**REPUBLIC OF TURKEY**

**YILDIZ TECHNICAL UNIVERSITY**

**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

# SYNTHESIS AND CHARACTERIZATION OF ULTRAVIOLET AND THERMAL CURABLE PHOSPHORUS CONTAINING FLAME RETARDANT POLYMER

**Dilek KACMAZ**

MASTER OF SCIENCE THESIS

Department of Chemistry

Chemistry Program

Advisor

Prof. Dr. Tarık EREN

July, 2019

**REPUBLIC OF TURKEY**

**YILDIZ TECHNICAL UNIVERSITY**

**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

# SYNTHESIS AND CHARACTERIZATION OF ULTRAVIOLET AND THERMAL CURABLE PHOSPHORUS CONTAINING FLAME RETARDANT POLYMER

A thesis submitted by Dilek KACMAZ in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE is approved by the committee on 19.07.2019 in Department of Chemistry, Chemistry (Eng.) Program.

Prof. Dr. Tarık EREN

Yıldız Technical University

Advisor

**Approved By the Examining Committee**

Prof. Dr. Tarık EREN, Advisor
Yıldız Technical University _____

Assoc. Prof. Dr. Sevnur KESKIN DOGRUYOL, Member
Yıldız Technical University _____

Assoc. Prof. Dr. Ferda HACIVELIOGLU, Member
Yıldız Technical University _____

I hereby declare that I have obtained the required legal permissions during data collection and exploitation procedures, that I have made the in-text citations and cited the references properly, that I haven't falsified and/or fabricated research data and results of the study and that I have abided by the principles of the scientific research and ethics during my Thesis Study under the title of Synthesis and Characterization of Ultraviolet-Curable Phosphorus Containing Flame Retardant Polymer supervised by my supervisor, Prof. Dr. Tarık EREN. In the case of a discovery of false statement, I am to acknowledge any legal consequence.

Dilek KACMAZ

Signature

This study was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) Grant No: 2210.

*Dedicated to my family*

*and my best friend*

# ACKNOWLEDGEMENTS

I would like to acknowledge my advisor, Prof. Dr. Tarık Eren, who went above and beyond the duties of a thesis chairperson. He is a mentor by both advice and example. I am sincerely grateful for his selfless devotion towards my success as a graduate student.

I am also appreciative of Prof. Dr. Duygu Avci Semiz and her research group at BOUN to allow me to use their photo-DSC instrument. I would like to thank Tugce Nur Eren for her assistance with photo-DSC instrumentation.

I would like to acknowledge my peers for making me a more well-rounded scientist and teaching me throughout my graduate career: N. Ceren Süer, Ali Bayir, M. Nazrul Islam and, I. Ceren Acar.

Finally, I would like to thank my parents Sevda & Mustafa Kacmaz, my brother Ismail Kacmaz, and my close friends for their endless support and being there for me whenever I need encouragement.

