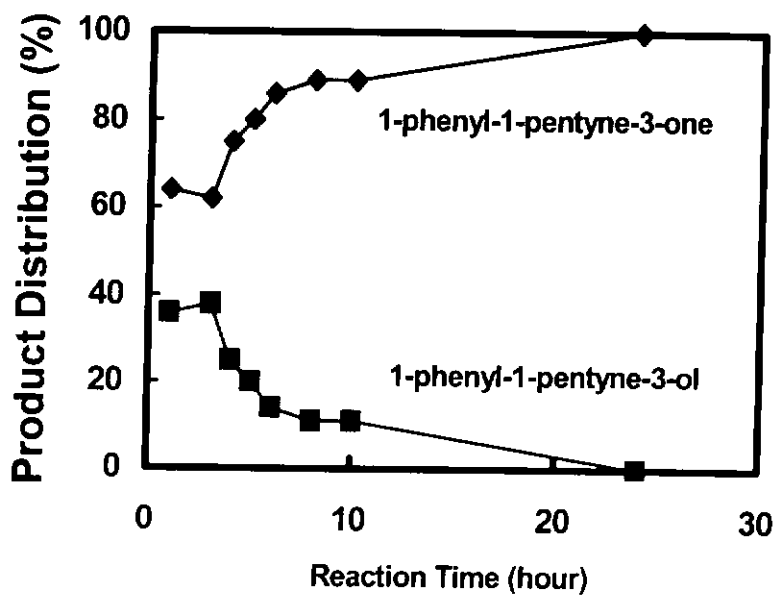


Figure 2.6 Product distribution during the oxidation of 1-phenyl-1-pentyne

2.5 Conclusion

Alkynes were successfully converted to α , β -conjugated acetylenic ketones through copper-catalyzed aerobic oxidation using *t*-BuOOH under mild conditions. The optimal reaction conditions were obtained by systematic study of various reaction parameters including the metal catalyst, and its concentration, *t*-BuOOH concentration, as well as addition methods. A wide range of alkynes could be selectively converted to the corresponding conjugated acetylenic ketones, while electron-deficient alkynes failed. The reaction proceeded through a hydrogen atom abstraction by radicals and acetylenic ketone was formed.

The present method provides a facile method for preparing α , β -conjugated acetylenic ketones from alkynes with high reactivity and selectivity.

Chapter 3

Synthesis and Properties of Poly(2,6-dimethyl-1,4-phenylene oxide) Containing Acetoxy Pendant Group

3.1 Introduction

Modification of existing polymers rather than development of new polymers have been the trend of this decade. The prime aim of polymer modification is to produce materials with new and improved properties such as enhanced thermal stability, solubility, microbial resistance, compatibility, flexibility, rigidity and so on. Polymer modification can be divided into two categories, namely, physical modification and chemical modification. Physical modification includes entrapment and radiation-induced changes, whereas in the case of chemical modification, reactions on the preformed polymers are involved³⁵. This part of the thesis is focused on the chemical modification of Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) via metal-catalyzed oxidation.

3.1.1 Background of poly(2,6-dimethyl-1,4-phenylene oxide)

Poly(2,6-dimethyl-1,4-phenylene oxide) (Fig.3.1) was developed in 1964 by Allan S. Hay. It belongs to the class of thermally stable engineering plastics characterized by a high glass transition temperature ($T_g=212^\circ\text{C}$) and good thermal stability under nonoxidizing conditions⁴³.

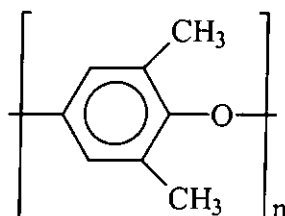


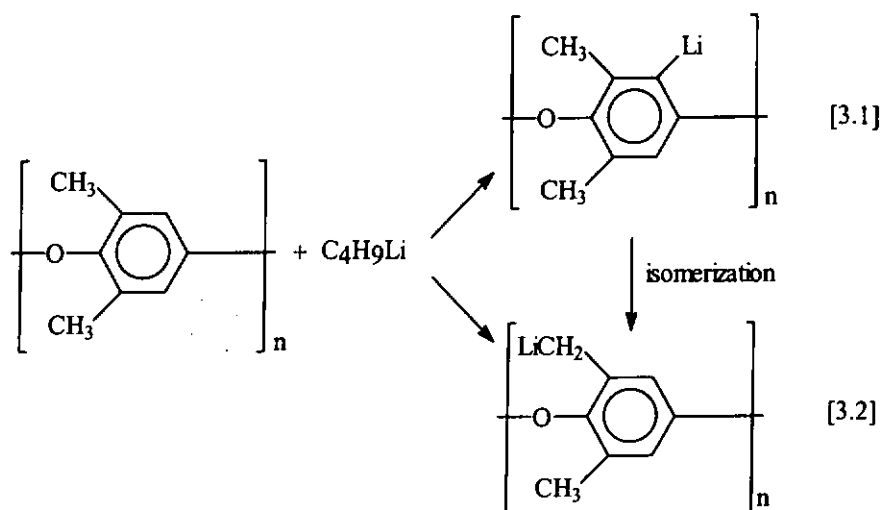
Fig. 3.1 Chemical Structure of PPO

One of the most interesting properties of PPO is its rather unique gas permeation characteristics. Among the many aromatic polymers which possess high T_g, PPO shows the highest permeability to gases. However, this distinct permeation property of PPO has not been fully utilized. This may be due to two disadvantages associated with PPO when compared with polysulfone which is currently used in gas separations. First, PPO has lower selectivity to gases. Second, PPO is not soluble in dipolar aprotic solvents, which are the most conventional solvents used in the membrane fabrication process. Hence many chemical modifications of PPO to give better gas selectivity and solubility in aprotic solvents have been developed and are summarized in the following section.

3.1.2 Literature Methods of PPO Modification

3.1.2.1 Direct Metalation

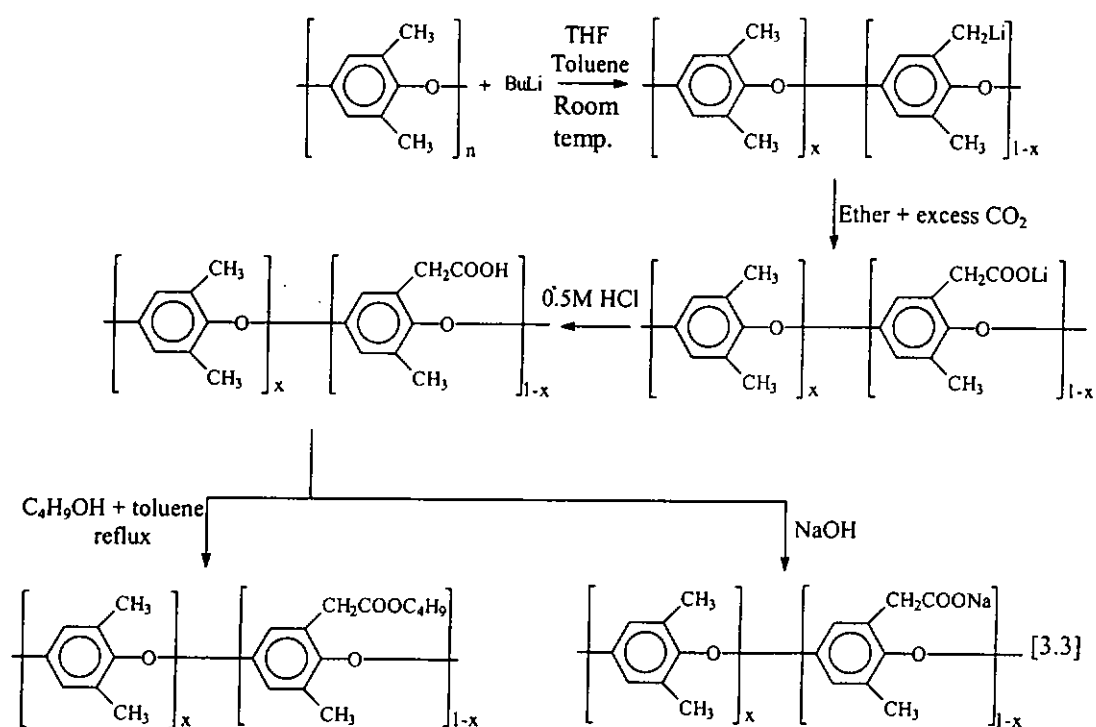
Chalk and Hay first reported that PPO was metalated with butyllithium in THF or with N, N, N', N'-tetramethylethylenediamine (TMEDA) complex of butyllithium in a variety of solvents^{8,17}. Metalation occurred on both the ring [3.1] and side chain positions [3.2], the former one being preferred initially. Subsequently, there was an isomerization in favor of the side chain. When sodium and potassium alkyls were used, only side-chain metalation was observed. The metalated polymer as a typical organometallic reacts with a wide variety of reagents. For example, the metalated PPO could react with trimethylchlorosilane [(CH₃)₃SiCl], ketones, organometallic halides, carboxyl, acid anhydrides, acid chlorides and vinyl monomers.



Chalk and Hoogeboom employed lithiated PPO as an initiator for the graft polymerization of isoprene and methylacrylate⁹. The trigraft terpolymers were also obtained via the anionic polymerization of methyl methacrylate (MMA) from lithiated PPO followed by trans-esterification of oligomeric methoxy polyethylene glycol (MPEG) on the MMA side chains.

Macknight et al have reported the synthesis and properties of carboxylated PPO which was prepared by first metalating PPO with butyllithium in a mixed solvent of THF and toluene, followed by treating it with carbon dioxide²². A range of polymers containing carboxyl groups from 1.5 to 41.7% were examined. These carboxylic acid polymers could further react via esterification or metalization to form esters and sodium salt. The reaction schemes are shown in reaction scheme [3.3].

During the metalation of PPO with butyllithium, a mixture of metalated PPO at both the ring and side chain was obtained, causing many complications in the subsequent reactions.



3.1.2.2 Bromination

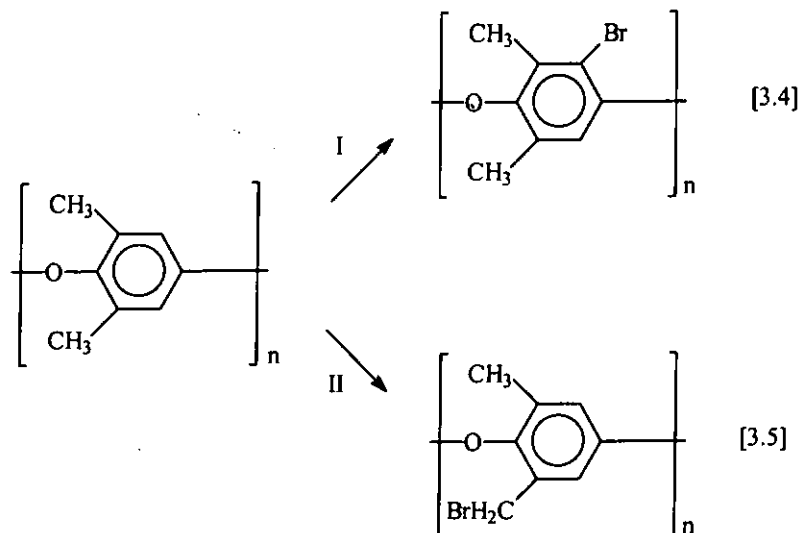
The introduction of halogen atoms, especially bromine atom, onto the PPO has received a considerable attention because of the following two reasons:

1. Halogen can have effect on the flammability and thermal properties of the polymers.
2. Halogenated PPO can be used as a useful precursor for polymers by further reactions to incorporate other functional groups.