Dilek KACMAZ

# TABLE OF CONTENTS

**LIST OF SYMBOLS** VIII

**LIST OF ABBREVIATIONS** IX

**LIST OF FIGURES** XI

**LIST OF TABLES** XIII

**ABSTRACT** XIV

**ÖZET** XVI

**1 Introduction** 1

1.1 Literature Review . . . . . 1

1.2 Objective of the Thesis . . . . . 5

1.3 Hypothesis . . . . . 7

**2 Flame Retardants** 9

2.1 The Importance of Flame Retardants . . . . . 9

2.2 Common Flame Retardants in the Market. . . . . 9

2.3 Phosphorus Containing Flame Retardant Polymers (P-FRs) . . . . . 12

**3 Phospha-Michael Addition** 18

3.1 Michael Addition of H-Phosphonates (Phospha Michael Addition) . . . . 18

3.2 Microwave Assisted Phospha-Michael Addition . . . . . 21

**4 Kinetics of Polymers** 23

4.1 Radical Chain Reaction . . . . . 23

4.1.1 Radical Chain Growth Polymerization . . . . . 24

4.2 Copolymerization . . . . . 27

4.2.1 Reactivity Ratio . . . . . 27

4.3 Finemann-Ross Method . . . . . 28

4.4 Kelen-Tudos Method (KT) . . . . . 31

4.5 Extended Kelen-Tudos Method (EKT). . . . . 31

**5 Experimental** 33

5.1 Materials and Methods . . . . . 33

5.1.1 Reagents . . . . . 33

5.1.2 Characterization . . . . . 33
5.2 Procedure for Synthesis of DK-2 Monomer . . . . . 33
5.3 Procedure for Microwave Assisted Synthesis of DK-2 Monomer . . . . . 34
5.4 Photopolymerizaton Procedure for DK-2 Monomer and DK-2:HEMA Copolymer . . . . . 34
5.4.1 Photopolymerizaton Procedure for DK-2 Homolpolymer . . . . . 34
5.4.2 Photopolymerization Procedure for DK-2: HEMA (1:1) Copolymer . . . . . 34
5.5 Synthesis of PAN:DK-2 (8:2) Copolymer via Free Radical Polymerization . . . . . 35
5.6 Kelen-Tudos/Finemann-Ross Calculation . . . . . 35
5.7 Microscale Combustion Calorimetry (MCC) Analysis for PAN:DK-2 (8:2) Copolymers . . . . . 35
**6 Results and Discussion** 36
6.1 Synthesis of DK-2 Monomer. . . . . 36
6.2 Synthesis of PAN:DK-2 (8:2) Copolymer . . . . . 37
6.2.1 Thermal Properties of PAN:DK-2 . . . . . 45
6.3 Photopolymerization of DK-2 Monomer and DK-2:HEMA (1:1) Copolymer . . . . . 47
6.4 Finemann-Ross & Kelen-Tudos Calculation for PAN:DK-2 (8:2) Copolymer. . . . . 50
6.5 MCC Analysis for PAN:DK-2 (8:2) Copolymers . . . . . 52
6.6 Conclusion . . . . . 52
**References** 54
**Publication from the Thesis** 63

# LIST OF SYMBOLS

| | |
|---|---|
| °C | Celsius Degree |
| δ | Chemical Shift Unit in Ppm |
| f | Feed Ratios of Copolymers |
| $T_g$ | Glass Transition Temperature |
| Q/s | Heat Flow per Second |
| h | Hour |
| Kcal | Kilocalorie |
| L | Liter |
| MHz | MegaHertz |
| mg | Miligram |
| ml | Mililiter |
| min | Minute |
| F | Mol Fractions of Copolymers |
| M | Molar Mass of the Monomer |
| nm | Nanometer |
| ppm | Parts per Million |
| $R_p$ | Polymerization Rate |
| $k_p$ | Rate Constant for Propagation |
| $k_t$ | Rate Constant for Termination |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| AHM | 3-(Acryloyloxy)-2-hydroxypropyl methacrylate |
| AIBN | Azobisisobutyronitrile |
| APP | Ammonium Polyphosphate |
| BSA | Bis(trimethylsilyl)acetamide |
| CPSC | Consumer Product Safety Commission |
| $CDCl_3$ | Deuterated Chloroform |
| DABCO | 1,4-Diazabicyclo[2.2.2]octane |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene |
| DK-2 | Synthesized Monomer Code |
| DMF | Dimethylformamide |
| DSC | Differential Scanning Calorimetry |
| DOPO | 9,10-Dihydro-9-oxa-phosphaphenthrene-10-Oxide |
| EKT | Extended Kelen-Tudos Method |
| EMDAT | Emergency Events Database |
| FR | Flame Retardants |
| FT-IR | Fourier Transform Infrared Spectrometer |
| GPC | Gel Permeation Chromatography |
| HEMA | 2-Hydroxyethyl Methacrylate |
| HRR | Heat Release Rate |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectrometry |
| Irgacure 651 | 2,2-Dimethoxy-2-phenylacetophenone |
| KT | Kelen-Tudos Method |
| LOI | Limiting Oxygen Index |

| | |
|---|---|
| MCC | Microscale Combustion Calorimetry |
| NIFC | National Interagency Fire Center Statistics |
| NIST | National Institute of Standards and Technology |
| NMR | Nuclear Magnetic Resonance |
| PAN | Polyacrylonitrile |
| PFRs | Phosphorus Containing Flame Retardants |
| PI | Polyimides |
| PU | Polyurethane |
| RoHS | Restriction of Hazardous Substances |
| SPR | Smoke Production Rate |
| TBD | Triazabicyclodecene |
| THF | Tetrahydrofuran |
| TEOS | Tetraethyl Orthosilicate |
| THR | Total Heat Release |
| TGA | Thermogravimetric Analysis |
| TLC | Thin Layer Chromatography |
| WEEE | Waste Electrical and Electronic Equipment |

# LIST OF FIGURES


**Figure 1.1** Area Burned, Number of Fires and Suppression Costs (Inflation Adjusted to 2016 Equivalent) for the USA with Linear Trend Lines ((NIFC) 1991-2015) [4] ..... 2

**Figure 1.2** Structure of Polyacrylonitrile ..... 5

**Figure 2.1** Structures of Ammonium Phosphate (left) and Aliminium Hydroxide (right) ..... 11

**Figure 2.2** Industrial Pathways to Various P-Based FRs from Phosphate Rock [1] ..... 13

**Figure 2.3** Renewable Sources for Phosphorus Containing Flame Retardants [1] ..... 14

**Figure 2.4** Flaming Combustion of Polymeric Material and the Role of P-FRs [1] ..... 16

**Figure 2.5** DOPO (a), DOPO-Based Hardener (b), Nonreactive Analog (c) [74] ..... 17

**Figure 2.6** Reaction Scheme of Phosphorus/Nitrogen Containing hb FRs ..... 18

**Figure 3.1** Examples of Phospha-Michael Addition Reactions [81] ..... 19

**Figure 3.2** Two Tautomeric Forms of H-Phosphonates ..... 21

**Figure 3.3** Reaction of Methyl Acrylate with Diethyl Phosphonate [96] ..... 21

**Figure 3.4** Microwave Assisted Phospha-Michael Addition Reaction Scheme of Phosphine Oxide-DOPO ..... 23

**Figure 3.5** $HP(O)Ph_2$ Addition to Alkenes [127] ..... 23

**Figure 4.1** Polymerization of an Alkene Species [128] ..... 24

**Figure 4.2** Subsequent Reactions of Some Radical Initiators [128] ..... 25

**Figure 4.3** Initiation and Propagation Steps in Radical Polymerization [128] ..... 25

**Figure 4.4** Combination and Disproportionation Chain Termination Reactions [128] ..... 27

**Figure 4.5** Inter- and Intra-Molecular Chain Transfer Reaction Polymerizations [128] ..... 28

**Figure 4.6** (a) Random Copolymerization, (b) Alternating Copolymerization, (c) Block Copolymerization, (d) Graft Copolymerization Chain Configuration [129] ..... 28
**Figure 4.7** Copolymer Structures According to Reactivity Ratios ..... 29
**Figure 4.8** Finemann-Ross Graph ..... 29
**Figure 4.9** Change in Copolymer Composition against Initial Monomer Composition (a) $r_1=r_2=1$; (b1) $r_1=8$, $r_2=0.125$; (b2) $r_1=0.125$, $r_2=8$; (c) $r_1=10$, $r_2=0.9$ ; (d) $r_1=0.9$, $r_2=10$; (e) $r_1=0.1$, $r_2=0.005$; (f) $r_1=20$, $r_2=10$ ..... 31
**Figure 6.1** Reaction Scheme of DK-2 Monomer ..... 39
**Figure 6.2** $^{1}H$ NMR Spectra of Starting Reagent AHM ..... 39
**Figure 6.3** $^{1}H$ NMR Spectra of DK-2 Monomer ..... 40
**Figure 6.4** $^{13}C$ NMR Spectra of DK-2 Monomer ..... 40
**Figure 6.5** $^{31}P$ NMR Spectra of DK-2 Monomer ..... 41
**Figure 6.6** Reaction Scheme of PAN:DK-2 Copolymer ..... 42
**Figure 6.7** $^{1}H$ NMR Spectra of PAN:DK-2 Copolymer ..... 43
**Figure 6.8** $^{31}P$ NMR Spectra of PAN:DK-2 Copolymer ..... 43
**Figure 6.9** FT-IR Spectra of PAN:DK-2 Copolymer ..... 44
**Figure 6.10** PAN:DK-2 (1) Integrated NMR Data ..... 45
**Figure 6.11** PAN:DK-2 (3) Integrated NMR Data ..... 45
**Figure 6.12** PAN:DK-2 (4) Integrated NMR Data ..... 46
**Figure 6.13** TGA Graph (Air) for PAN, PAN:DK-2 (1), PAN:DK-2 (2), PAN:DK-2 (4) Copolymers ..... 47
**Figure 6.14** TGA Graph ($N_2$) for PAN, PAN:DK-2 (1), PAN:DK-2 (2), PAN:DK-2 (4) Copolymers ..... 47
**Figure 6.15** Photopolymerization Reaction Scheme of HEMA and DK-2 Monomer ..... 46
**Figure 6.16** Conversion (top) and Polymerization Rate (bottom) Graphs for DK-2 Homopolymer and DK-2:HEMA Copolymer at 25°C and 70°C ..... 49
**Figure 6.17** Conversion (top) and Polymerization Rate (bottom) Graphs for PAN:DK-2 Copolymer at 25°C, 40°C and 70°C ..... 50