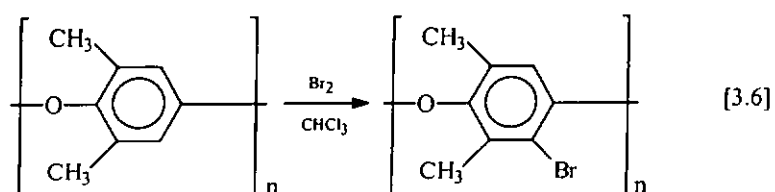
PPO can be selectively brominated either on the benzene ring or on the methyl group, depending on the reaction conditions.

(I) Electrophilic substitution on phenyl ring [3.4].

(II) Radical substitution on methyl groups [3.5].

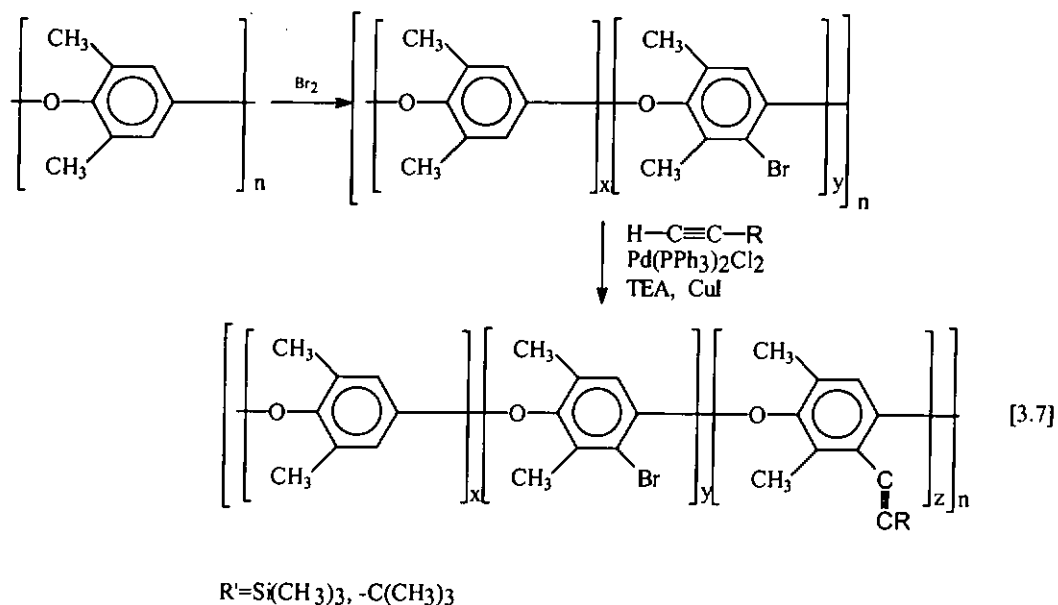


PPO was directly brominated on the phenyl ring in solution⁶³, and the reaction scheme is shown in [3.6].



The brominated PPO resulted in a decrease in intrinsic viscosity, which might be caused by the chain cleavage reaction. On the other hand, the CO₂ permeability of the brominated PPO was found to be twice as high as PPO, while retaining the same selectivity for CO₂/CH₄ mixture.

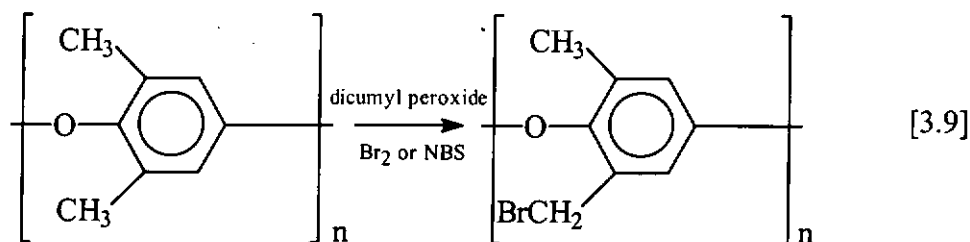
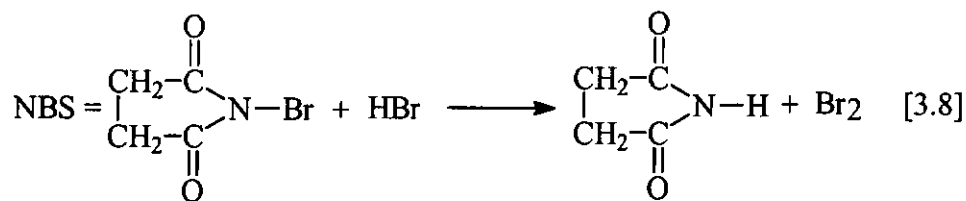
Bonfanti utilized the brominated PPO to react with substituted acetylenes using a palladium as a catalyst³ [3.7]. Bulky substituent on the phenyl ring was introduced which could be a useful tool for increasing the gas permeability of PPO.



Although displacement of bromine with substituted acetylenes decreased the T_g values as compared to the brominated PPO, it indeed increased the gas permeability.

3.1.2.3 Bromomethylation

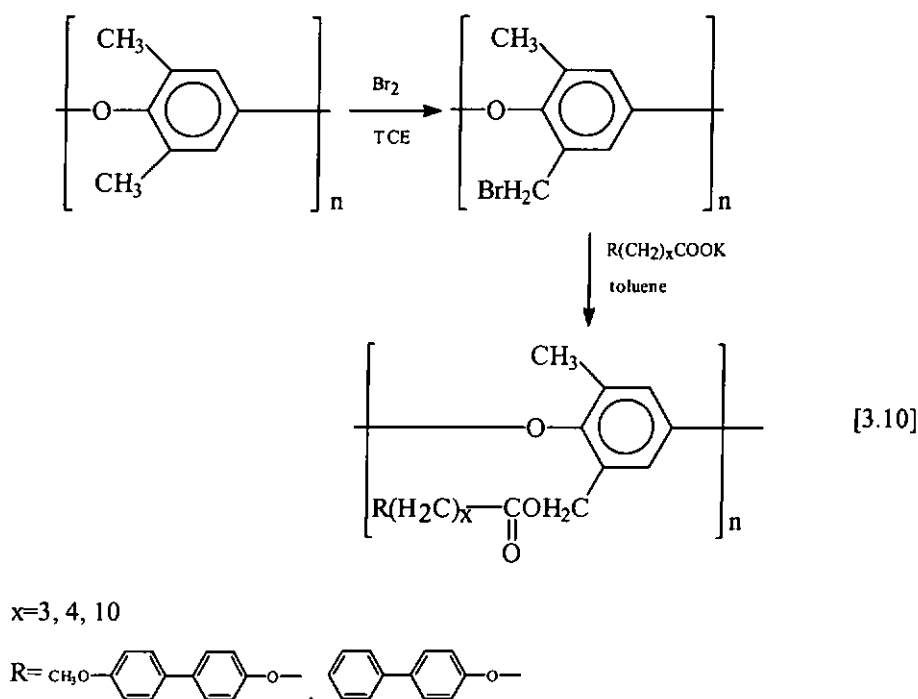
Liska et al found that bromination of the methyl group of PPO could take place using molecular bromine or brominating agent in chlorobenzene with dicumyl peroxide initiator at 132°C³². Under these conditions, no phenyl-brominated product was obtained [3.9].



The parallel bromination of the phenyl group and the methyl group of PPO, however, occurred at the temperature below 130°C with either molecular bromine or N-bromosuccinimide (NBS). But reaction temperature above 150°C led to cross-linking of PPO together with the bromination. In other words, the presence of peroxide accelerated the radical initiation, thus methyl bromination was preferred over electrophilic attack and the degree of bromination was enhanced. However, the extent of cross-linking reaction was increased at high temperature as well.

Radical bromination of PPO methyl groups to a corresponding polymer, bromobenzyl group, has been an important process for preparing various functionalized PPO. For example, Pugh and Percec have synthesized thermotropic side-chain liquid crystalline polymers containing PPO main chain as shown in [3.10]⁴⁷. The bromobenzyl groups were then esterified under phase-transfer-catalyzed reaction conditions with potassium ω-(4-oxybiphenyl)alkanoates and

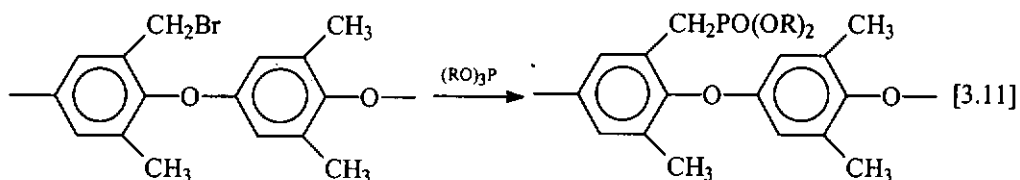
potassium ω -(5-methyl-4'-oxybiphenyl) alkanooates. The glass transition temperatures of most of the substituted PPO were lower compared with ordinary PPO. The results demonstrated that thermoplastic side-chain liquid crystalline polymers could be prepared from any polymer backbone, including rigid ones, provided that a long enough spacer was employed.



Percec and Auman also reported a method for synthesizing PPO containing pendant vinyl groups via chloro- or bromomethylated PPO⁴⁵. The halogenated PPOs were then transformed into phosphonium salts, and subject to a phase transfer-catalyzed Wittig reaction to provide polymers with vinyl groups.

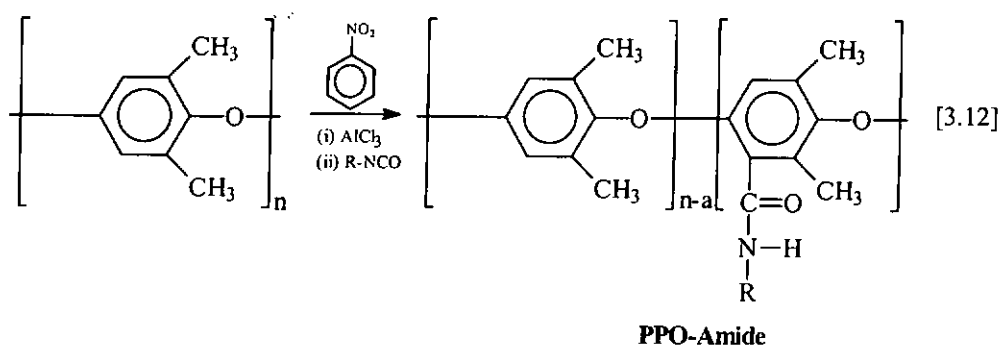
The phosphonylation in the brominated methyl group was reported by Cabasso et al. The reaction took place via the Michaelis-Arbuzov reaction [3.11]⁶. The organic phosphorous group in the side chain of PPO lowered the glass

transition temperature of PPO, acting as a plasticizer by loosening the chain packing and lowering the intermolecular forces.