**Figure 6.18** G-H Graph Calculated from F-R Parameters.....52
**Figure 6.19** η-ξ Graph Calculated from K-T Parameters .....52

# LIST OF TABLES

**Table 1.1** Total Reported Fire Statistical Data, by Country, 1993-2016[3]..... 3

**Table 1.2** Human and Economic Losses from Wildfire Disasters by Global Region 1984 to 2013 [5] ..... 5

**Table 4.1** Propagating Site of Reactivity According to Polymerization Type.....25

**Table 6.1** Amount of Reagents Used in Copolymerization Reaction.....42

**Table 6.2** ICP-OES Analysis Values for P Element in PAN:DK-2 copolymer.....44

**Table 6.3** Monomer Feed Ratio and Monomer Mol Fractions.....51

**Table 6.4** Parameters for Kelen-Tudos and Finemann-Ross.....51

**Table 6.5** MCC Parameters for PAN:DK-2 Polymers.....53

# ABSTRACT

## Synthesis and Characterization of Ultraviolet and Thermal Curable Phosphorus Containing Flame Retardant Polymer

Dilek KACMAZ

Department of Chemistry

Master of Science Thesis

Advisor: Prof. Dr. Tarık EREN

Researchers are in quest of halogen free flame retardants such as phosphorus containing flame retardants (P-FRs) as they are the prominent alternatives to their counterparts. Stringent precautions for environment shifted the market toward environmentally-friendly formulations that prompt the use of nonleachable, covalently attached flame retardants to the polymer matrix attracted attention because of reducing the environmental pollution impact. Reactive functional phosphorus containing monomer makes it unprecedented for tailoring the properties of FRs that provide inherent flame retardancy to the materials. In this study, methacryl functional phosphorus containing monomer was synthesized and used further in free radical polymerization. DK-2 monomer synthesis was followed by using 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM) and diphenylphosphine oxide via phospha-Michael addition. DK-2 monomer and acrylonitrile were mixed in different feed ratio and polymerized via free radical pathway. Finemann-Ross and Kelen-Tudos methods were applied to calculate the reactivity ratios. The polymers were characterized by $^{1}H$, $^{13}C$, $^{31}P$ NMR, TGA, and

photopolymerization properties of DK-2 were conducted via photo-DSC experiment. Increasing the phosphorus monomer in the formulation resulted in increasing thermal properties of the materials.

**Keywords:** Flame retardant, phosphorus, polyacrylonitrile, free radical polymerization

# ÖZET

## Ultraviyole ve Isıl Kürleştirilebilen Fosfor İçerikli Alev Geciktirici Polimer Sentezi ve Karakterizasyonu

Dilek KAÇMAZ

Kimya Bölümü

Yüksek Lisans Tezi

Danışman: Prof. Dr. Tarık EREN

Son yıllarda araştırmacılar halojen içerikli alev geciktiricilerin önde gelen alternatifi fosfor içerikli olan halojensiz alev geciktirici arayışındadırlar. Sıkı çevresel önlemlerden dolayı alev geciktirici piyasası daha doğayla dost formülasyonlar içeren, çevre kirliliğinin etkisini azalttığı için fazlasıyla dikkat çeken, polimer matriksinde kovalent bağlanmış olarak bulunan alev geciktiricilerin kullanımını teşvik etmektedir. Reaktif fonksiyel fosfor içeren monomerler doğasında var olan alev geciktirici özelliklerinden dolayı, alev geciktiricilerdeki özelliklerin ayarlanılabilinirliği açısından benzersiz bir olanak sağlar. Bu çalışmada, metakril fonksiyonel fosfor içerikli monomer sentezlenerek serbest radikal polimerizasyonunda kullanılması amaçlanmıştır. Monomer 3-akriloiloksi-2-hidroksipropil metakrilat (AHM) ve difenilfosfinoksit ile fosfa-Michael katılması reaksiyonu ile sentezlenmiştir. DK-2 monomeri ve akrilonitril farklı ilerleme oranında karıştırılmış ve serbest radikal polimerizasyonu yöntemi ile polimerizasyon reaksiyonu gerçekleştirilmiştir. Finemann-Ross ve Kelen-Tudos metodları kullanılarak polimerizasyon hızı hesaplanmıştır. Farklı besleme oranına sahip polimerler elde edilerek $^{1}H$, $^{13}C$, $^{31}P$ NMR (nükleer manyetik rezonans) ile