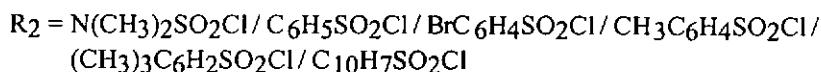
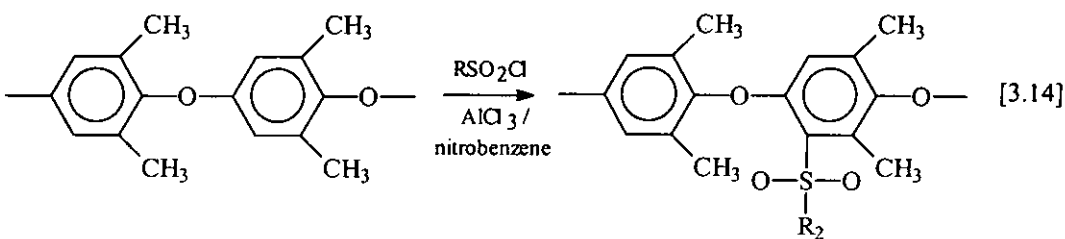
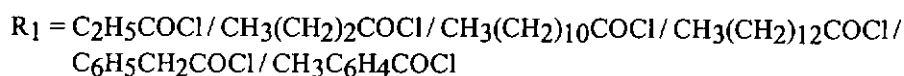
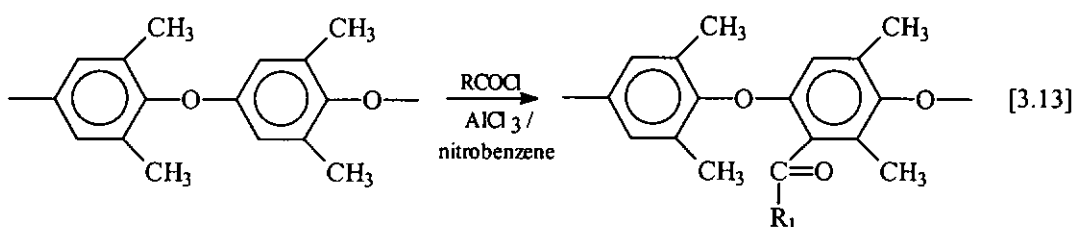
3.1.2.4 Friedel-Crafts reactions

Mahajan et al reported the modification of PPO by the incorporation of amide groups on PPO aromatic units by electrophilic substitution reaction with isocyanates in the presence of aluminum trichloride³⁴. This modification led to a series of random copolymers as shown in the following reaction scheme [3.12]:



The modified PPO was soluble in dipolar aprotic solvents like dimethyl sulfoxide (DMSO), N, N-dimethyl formamide (DMF), and N, N-dimethylacetamide.

Friedel-Crafts sulfonylation and acylation of the aromatic ring of PPO have also been investigated by Percec et al⁴³. Since the tetrasubstituted aromatic units of the PPO backbone were very nucleophilic, the substitution of the first available position from the aromatic ring could occur easily in one step by treatment with PPO and acid chlorides [3.13] or sulfonyl chlorides [3.14]. The deactivating effect and increased steric hindrance from the second electrophilic substitution on the sample PPO phenyl ring proceeded with great difficulty.



The T_g 's of PPOs modified with *p*-toluenesulfonyl chloride and dimethylsulfamoyl chloride are 265°C and 245°C, respectively. This result shows that substitution of PPO with rigid and bulky side groups decrease the flexibility of the polymer chain and thus the T_g of modified PPO increases. However, the T_g of

PPO modified with myristoyl chloride is only 116°C which is much lower than PPO's. It is due to the substituted flexible side groups which increase the intermolecular distances. Thus the Tg is lowered.

The solubility results show that most of the sulfonated PPOs and some acetylated PPOs become soluble in dipolar aprotic solvents such as N, N-dimethylformamide (DMF), and N, N-dimethylacetamide (DMA), and etc.

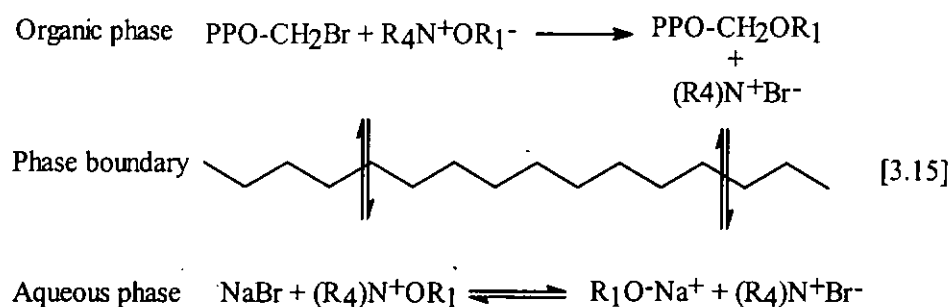
PPO substituted with *p*-toluenesulfonyl chloride or dimethylsulfamoyl chloride has an increase in permeability together with an increase in selectivity for CO₂ / CH₄.

3.1.2.5 Phase transfer catalysis

Chemical modification of PPO has been performed under phase transfer catalyzed (PTC) conditions⁴⁴. Four types of reactions, that is Williamson etherification, cyanide displacement, esterification, and heterocyclic group transfer, have been examined.

(1) Williamson Etherification Reactions

In the two-phase Williamson ether reaction, the base used was concentrated aqueous sodium hydroxide. The alcohol or the alkyl phenol was deprotonated by hydroxide either in the aqueous phase or at the interface, and then solubilized in the organic phase by ion pairing with the quaternary ammonium ion [3.15].



(2) Cyanide Displacement Reaction

The cyanide displacement reaction was performed by using crown ether with KCN and NaCN. The KCN gave the highest degree of substitution of PPO.

(3) Esterification Reaction

The phase transfer method facilitated the dissolution of carboxylates in nonpolar media. In this reaction, 18-crown-6 and tetrabutylammonium hydrosulphate (TBAS) have been used.

(4) Heterocyclic Group Displacement

Nucleophilic substitution of methyl brominated PPO with carbazole and indazole has been done. Under the same reaction conditions, the substitution of carbazole was higher than that of indazole.

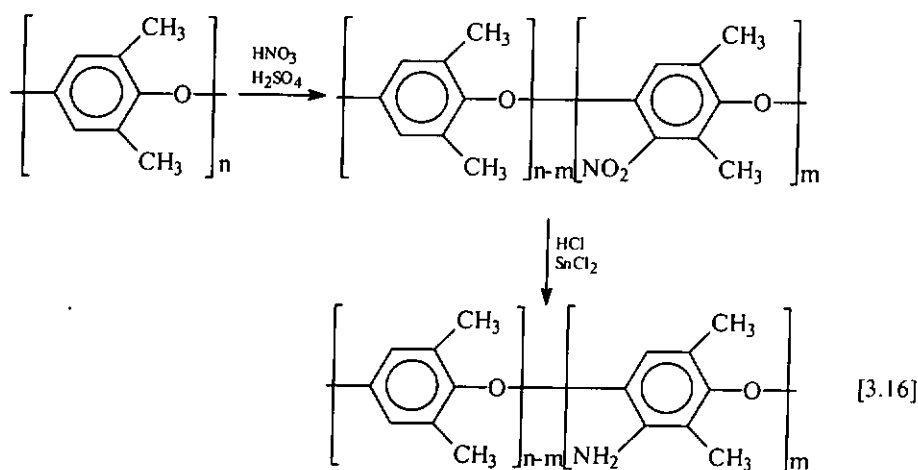
3.1.2.6 By Amination

Huang et al reported the modification of PPO by incorporating an amine group into the PPO backbone⁴¹. A maximum monosubstitution of 65 mol % was achieved. The reaction scheme is shown in [3.16].

The properties of aminated and nitrated PPO were investigated by DSC, solubility test, and X-ray diffraction.

Nitrated PPO with a monosubstitution degree below 28 mol % had two glass transitions, which were caused by the polar group that impeded the local chain segment movement, so there was another higher Tg besides a Tg mainly due to PPO. However, if the monosubstitution degree exceeded 28 mol %, only one exothermic peak appeared which might be due to the cross-linking that impeded all the chain segment movement. On the other hand, aminated PPO did not have Tg, but had a broad endothermic peak which was caused by intermolecular association that impeded the chain segment movement.

In solubility test, aminated PPO tends to be soluble in dipolar aprotic solvents with an increasing molar monosubstitution degree of the amino group. From the X-ray diffraction studies, the nitrated and aminated PPOs showed the pattern typical of amorphous materials.

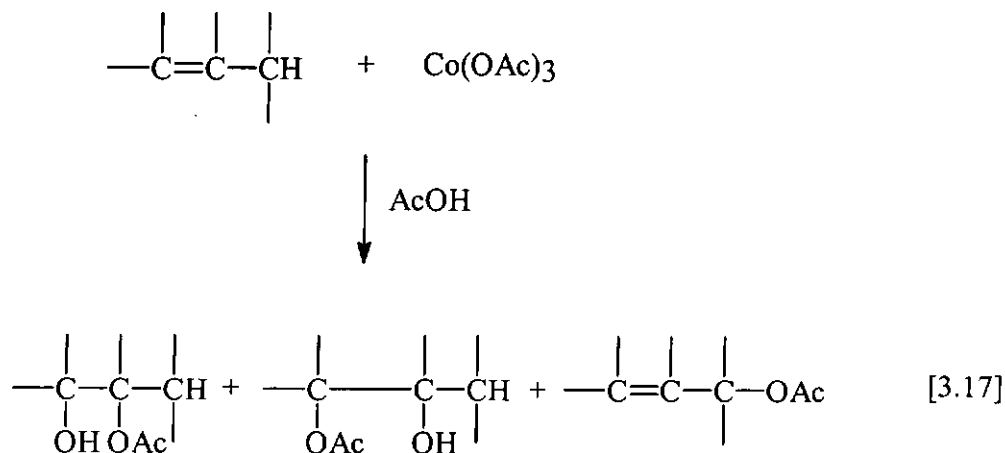


3.1.3 Examples of using cobalt(III) as an oxidant

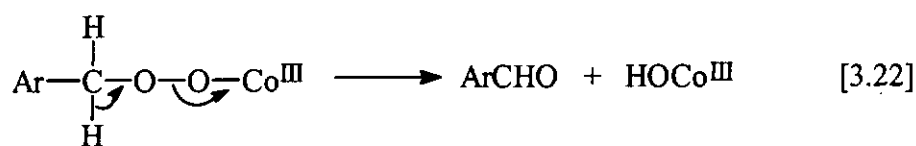
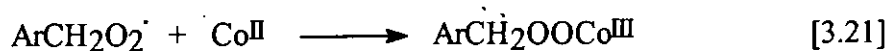
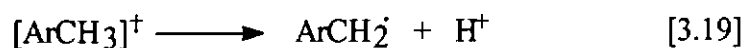
Cobalt(III) salts are potent reagents for the oxidation of various compounds such as aldehydes, alcohols, alkanes, alkylaromatics, and olefins¹⁹.

Morimoto et al reported that oxidation of styrene with cobalt(III) acetate in acetic acid at 60 °C under nitrogen¹⁹ gave six products: benzaldehyde, benzylidene diacetate, 1-phenylethane-1,2-diol 1-acetate, 1-phenylethane-1,2-diol 2-acetate, 1-phenylethane-1,2-diol diacetate and benzoic acid.

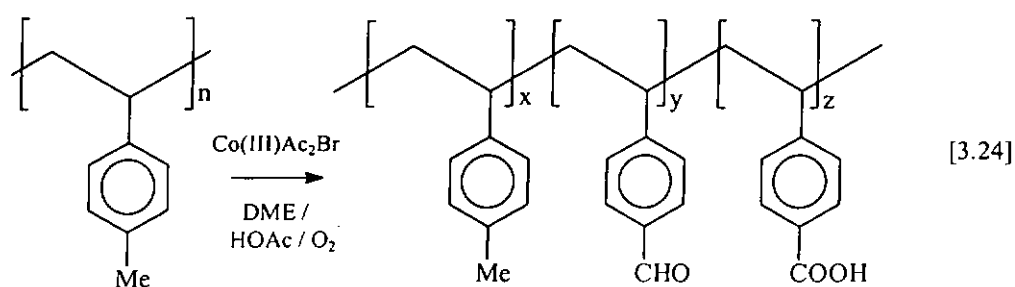
Morimoto et al have also reported that oxidation of alkenes by cobalt(III) acetate in acetic acid³⁷ is found to give allylic acetates and glycol monoacetates, the product ratios of which depend on the structure of the olefins. The general reaction scheme is shown as below [3.17]:



Another example is the oxidation of *p*-xylene to *p*-toluic acid by air in the presence of a cobalt catalyst¹, a reaction of practical importance since it forms the first step in Shell process for manufacturing terephthalic acid. The possible propagation cycle is shown in the reaction scheme:



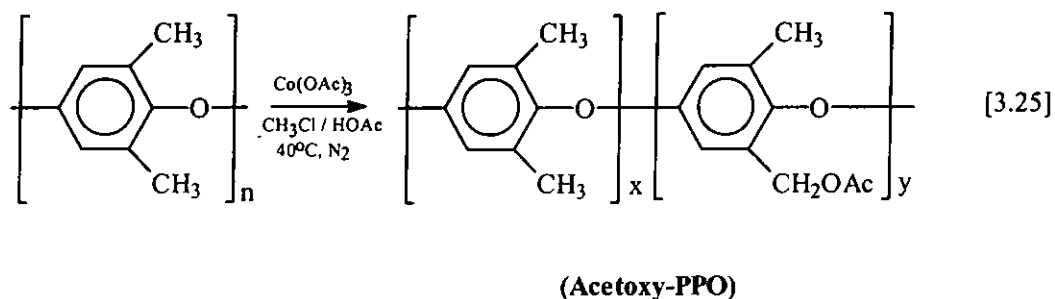
However, chemical conversion of polymeric alkyl aromatic compounds using cobalt(III) has received less attention. For example, selective oxidation of poly(4-methylstyrene) by cobalt(III) diacetate bromide complex in a mixture of acetic acid and 1,2-dimethoxyethane at 80°C under O₂ has been reported by Stover et al⁵². The general reaction scheme is shown as below [3.24]:



The modified poly(4-methylstyrene)s have molecular weights from 2,000 to 16,500 and contain up to 20% aldehyde and 90% carboxylic acid groups.

3.2 Objective

The selective modification of commodity polymers into reactive polymers bearing a range of functional groups is both of academic and industrial interest. In the first part of the thesis, selective oxidation of alkynes to the corresponding α , β -conjugated acetylenic ketones has been extensively studied via metal-catalyzed autoxidation. In this part of the thesis, functionalization of PPO to the corresponding acetoxy substituted PPO is investigated through a direct homolytic oxidation by metal complex [3.25]. Our objective is twofold: First, to develop a facile synthetic method to incorporate the pendant acetoxy functional groups onto PPO. Second, to investigate the effect of the functional groups and concentrations on their chemical and physical properties of the modified PPOs.



The modified PPO is characterized by FTIR spectroscopy and $^1\text{H-NMR}$. Physical properties of the modified PPOs are also studied including their thermal properties, intrinsic viscosity and average molecular weight.

3.3 Experimental Section

3.3.1 Materials

Commercially available PPO (Aldrich) was purified by precipitation with four fold excess methanol from chloroform solution. $\bar{M}_n = 23,400$, $\bar{M}_w = 36,000$, $\bar{M}_w/\bar{M}_n = 1.54$ (determined by gel permeation chromatography in THF, using polystyrene as standard). Cobalt (II) acetate (99%, Riedel-de-Haen), potassium permanganate (99.5%, Panreac), sodium oxalate (99%, M & B Lab Chemicals), ammonium iron (II) sulfate hexahydrate (Acros) and solvents were all used without further purification.

3.3.2 Procedures for preparing cobalt(III) acetate

3.3.2.1 Preparation of cobalt(III) acetate

Cobalt (III) acetate was prepared according to literature method with slight modification³¹: $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (16 g) was dissolved in a mixture of 170 mL of glacial acetic acid and 10 mL of acetic anhydride under vigorous stirring. Ozone was bubbled into the solution for about 7 days at room temperature (The ozone generator was set at 200 mg /hr). Color of the solution changed from pink to dark green during the reaction. After removing solvents by a rotary evaporator, a dark green solid which contained a mixture of Co(II) and Co(III) acetate was crushed into fine powder, and mixed with chloroform. The mixture was then filtered, followed by washing the filtrate (crude Co(III) acetate) with 1,2-dimethoxyethane (DME) to give shiny dark green crystal⁵⁹.

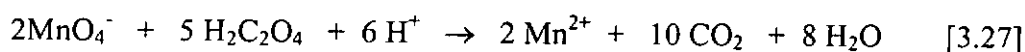
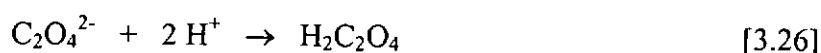
3.3.2.2 Preparation and standardization of 0.02M potassium permanganate⁶²

Preparation of 0.02 M potassium permanganate solution

Potassium permanganate, KMnO_4 (3.2 g) was transferred to a 1.5 L beaker. Deionized water (1 L) was added to the beaker, and covered it with a watch glass. The solution was then boiled gently about 15-30 minutes. After cooling the solution down to room temperature, it was filtered and stored in a glass-stoppered bottle in a dark place.

Standardization of KMnO_4 solution prepared with sodium oxalate

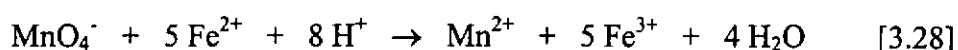
Sodium oxalate (1.70 g) was transferred into a 250 mL volumetric flask, and make up to the mark by adding deionized water. Shake the solution until all the sodium oxalate was completely dissolved. 25 mL of this solution and 150 mL of *ca* 1 M sulphuric acid were used for subsequent titration. The prepared KMnO_4 solution was titrated with oxalate solution at the room temperature until the first pink color appeared, the solution was further stirred until colorless, then warmed it to 50-60°C. The titration was continued until a permanent faint pink color appeared. The reaction took place according to the following equations [3.26] & [3.27]:



Standardization of 0.01 M ammonium iron (II) sulfate by 0.02 M potassium permanganate

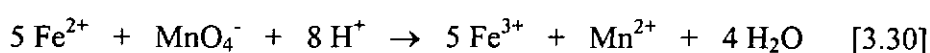
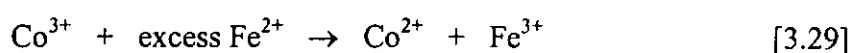
Ferrous ammonium (9.8 g) was transferred to a 250 mL volumetric flask, followed by the addition of 5 mL of concentrated sulphuric acid. The flask was

made up to 250 mL with deionized water and was shaken until the ferrous ammonium completely dissolved. The stock solution (25 mL) was acidified with 25 mL of 1 M sulphuric acid per titration. The solution was titrated with standardized 0.02 M potassium permanganate until the permanent pink color appeared. The reaction was taken place according to the following equation [3.28]:



3.3.2.3 Determination of cobalt(III) acetate concentration⁵¹

A cobalt (II)/(III) acetate mixture (0.266 g) was dissolved in deionized water and made up to 100 mL in a volumetric flask. The stock solution (25 mL) mixed with 25 mL standardized ammonium iron (II) sulfate was titrated with 0.02 M potassium permanganate until a faint permanent pink color formed. The reaction took place based on the following equations [3.29] & [3.30].



3.3.3 General Procedures for Optimization of reaction conditions

3.3.3.1 Purification of PPO

PPO (5.0 g) was dissolved in 200 mL chloroform, and then PPO was precipitated in 1 L of methanol (5 fold excess). The precipitated PPO was filtered by suction filtration and dried in a vacuum oven at room temperature for 24 hours.

3.3.3.2 Chemical modification of PPO by cobalt (III) acetate

Cobalt(III) acetate (68%) (0.033 mol, 13.56 g) was dissolved in 100 mL of acetic acid in a 3-neck round bottom flask equipped with a mechanical stirrer, condenser and an nitrogen inlet. 150 mL of chloroform solution containing 2 g of PPO (0.017 mol) was added into the reaction flask, followed by stirring of the mixture at 40 °C under nitrogen for 24 hours. After removing all solvents by a rotary evaporator at the end of reaction, the residue solid was re-dissolved in 100 mL of chloroform, followed by addition of 5 mL of 0.1 M NaOH solution in order to neutralize any acid presence. After washing the chloroform layer with the base, it was further washed with an excess amount of deionized water to remove all the cobalt (II) and cobalt (III) salts. The chloroform layer was then dried with anhydrous calcium chloride. Finally, an orange solid product (bulk) was obtained in a near quantitative solid recovery.

The orange solid product was re-dissolved in 50 mL of chloroform and re-precipitated in six folds of methanol. The precipitated PPO was separated by suction filtration, giving a yellowish solid which was the acetoxy-PPO. For the solution phase, methanol was removed by a rotary evaporator and a yellow gum-like product was obtained. Both samples were then dried in a vacuum oven at about 50°C for 48 hours.

3.3.3.3 Effect of reaction temperature on modification of PPO

The procedure was similar to Procedure 3.3.3.2, except that the reaction temperature was varied at room temperature, 40°C, 60°C and 80°C.

3.3.3.4 Effect of phase transfer agent and mixing, magnetic vs mechanical stirring on modification of PPO

The procedure was similar to Procedure 3.3.3.2, except adding 0.1 mol % of phase transfer agent. Mechanical and magnetic stirring were also examined.

3.3.3.5 Effect of solvents and solvent ratio on modification of PPO

The procedure was similar to Procedure 3.3.3.2, except using TFA or a mixture of acetic acid and acid anhydride. Furthermore, volume ratio of acetic acid and chloroform was altered as shown in Table 3.1.

Table 3.1 Effect of solvent ratio on modification of PPO

Experiment No.	Acetic acid (mL)	Chloroform (mL)	Solvent Ratio (acetic acid : chloroform)
1	15	30	1 : 2
2	18	27	1 : 1.5
3	20	25	1 : 1.25

3.3.3.6 Effect of cobalt(III) to PPO ratio on modification of PPO

The procedure was similar to Procedure 3.3.3.2 except the concentration of cobalt(III) acetate was varied as shown at Table 3.2.

Table 3.2 Effect of cobalt(III) acetate concentration.

Experiment No.	Mole Ratio of PPO to Cobalt(III) Acetate
5	1 : 3
6	1 : 2
7	1 : 1
8	1 : 0.5

3.3.3.7 Kinetic study of the modification of PPO

Similar to Procedure 3.3.3.2, except that about 5 mL of mixture was withdrawn at different time intervals.

3.3.4 Characterization of the modified PPO

Infrared spectra were recorded on a Nicolet Magna-IR 750 FTIR spectrophotometer using KBr disks. ¹H-NMR spectra were measured on a Fourier Transform Magnetic Resonance Spectrometer (Bruker DPX400 NMR) in CDCl₃. The percentage of acetoxy-benzyl groups was calculated on a basis of integration of aromatic and methylene protons. Gel permeation chromatograms (GPC) were taken on a Water's 410 GPC system with differential refractometer. Tetrahydrofuran was used as the eluent at a rate of 1 mL/min at 30°C. The GPC was calibrated with polystyrene standard samples, and the apparent molecular weights were calculated with the Waters baseline 810 software. Differential scanning calorimetry (DSC) was measured under nitrogen on a Mettler DSC30 at a heating rate of 20°C/min. Before the first heating scan was recorded, all samples

were heated to 300°C and slowly cooled down to room temperature. Intrinsic viscosity of PPO and modified PPO were determined using toluene as solvent in a Ubbelohde Viscometer at 25°C water bath.