karakterize edilmiş ve TGA (termogravimetrik analiz) yapılmış ve foto-DSC deneyleri yapılarak fotopolimerizasyon özellikleri incelenmiştir. Monomer formülasyonunda bulunan fosfor miktarının artırılması sonucunda materyallerin termal özelliklerinin arttığı bulunmuştur.

**Anahtar Kelimeler:** Alev geciktirici, fosfor, poliakrilonitril, serbest radikal polimerizasyonu

# 1
# Introduction

## 1.1 Literature Review

There is variety of applications where polymeric materials are used in nearly all area of modern life. However, hydrocarbon based polymers have a large fire load and high flammability, which create an inherent risk of fire as a drawback [1].

Due to being potentially exposed to impact of a fatal accident and toxic pyrogenic thermal stress; firefighters, drivers of toxic gas transporters, professionals handling these toxic gases, petrochemical factory workers are under high risk with the 36% of the total accidents [2].

There is a wide extant literature for fire statistics by plenty of organizations in recent years that pervades media reports around the world (Figure 1.1). An overview of the fire problem in the world for 1993-2016 is presented in Table 1.1 [3], and data by National Interagency Fire Center Statistics (NIFC) between 1991-2015 demonstrate burned area, number of fires and suppression costs [4] while the Emergency Events Database (EM-DAT) demonstrates that over the period 1901-2014 wildfire killed 3753 people (Table 1.2) [5].

Polymers' flammability behavior is defined based on several processes and/or parameters, such as ignition characteristics (delay time, ignition temperature, critical heat flux for ignition), smoke production, distribution of the product (in particular, toxic species emissions), burning rates (solid degradation rate and heat release rate), spread rates (flame, pyrolysis, burn-out, smolder), etc. [6].

Different methods can be used to protect materials against fire attack more effectively. High-performance polymers are categorized as polymers with a continuous operating temperature between 180 °C and 300 °C (or higher) and a temperature of degradation above 350 °C. Limiting oxygen index (LOI), cone

calorimetry, UL-94 are some of the usual fire testing methods that define the flame retardant ability of the polymers [7-9].