Calculation of acetoxy % of acetoxy-PPO by using ¹H-NMR spectrum is shown as below:

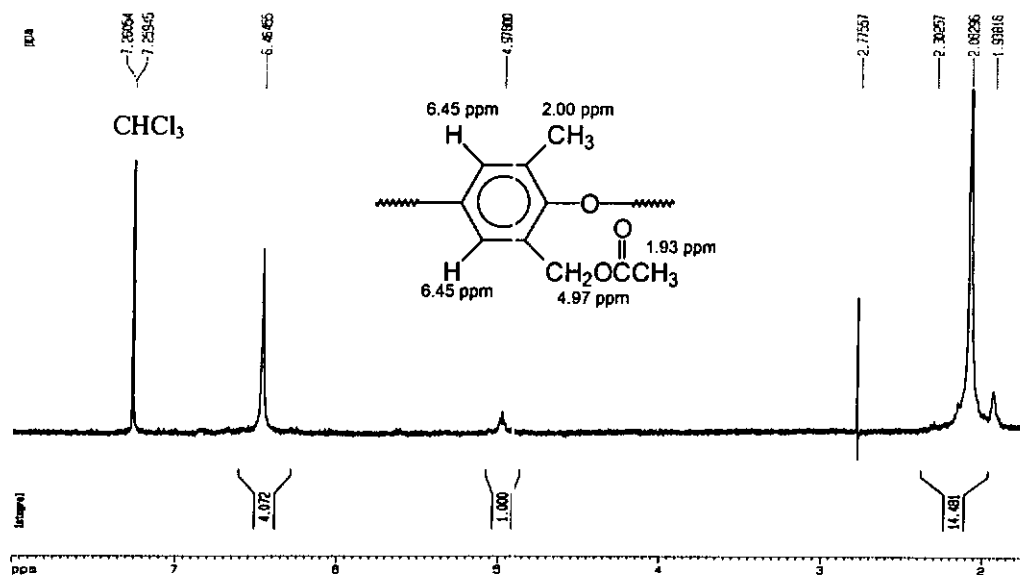


Fig. 3.2 ¹H-NMR spectrum of acetoxy-PPO in d-Chloroform

General equation:

$$\% \text{ of acetoxy} = \frac{\text{Integral of acetoxy-substituted benzyl protons}}{\text{Integral of aromatic protons}}$$

For example,

$$\begin{aligned} \% \text{ of acetoxy} &= \frac{1}{4.072} \\ &= 25 \% \end{aligned}$$

From the above spectrum, the % acetoxy of acetoxy-PPO is about 25 %.

3.3.4.1 Intrinsic viscosity measurement by Ubbelohde viscometer

Preparation of PPO and modified PPO stock solutions (2 g/dL)

PPO (0.5 g) and modified PPO (0.5 g) was dissolved in 25 mL toluene in a volumetric flask.

Determination of viscosity

Toluene (14 mL) was pipetted and transferred to a Ubbelohde viscometer that fasten vertically in a 25 °C water bath for about 10 minutes. The liquid was brought above the graduation mark of bulb, then was allowed to drain down the capillary. The timer was started exactly as the meniscus passed the upper graduation mark, and was stopped exactly as the meniscus passed the lower graduation mark. The efflux time was determined at least 3 times to give agreement within 0.1 sec or 0.1% of their mean.

Polymer solution (2 mL) was added exactly to the Ubbelohde viscometer. The solution was mixed well, and the draining time was recorded in the same way as stated above. Another aliquot of solution (2mL) was added in the viscometer again. The procedure was repeated for four times.

3.3.4.2 Analysis of the degraded PPO

2,4-Dinitrophenylhydrazine test^{A2}

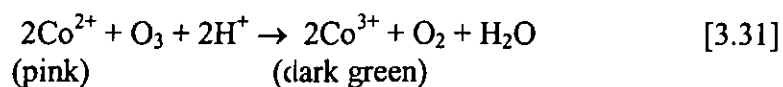
2,4-Dinitrophenylhydrazine (3.0 g) was dissolved in 15 mL of concentrated sulfuric acid. This solution was added into a mixture of 20 mL water and 70 mL of 95% ethanol. The solution was mixed thoroughly and filtered.

The above 2,4-dinitrophenylhydrazine solution (5 mL) was placed in a test tube, followed by addition of degraded PPO (3 mg) dissolved in a minimum amount of ethanol. The test tube was then shaken vigorously, and the solution was allowed to stand for about 15 minutes for precipitation. The formation of a yellow to orange-red precipitate was considered a positive result of 2,4-dinitrophenylhydrazine. The precipitate was filtered and washed with ethanol, then dried in a vacuum oven at room temperature. The dried precipitate was characterized by FTIR.

3.4 Results and Discussions

3.4.1 Determination of cobalt(III) acetate concentration

Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate in a mixture of acetic acid and acetic anhydride at room temperature for 7 days according to the following reaction [3.31].



The colour of suspension changed slowly from pink to dark green during the reaction. After removing the solvents, the crude cobalt(III) acetate was purified with chloroform, and then washed with 1,2-dimethoxyethane to give shiny dark green crystal.

Table 3.3 Results of determination of cobalt(III) acetate concentration^a

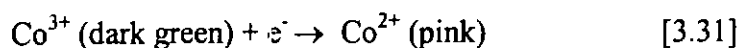
Experiment no.	% of Cobalt(III) acetate ^b
1	43%
2	55%
3	52%
4	56%
5	38%
6	35%
7	44%

^aConditions: cobalt(II) acetate (16 g) in 170 mL acetic acid and 10 mL acetic acid bubbled with ozone for 7 days at room temperature

^bPercentage of cobalt(III) acetate was determined by back titration of ferrous ammonium sulphate (0.01 M) with potassium permanganate (0.02 M)

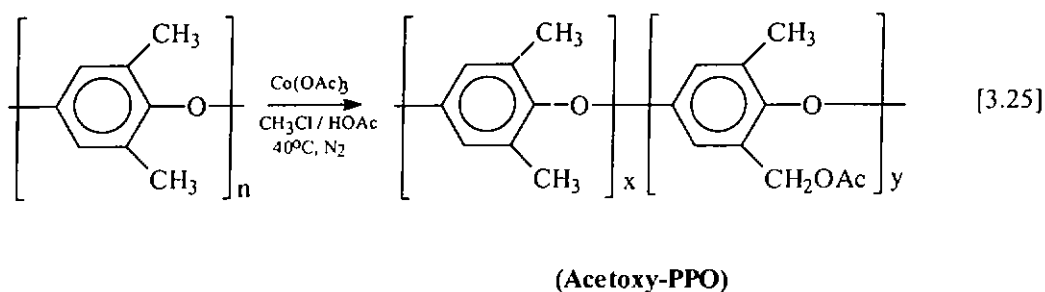
The conversion of cobalt(II) to cobalt(III) acetate was determined by adding excess ferrous ammonium sulphate solution, and back titrated with standardized 0.02 M potassium permanganate. This cobalt(III) acetate has been prepared several times and the results are summarized in Table 3.3.

Unfortunately, high percentage of cobalt(III) acetate was difficult to achieve even with prolonged time. Two possible factors may attribute to such a low conversion: (1) output power of ozone generator and (2) equilibrium between Co^{2+} and Co^{3+} in acetic acid. It was found that cobalt(III) acetate was quite unstable that could react with water to form oxygen in a redox reaction, and reduced back to Co(II) [3.31].



In order to achieve a better conversion and consistent result, only cobalt(III) acetate over 50% cobalt(III) content will be used in modification of PPO.

3.4.2 Optimization of reaction conditions



Reaction conditions studied:

- Temperature
- Phase transfer agent and mixing
- Solvent
- Solvent ratio
- Cobalt(III) concentration

3.4.2.1 Effect of reaction temperature on modification of PPO

The effect of reaction temperature on the conversion was investigated by carrying out the reaction at room temperature, 40°C, 60°C, and 80°C. At room temperature, only a trace acetoxy substitution occurred. When the temperature was raised to 40°C, percentage of acetoxy substitution increased to 24%. Similar result was obtained at 60°C. However, when temperature was further increased to 80°C, the percentage of acetoxy substitution was actually lowered. This observation might be explained by the conversion of active cobalt(III) back to cobalt(II) ions at higher temperature.

3.4.2.2 Effect of phase transfer agent and mixing, magnetic vs mechanical stirring on modification of PPO

Since the reaction was taken place in two phases, the conversion of PPO was generally low. In order to facilitate the electron transfer in two phases, cationic phase transfer agents such as tetrabutylammonium bromide and tetraheptylammonium bromide were added to the reaction mixture. Nonionic

phase transfer agent like poly(ethylene glycol) (PEG-400) was also examined. Unfortunately, addition of these phase transfer agents could not improve the conversion.

Interestingly, when a mechanical stirrer was used instead of magnetic stirrer, the percentage of acetoxy group was greatly enhanced from about 8% to over 20% under the same reaction conditions. Thus thorough mixing is very crucial for this reaction.

3.4.2.3 Effect of solvent on modification of PPO

According to the PPO solubility test, PPO could be dissolved in some aromatic and halogenated solvents, such as toluene, benzene, chlorobenzene, dichloroethane, and chloroform. However, cobalt(III) acetate could only be dissolved in polar solvents, such as acetic acid, acetic anhydride and trifluoroacetic acid. As a result, the reaction had to take place in two immiscible phases. In order to obtain higher conversion, different solvents of both phases were investigated.

For the cobalt(III) acetate phase, the use of acetic acid alone, or a mixture of acetic acid and acetic anhydride gave a comparable conversion, while using trifluoroacetic acid (TFA) as the solvent resulted in no reaction. The colour of the mixture changed from dark green to pink immediately after addition of TFA. This colour change indicated that the cobalt(III) ions were totally reduced to cobalt(II) ions. Therefore, no reaction could occur. For the organic solvents of PPO, although PPO dissolved well in chlorobenzene, dichloroethane and chloroform, they all gave a similar conversion, chloroform being finally selected because of its

easy removal after reaction. Thus, acetic acid and chloroform were selected as the solvents of cobalt(III) acetate and PPO, respectively.

3.4.2.4 Effect of solvent ratio on modification of PPO

In order to determine the effect of solvent ratio in modification of PPO, four different ratios of acetic acid and chloroform have been examined and is shown in Table 3.4.

Table 3.4 Effect of solvent ratio on modification of PPO^a

Experiment no.	Acetic acid (mL)	Chloroform (mL)	Solvent ratio (acetic acid : chloroform)	Acetoxy ^b (%)
3	15	30	1 : 2	26
4	18	27	1 : 1.5	25
5	20	25	1 : 1.25	30
6	20	20	1 : 1	ppt formed

^aReaction conditions: Mole ratio of PPO to cobalt(III) acetate = 1 : 1. Reaction was carried out at 40 °C under nitrogen for 24 hours.

^bPercentage of acetoxy was calculated based on ¹H-NMR spectrum.

According to the results, the ratio of acetic acid to chloroform of 1 : 1.25 gave the highest conversion. However, it is important to note that the volume of chloroform must be greater than the volume of acetic acid, otherwise PPO is precipitated out in an excess amount of acetic acid. In addition, the total volume of solvents should not be less than 40 mL in order to ensure a good mechanical stirring.

3.4.2.5 Effect of cobalt(III) acetate concentration

The cobalt(III) concentration was found to affect the conversion of PPO. Table 3.5 shows that increasing the PPO : Co (III) ratio from 1 : 0.5 to 1 : 2 increased the percentage of acetoxy substitution, but decreased when the ratio was further increased to 1 : 3. One possible cause might be that an excess amount of cobalt(III) acetate could not be completely dissolved in acetic acid which affected the homogeneity of the reaction system. In addition, the undissolved cobalt(III) acetate might affect the stirring efficiency.

Table 3.5 Effect of cobalt(III) acetate concentration on modification of PPO

Experiment no.	Mole ratio of PPO : Co ³⁺	Colour change	Acetoxy (%)
6	1 : 3	Dark green	16
7	1 : 2	Dark green	26
8	1 : 1	Dark brown	24
9	1 : 0.5	Pink	20

^aReaction conditions: Ratio of acetic acid to chloroform is 1 : 1.25. Reaction was carried out at 40 °C under nitrogen for 24 hours.

^bPercentage of acetoxy was calculated based on ¹H-NMR spectrum.

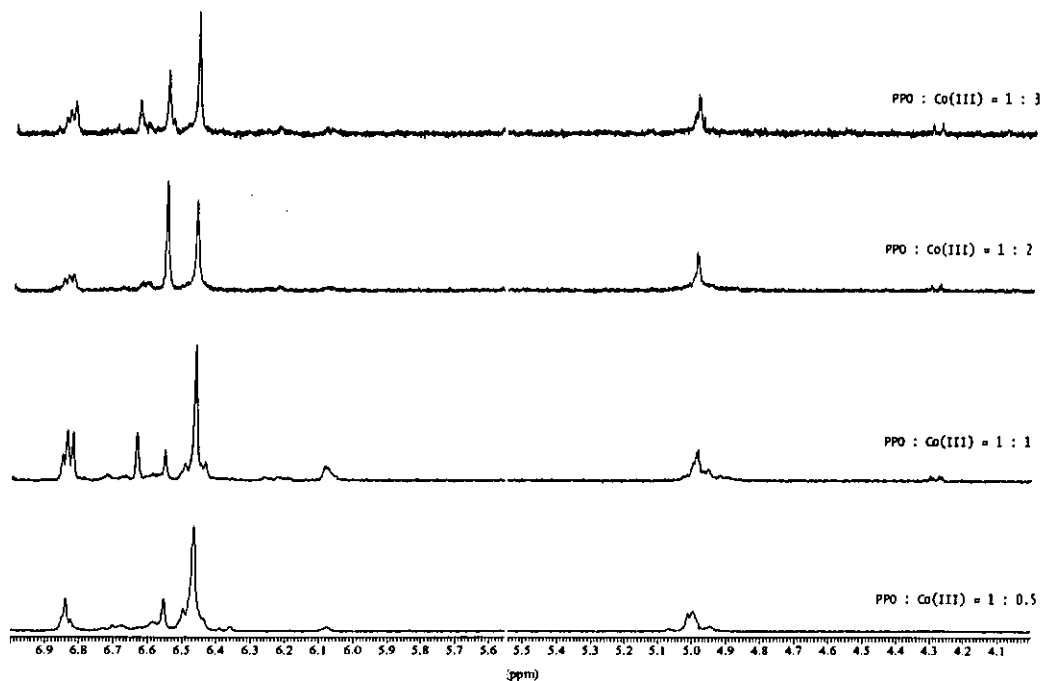


Fig 3.3 ¹H-NMR spectra of modification of PPO at different cobalt(III) acetate concentration

The ¹H-NMR spectra of the crude products prepared by different ratios of PPO to cobalt(III) acetate are illustrated in Fig. 3.3. It was found that PPO : Co(III) = 1 : 2 gave two major peaks at 6.45 and 6.55 ppm, while other ratios resulted in several peaks in 6.4 – 6.9 ppm. Furthermore, the splitting pattern of the peak at 5.0 ppm suggested the presence of acetoxy-substituted methylene. Hence, PPO : Co(III) = 1 : 2 was selected as the optimal ratio for subsequent studies.

3.4.2.6 Kinetic study of modification of PPO

Reaction kinetics was studied by withdrawing samples from the reaction mixture at 2 hours intervals. The crude product was isolated by precipitating the sample solution into an excess amount of methanol. The precipitate obtained was a yellowish solid, being the acetoxy-PPO. After removing the excess methanol, an orange-yellow gel-like residue was obtained, being the degraded PPO. Surprisingly, almost half of the PPO was degraded within one hour. But the degradation seemed to be slow down with prolonged reaction time. Details of degraded products and mechanism will be discussed in 3.4.3.7.

Fig. 3.4 demonstrates the percentage of acetoxy substitution as a function of reaction time. The percentage of acetoxy-substitution increased significantly up to 16 hours, while a further increase in reaction time had only a slight effect.

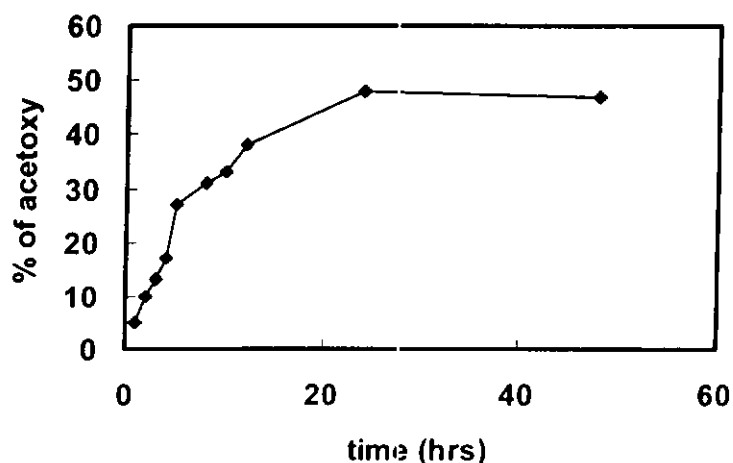


Fig. 3.4 Reaction kinetic based on the optimal conditions

3.4.2.7 Proposed reaction mechanism of modification of PPO

The proposed reaction mechanism for the formation of acetoxy-PPO is given in Fig. 3.5. PPO first interacted with cobalt(III), forming a cationic radical, followed by loss of a proton to a benzyl radical. The benzyl acetate is derived from the subsequent reaction of the benzyl radical with cobalt(III), then acetic acid.

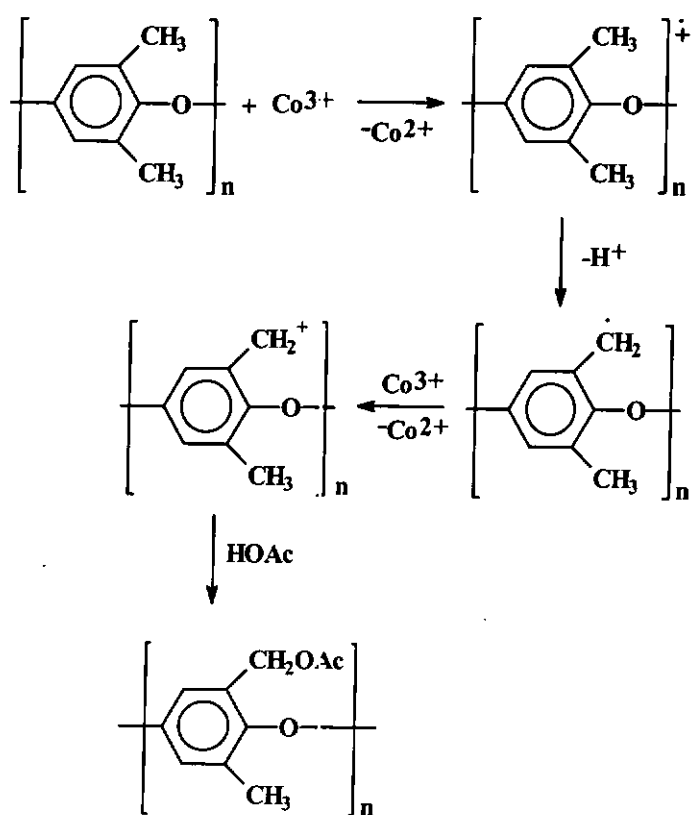


Fig 3.5 Proposed mechanism of modification of PPO

3.4.3 Characterization of the modified PPO

3.4.3.1 By $^1\text{H-NMR}$

Fig. 3.6 compares the $^1\text{H-NMR}$ spectrum of crude product, acetoxy-PPO and degraded PPO.

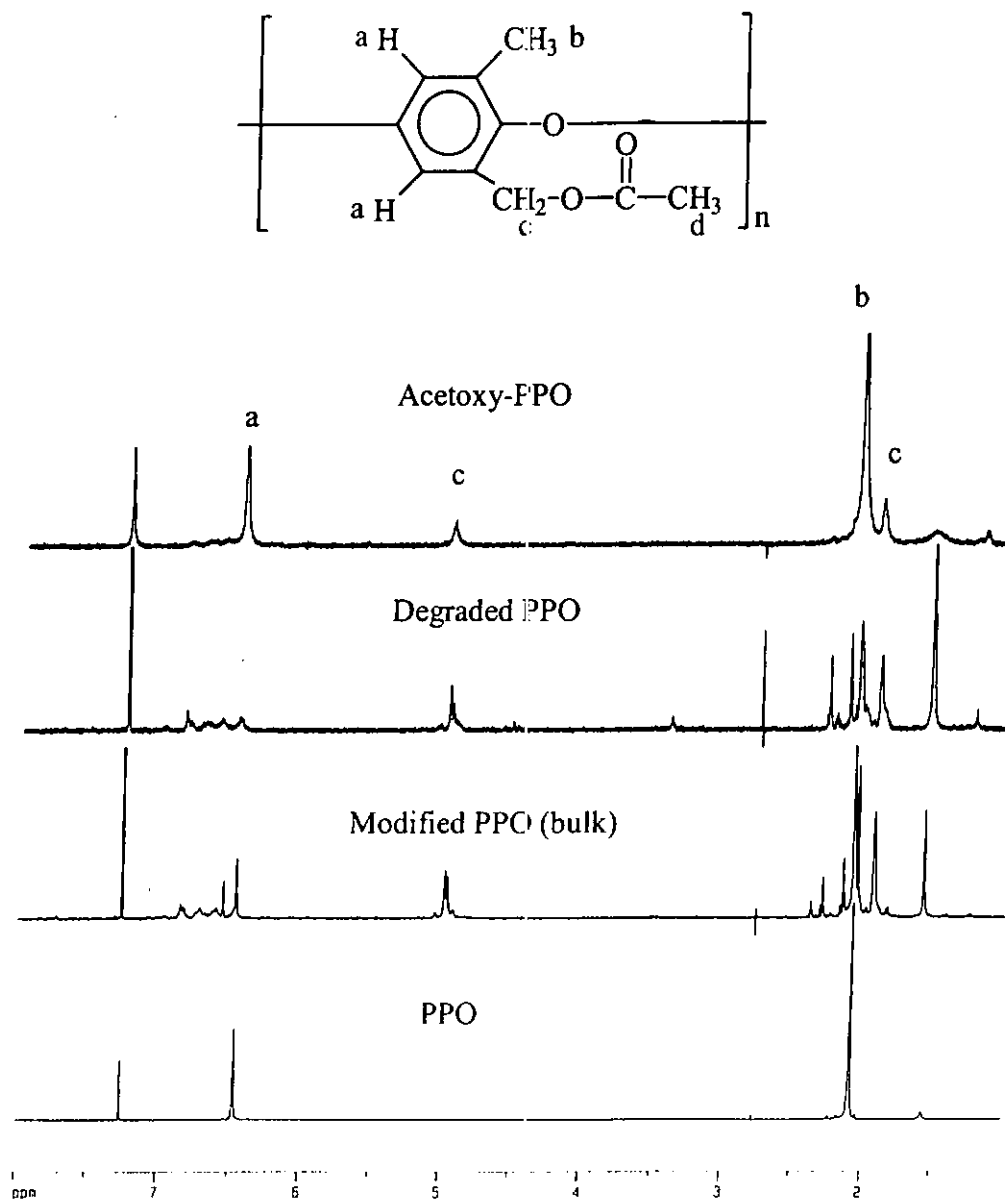


Fig. 3.6 $^1\text{H-NMR}$ spectra of PPO and modified PPOs

For the modified PPO (ppt), new peaks were found at 5.0 ppm as compared to pure PPO, which arised from the acetoxy-substituted benzyl protons (c). Peak at 6.5 ppm represents the aromatic protons (a) of the modified PPO. Single peaks at 2.0 ppm and 1.9 ppm are due to the methyl protons of (b) and (d).