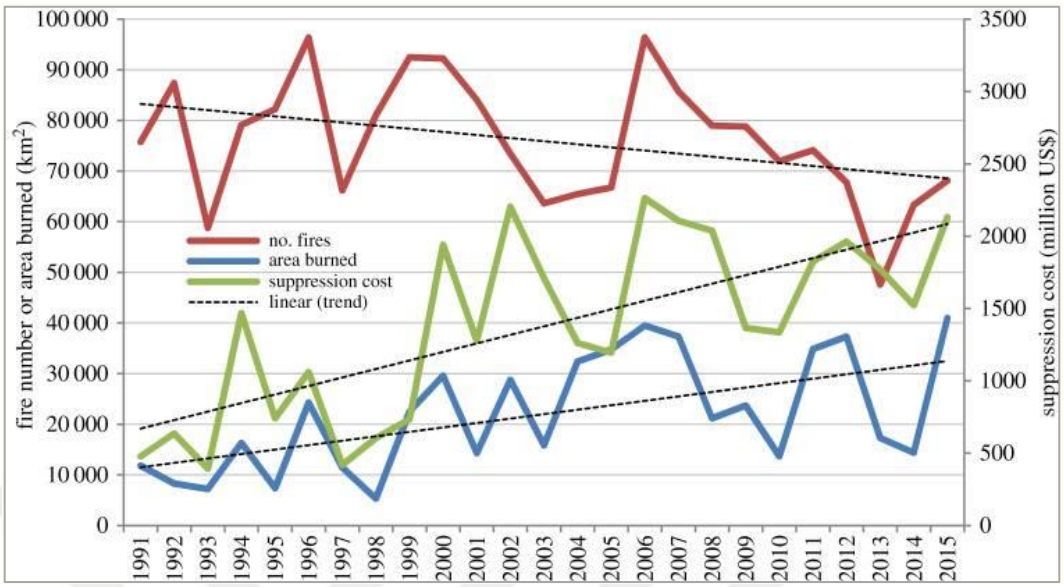



**Figure 1.1** Area Burned, Number of Fires and Suppression Costs (Inflation Adjusted to 2016 Equivalent) for the USA with Linear Trend Lines ((NIFC) 1991-2015) [4]

The use of specific materials as high performance polymers or inherently FR polymers does not mean they have suitable properties in terms of aging, cost, etc.; however, they may show low flammability and good efficiency [10].

Thermoset resins such as phenolics, polyimides, bismaleimides, and epoxies have inherent flame retardancy, and their fire resistance ranking is: phenolic > polyimide > bismaleimide > epoxy.

For instance, in the presence of a flame, polyimides (PI) cannot be ignited and are incandescent. They are significant heterocyclic polymers with diverse applications. With their degree of linking, the tendency of the organic inherently FR polymers to char increases due to the formation of gaseous decomposition products and as a result; the tendency to burn with an open flame diminishes [11].

**Table 1.1** Total Reported Fire Statistical Data, by Country, 1993-2016[3]

| Year | Number of Countries | Total population | Number of fires | Number of fire deaths | Average number of fires | Average number of fire deaths | |
|---|---|---|---|---|---|---|---|
| | | | | | | Per 100000 inh. | Per 100 fires |
| 1993 | 39 | 2.4 | 3.9 | 30.2 | 1.6 | 1.3 | 0.8 |
| 1994 | 27 | 1.1 | 4.0 | 29.5 | 3.6 | 2.7 | 0.7 |
| 1995 | 42 | 1.2 | 4.5 | 32.5 | 3.8 | 2.7 | 0.7 |
| 1996 | 43 | 0.9 | 4.0 | 29.1 | 4.4 | 3.2 | 0.7 |
| 1997 | 48 | 2.8 | 3.7 | 57.6 | 1.3 | 2.1 | 1.6 |
| 1998 | 47 | 3.0 | 3.6 | 51.7 | 1.2 | 1.7 | 1.4 |
| 1999 | 52 | 3.1 | 3.9 | 51.6 | 1.3 | 1.7 | 1.3 |
| 2000 | 57 | 3.3 | 4.5 | 56.2 | 1.4 | 1.7 | 1.2 |
| 2001 | 46 | 3.5 | 3.8 | 61.9 | 1.1 | 1.8 | 1.6 |
| 2002 | 41 | 3.5 | 4.3 | 62.3 | 1.2 | 1.8 | 1.4 |
| 2003 | 39 | 3.5 | 4.5 | 61.1 | 1.3 | 1.7 | 1.4 |
| 2004 | 44 | 3.5 | 4.1 | 60.1 | 1.2 | 1.7 | 1.5 |
| 2005 | 45 | 3.5 | 4.3 | 57.4 | 1.2 | 1.6 | 1.3 |
| 2006 | 37 | 3.6 | 4.1 | 52.2 | 1.1 | 1.5 | 1.3 |
| 2007 | 40 | 3.8 | 4.0 | 52.5 | 1.1 | 1.4 | 1.3 |
| 2008 | 31 | 3.5 | 3.6 | 48.3 | 1.0 | 1.4 | 1.3 |
| 2009 | 31 | 3.4 | 3.3 | 44.7 | 1.0 | 1.3 | 1.4 |
| 2010 | 33 | 2.2 | 3.2 | 46.1 | 1.5 | 2.1 | 1.4 |
| 2011 | 34 | 2.3 | 3.3 | 48.2 | 1.4 | 2.1 | 1.5 |
| 2012 | 35 | 1.1 | 3.1 | 23.7 | 2.8 | 2.2 | 0.8 |