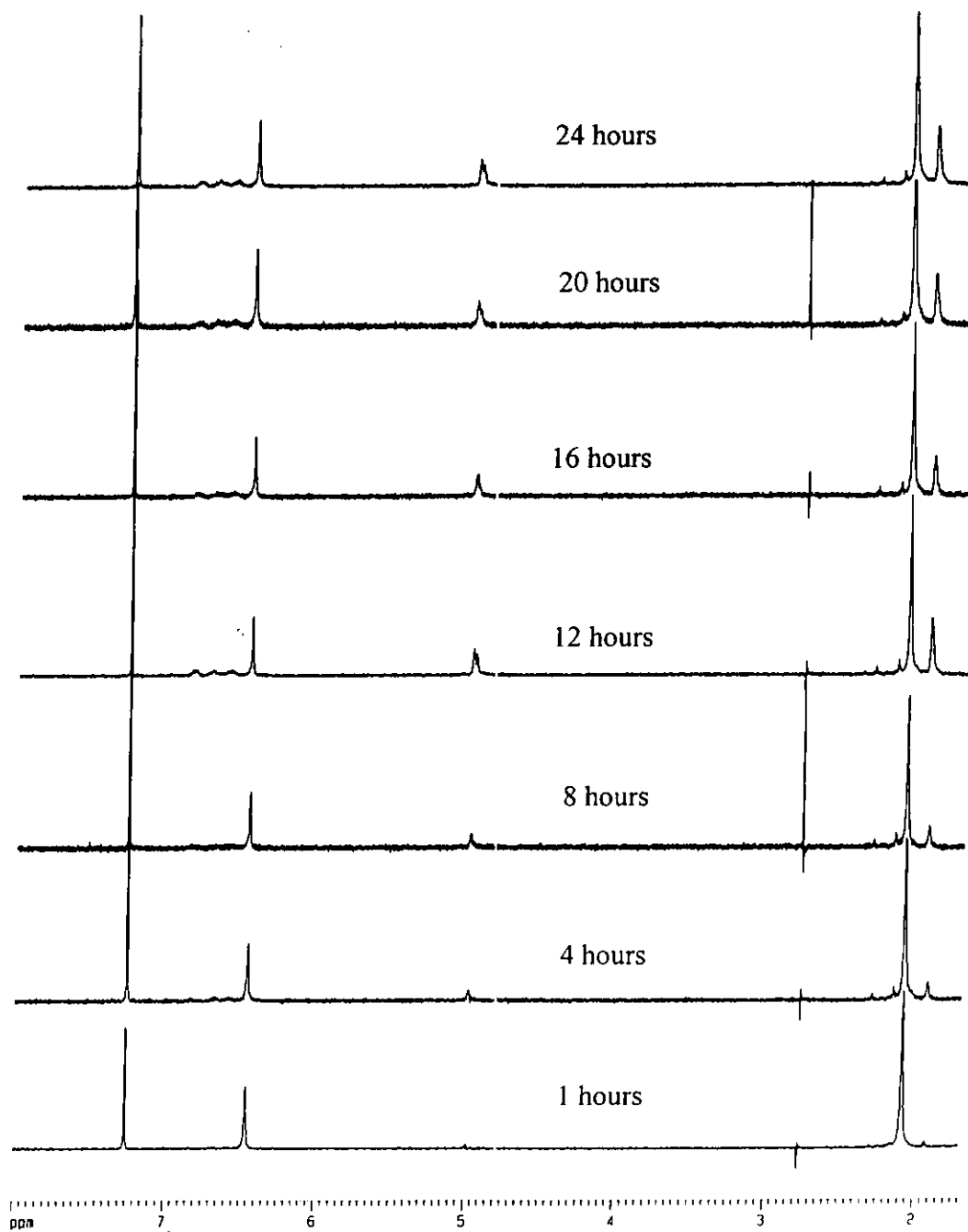


Fig. 3.7 ¹H-NMR spectra of modification of PPO as a function of time

Fig. 3.7 shows that peak intensive of benzyl protons (5.0 ppm) and acetate methyl protons enhanced with increasing the reaction time. These results suggested that the percentage of acetoxy substitution increased with time which is in good agreement with the kinetic study as discussed in 3.4.2.6.

3.4.3.2 By FTIR

Fig. 3.8 compares the FTIR spectra of PPO, modified PPO (bulk), acetoxy-PPO and degraded PPO.

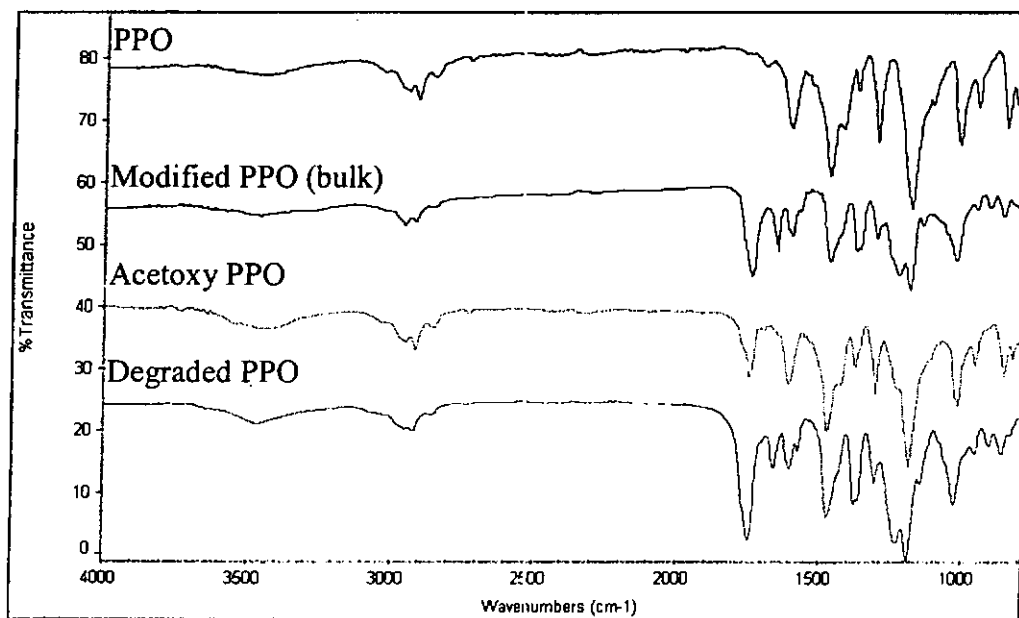


Fig. 3.8 FTIR spectra of PPO and modified PPOs

A strong new peak at 1743 cm⁻¹ was found in the acetoxy-PPO, which represents the C=O stretching of the acetoxy group. However, another peak at 1653 cm⁻¹, being quinone carbonyl group, was found to arise from the degraded PPO.

3.4.3.3 Thermal properties of the acetoxy-PPO

In the melt, thermal energy is sufficiently high for long segments of each polymer chain to move in random micro-Brownian motions. As the melt is cooled, a temperature is reached at which all long-range segmental motion ceases. This characteristic temperature is called glass transition temperature or T_g ¹⁴.

The T_g of polymer is strongly influenced by the chemical structure of the repeating unit. In general, several major factors affect the T_g of polymer, such as main chain flexibility, size of substituent, polarity of substituent as well as molecular weight.

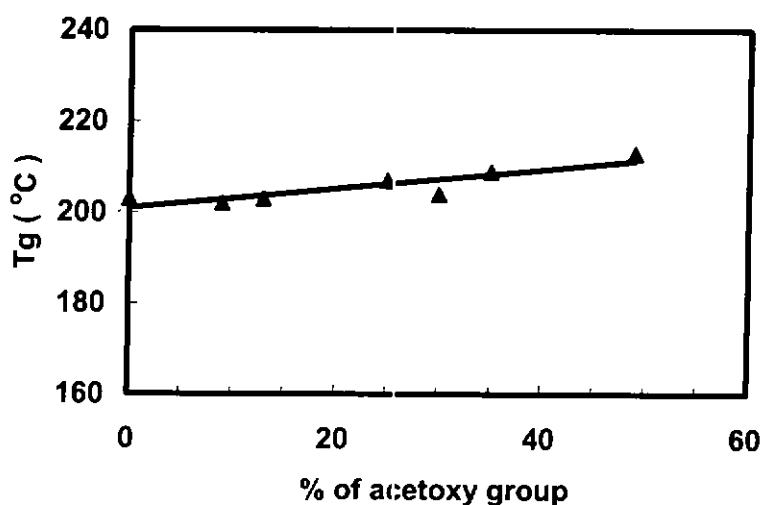


Fig 3.9 Relationship between % of acetoxy group of modified PPO and T_g

The T_g of modified PPO (ppt) was determined by differential scanning calorimetry (DSC). Fig. 3.9 shows that the T_g of modified PPO increased with increasing the % of acetoxy group. This effect may be due to the increase of

intermolecular force of the acetoxy-PPO as a result of the polarity of acetoxy group.

3.4.3.5 By intrinsic viscosity

Intrinsic viscosity of PPO, acetoxy-PPO and degraded PPO were determined using Ubbelohde viscometer at 25°C. Tables 3.7-3.9 summarize experimental data for the PPO. Fig 3.10 shows that by plotting $\eta_{sp} / \text{conc.}$, intrinsic viscosity $[\eta]$ was found by extrapolating the line to $c = 0$.

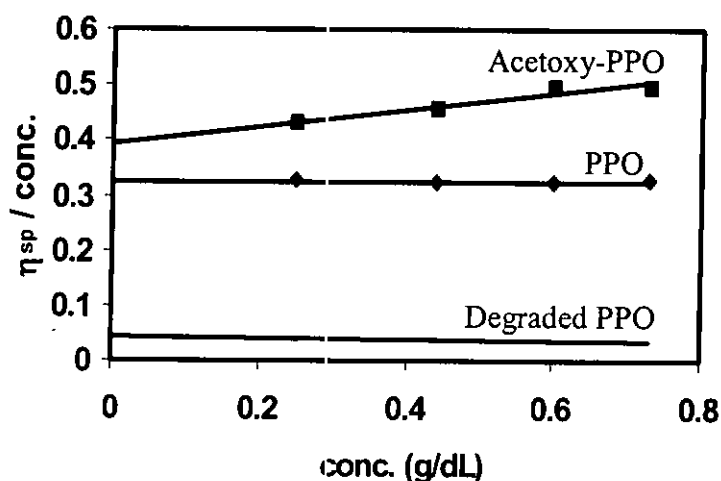


Fig 3.10 Determination of the PPO, acetoxy-PPO & degraded PPO Intrinsic viscosity from viscosity measurements at different concentrations

From Fig. 3.10, the intrinsic viscosity of PPO is determined to 0.3259 dL/g, which is comparable to the literature value. The intrinsic viscosity of acetoxy-PPO is 0.3941 dL/g which is slightly higher than PPO. However, the intrinsic viscosity of the degraded PPO is only 0.0438 dL/g, indicating that it has a very low molecular weight.

Table 3.6 Result of specific viscosity of PPO

Vol. of Solvent (mL)	Vol. of PPO solution added (mL)	Conc. of PPO (g/dL)	Average time (s)	η_{sp}	$\eta_{sp} / \text{conc.}$
14	0	0	8.9	-	-
14	2	0.25	9.63	0.0817	0.3266
14	2	0.44	10.17	0.1427	0.3243
14	2	0.60	10.63	0.1944	0.3240
14	2	0.73	11.01	0.2374	0.3265

Table 3.7 Result of specific viscosity of modified PPO (ppt)

Vol. of solvent (mL)	Vol. of PPO solution added (mL)	Conc. of PPO (g/dL)	Average time (s)	η_{sp}	$\eta_{sp} / \text{conc.}$
14	0	0	8.97	-	-
14	2	0.25	9.97	0.1078	0.4311
14	2	0.44	10.82	0.2011	0.4570
14	2	0.60	11.67	0.2966	0.4944
14	2	0.73	12.28	0.3622	0.4981

Table 3.8 Result of specific viscosity of degraded PPO

Vol. of Solvent (mL)	Vol. of PPO solution added (mL)	Conc. of PPO (g/dL)	Average time (s)	η_{sp}	$\eta_{sp} / \text{conc.}$
14	0	0	8.94	-	-
14	2	0.25	9.03	0.0101	0.0403
14	2	0.44	9.10	0.0179	0.0407
14	2	0.60	9.14	0.0224	0.0372
14	2	0.73	9.17	0.0257	0.0357

3.4.3.6 By gel permeation chromatography

One of the most widely used methods for the routine determination of molecular weight and molecular weight distribution is gel permeation chromatography (GPC).

The effects of % acetoxy groups (acetoxy-PPO) on the number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w) has been investigated by using GPC, and the results are shown in Table 3.9 and Fig. 3.11.

The result shows that the \bar{M}_n and \bar{M}_w decrease gradually as % of acetoxy increases. This might due to the degradation of PPO during the reaction.