| Year | Number of Countries | Total population | Number of fires | Number of fire deaths | Average number of fires | Average number of fire deaths | |
|---|---|---|---|---|---|---|---|
| | | | | | | Per 100000 inh. | Per 100 fires |
| 2013 | 31 | 1.1 | 2.5 | 21.7 | 2.3 | 2.0 | 0.9 |
| 2014 | 32 | 1.1 | 2.7 | 20.7 | 2.5 | 1.9 | 0.8 |
| 2015 | 31 | 1.0 | 3.5 | 18.4 | 3.5 | 1.8 | 0.5 |
| 2016 | 39 | 1.1 | 3.0 | 18.0 | 2.7 | 1.6 | 0.6 |
| Avg. | 39 | 2.5 | 3.7 | 43.2 | 1.5 | 1.7 | 1.2 |
| Total | | | 89.4 | 1036.0 | | | |

**Table 1.2** Human and Economic Losses from Wildfire Disasters by Global Region 1984 to 2013 [5]

| | No. events | People killed | Total people affected | Death rate/event | Economic cost (million US $) |
|---|---|---|---|---|---|
| Africa | 25 | 272 | 21 672 | 11 | 440 |
| America | 118 | 234 | 1 299 175 | 9 | 25 229 |
| Asia | 50 | 748 | 3 188 257 | 30 | 11 892 |
| Europe | 89 | 462 | 1 295 562 | 18 | 12 619 |
| Oceania | 21 | 224 | 74 320 | 9 | 2121 |
| Total | 303 | 1940 | 5 808 986 | 78 | 52 301 |

Polyacrylonitrile (PAN), an acrylate polymer family derivative, is a significant vinyl polymer [12]. Due to their properties such as radiation resistance, light resistance, and profound warmth retention, PAN is used widely in the textile industry.

Several techniques which include chemical reaction modification[13, 14] thermal oxidation [15] ,blending [16], and finishing [17] etc. have been applied in order to enhance the flame retardant properties of PAN fiber/fabrics.

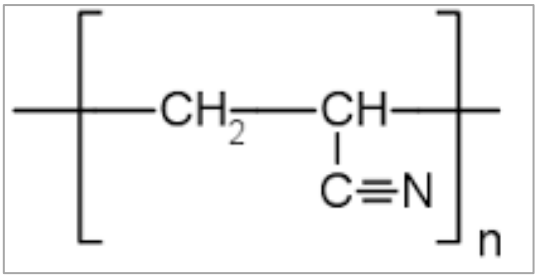



**Figure 1.2** Structure of Polyacrylonitrile

Studies have been conducted on the application of synergistic phosphorus-silica or phosphorus-nitrogen-silica to PAN fabrics. The effect of phosphoric acid on the flame retardant properties of PAN fabric using the tetraethyl orthosilicate (TEOS)-based sol-gel process was investigated by Necla Yaman [18] and the treated PAN fabrics showed nonflammable character. Ren Y. L. et al. also developed a sol-gel strategy [19] by using polyphosphorus acid containing organic-inorganic hybrid silica gel with P and N components to enhance the durability of the fire retardant PAN fabric; where the fabric exhibited decent flame retardancy when the heat release rate (HRR), smoke production rate (SPR), total heat release (THR) values were compared to the control sample. P and N doped hybrid $SiO_2$ matrix was formed on the surface of PAN fabrics, which was verified by several analytical techniques and the fire retardancy, morphology and structure were examined.

## 1.2 Objective of the Thesis

For the dynamics of Earth's climate and the development of biomass widespread, which has begun 350-440 million years ago, fire plays a significant role [20].

Humans coexisted with fire in the landscape, which affects the dynamics of the ecosystem and it can be used as an anthropogenic tool to comprehend these dynamics on a wide scale [21].

Fire has been a substantial factor for the rise of human societies whether it is a biomass burning or combustion practice of fossil fuels in engines and power stations [22].

According to the U.S. Fire Administration, in 2017, 1.3 million structure fires caused approximately 3,400 deaths, 14,670 injuries and 23 billion dollars in damages. Today's fire problem in lives and property diverts the researchers to find innovative fire protection resolutions [23].

Polymers have remarkable characteristics which include easy process and low weights for practical applications which cause an increase in their usage that can be proved with the ~9% increase in usage of plastics from 1950 to 2009 [24].

However, polymers burn easily under fire so, flame retardant type additives are added in the production of materials to increase heat resistivity.