Table 3.9 Molecular weight changes during reaction* (GPC)

Time (hrs)	% Acetoxy group	\bar{M}_n	\bar{M}_w	Polydispersity
0	0	23,400	36,000	1.56
1	5	16,813	25,180	1.50
2	10	12,251	21,481	1.75
3	13	12,306	24,811	2.02
4	17	10,172	21,278	2.10
8	31	9,964	21,509	2.16
10	33	10,077	21,571	2.14
12	38	10,227	21,665	2.12
24	48	9,477	20,225	2.13

*The samples (acetoxy-PPO) were obtained by reprecipitation in methanol

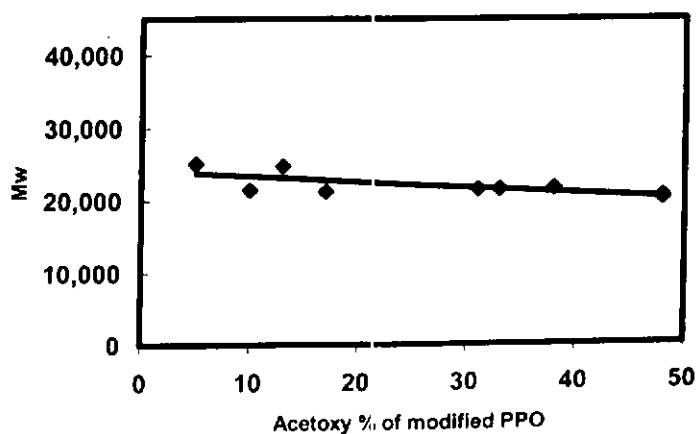


Fig. 3.11 Relationship between % acetoxy of modified PPO and \bar{M}_w

3.4.3.7 Analysis of the degraded PPO

Degradation of PPO to methanol soluble products was found during the reaction. It is especially serious in the beginning of the reaction. For example, after one hour, only about 50% of modified PPO were isolated by precipitation into methanol (Fig 3.12).

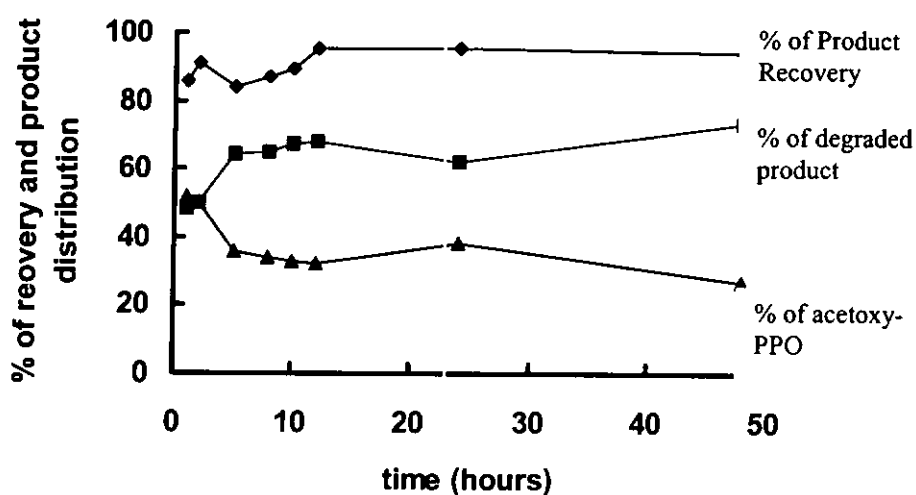


Fig. 3.12 Graph of % recovery and products distribution of modification of PPO

Appearance of the degraded PPO was similar to the appearance of benzoquinone. Therefore, 2,4-dinitrophenylhydrazine test was conducted to investigate the chemical structure of the degraded PPO.

2,4-Dinitrophenylhydrazine test

This test is originally used to test quinone. The formation of orange-red precipitate is considered as a positive test. The equation [3.32] is an example:

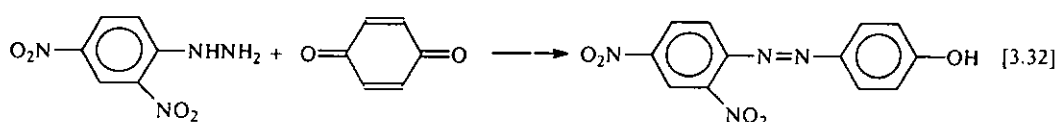


Fig. 3.13 shows that degraded PPO has two carbonyl peaks at 1744 and 1653 cm^{-1} . However, after the reaction with 2,4-dinitrophenylhydrazine, red-orange precipitate was formed and the peak at 1653 cm^{-1} disappeared.

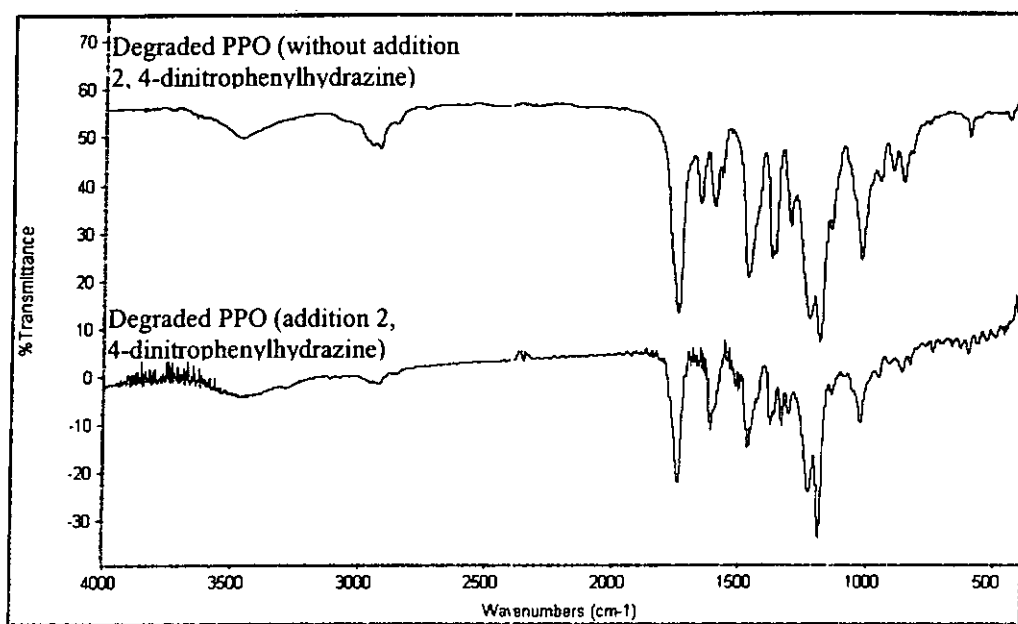
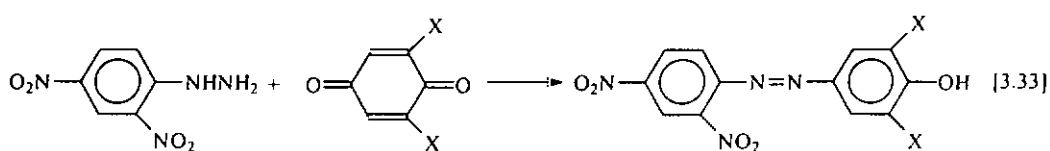


Fig. 3.13 FTIR spectra of degraded PPO and degraded PPO reacted with 2,4-dinitrophenylhydrazine

These results suggest that the degraded PPO contains benzoquinone derivatives. The proposed reaction scheme of 2,4-dinitrophenylhydrazine with of the degraded PPO is shown in [3.33].



X = CH₃ / CH₂OOCCH₃

3.4.3.8 Proposed reaction mechanism of degradation of PPO

The degradation may be caused by the reaction between the terminal hydroxy group of the PPO and cobalt(III) ions as shown in Fig. 3.14. In fact, Finkbeiner and Toothaker have reported that various oxidizing agents can attack PPO in acetic acid and produce either 4-acetoxy-phenols or *p*-benzoquinones¹⁵.

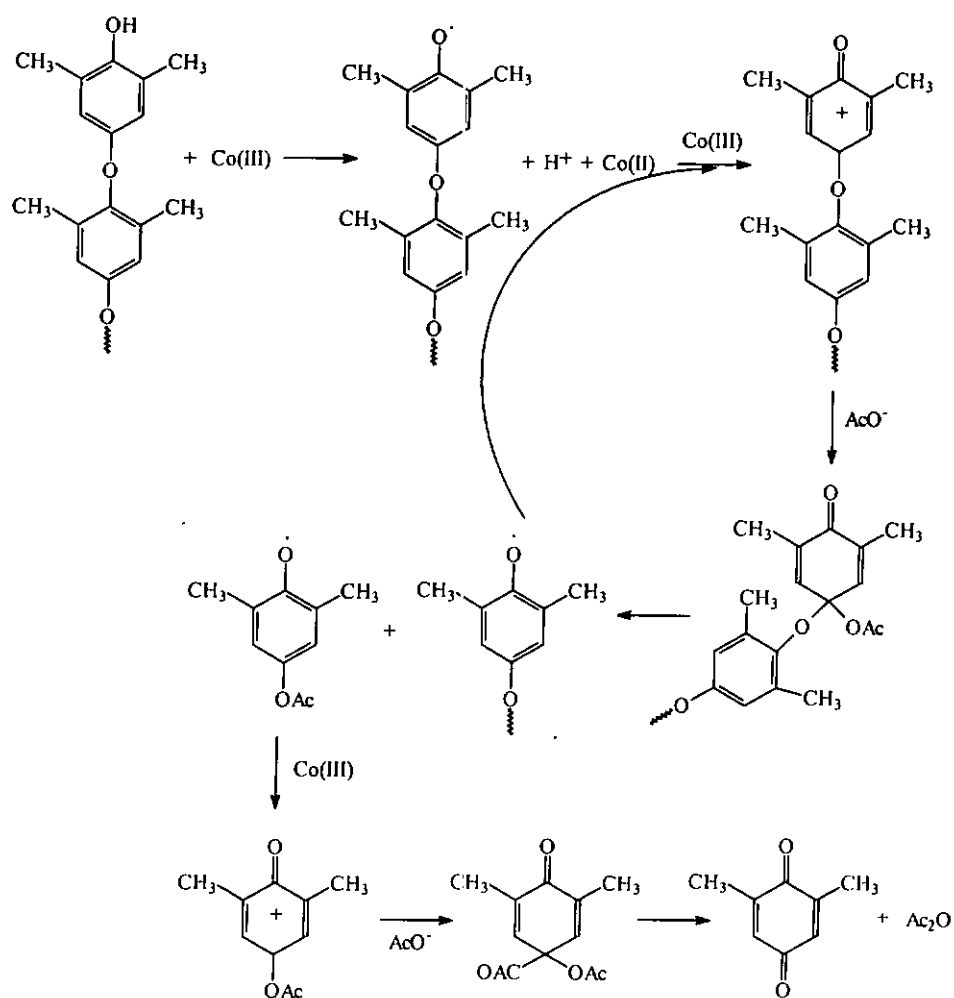


Fig 3.14 Proposed mechanism of degradation of PPO

3.5 Conclusion

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been successfully modified to acetoxy-PPO by using cobalt(III) acetate in a mixture of acetic acid and chloroform. By using optimal reaction conditions, i.e. PPO : Co(III) = 1 : 2, HOAc : CHCl₃ = 1 : 1.25 at 40°C with mechanical stirring, acetoxy-PPO with a range of percentage of acetoxy substituent on the benzyl could be obtained. It was found that T_g increased with increasing the percentage of acetoxy substituent, while the average molecular weight of the acetoxy-PPO decreased. During the reaction, degradation of PPO occurred, especially serious in the beginning of the reaction. This degradation may be caused by the reaction between the terminal hydroxy group of the PPO and Co(III) ions. For future study, it is suggested that terminal hydroxy group should be protected in order to prevent such degradation.

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