In 2018, 2.26 million tons of flame retardant polymers were manufactured [25] In this regard, phosphorus containing compounds, inorganic additives such as t-BuLi, $Al(OH)_3$, $Mg(OH)_2$ are mainly used in the market. However, non-leaching from matrix long lasting flame retardancy, formation of non-toxic gases are challenging in the field. Covalent attachment of flame retardant to the polymer backbone is one of approach to obtain inherent flame retardancy.

FRs main usage purpose is to prevent fire-related hazards and to protect materials by inhibiting ignition. National Bureau of Standards (The National Institute of Standards and Technology) conducted a comparison of room combustion tests for FR plastics and non-FR plastics and they revealed that FR materials provide less heat release and lower concentration of toxic gases, less smoke and longer escape time due to the decrease of the burning material amount [26].

It is a major challenge to improve the flame retardancy of polymers to extend their usage in most applications since their development has some regulations.

U.S. Consumer Product Safety Commission (CPSC) has set two standards that encourage innovative approaches to protect consumer goods from fire containing polyurethane foam. The first standard focuses on rate of heat release which is recognized as the main reason for a fire to spread out of control to flashover point by the fire safety experts. In order to meet the CPSC regulation, mattress industry collaborated with NIST to develop new standard method. According to CPSC

estimation, this new standard will prevent fire related 1,330 injuries and 270 deaths every year [27].

The second standard focuses on upholstered furniture and is in the regulatory progress. According to the acting chairman of the CPSC, this second standard will be addressing the fires of upholstered furniture without any fire retardant chemical requirement. This proposal promotes furniture manufacturers to use smolder-resistant cover fabrics and interior fire resistant barriers to prevent furniture's internal filling material [28].

FR systems that do not release toxic gases have become more preferable day by day since they are halogen free, recyclable and environmentally friendly. Restriction of hazardous substances (RoHS) and the waste electrical and electronic equipment (WEEE) directives can be given as an example since they limit the use of bromine based FRs [29].

The objective of this thesis was to develop safe, eco-friendly flame retardant polymer to replace halogenated flame retardants. In this context, phosphorus containing flame retardant polymer was synthesized and the characteristics of this polymer were investigated. Flame retardant which can be used in textile, casings for home & office electronics, and paper industries, etc. was developed.

## 1.3 Hypothesis

Although bromine and chlorine containing flame retardants are still used greatly in the flame retardant industry, it is foreseen from the renewals of policies and standards that they will be completely banned. In 2004, polybrominated diphenyl ether has been banned in Europe. It is a major problem that inorganic based flame retardants have poor distribution in polymer matrix and it poses a threat for environment and human health that they are released from the surface with time. The need for flame retardants that are non-leachable and environmentally friendly along with having a good heat resistivity is increasing day by day. Many commercial polymers used in the polymer industry such as polyethylene terephthalate, polypropylene, polyethylene, polyurethane do not have inherent flame retardancy and in order to have this trait, additives are used in their formulation. Recently, it is

aimed to synthesize polymers that have inherent flame retardancy without additives. These polymers will be non-leachable and disperse better in matrix. Also, they will be less hazardeous to environment and human health.

In this study, AHM (3-(Acryloyloxy)-2-hydroxypropyl methacrylate) was functionalized with diphenylphosphine oxide to obtain phosphorus containing environmentally-friendly monomer. This monomer was copolymerized with PAN (polyacrylonitrile) which also has an inherent flame retardancy and environmentally-friendly properties. The obtained copolymers were tested by using TGA, ICP-OES, MCC, GPC analyses.

As a result of this study, polymers themselves have flame retardant properties without addition of any flame retardant, here phosphorus containing monomer, enhance the long lasting flame retardant behavior; non-leaching from the matrix to the environment, well dispersion in polymer matrix are also important advantages of these type of polymers.

# 2
# Flame Retardants

## 2.1 Importance of Flame Retardants

Flame retardants (FRs) are one of the polymeric materials that can be either incorporated into plastic compounds such as thermoplastic and thermoset polymers for procuring the flammability protection by slowing down and/or inhibit the initial phase of fire that develops [30].

Flame protection does not solely mean that the material in question does not burn. Some materials may have the ability to delay the fire or be affected by the heat caused by a fire in other ways. The materials that delay fire are called as flame-retardants while materials that resistant to fire known as fire resistants. Flame resistants include a number of fibres that have superseded the flame retardants to some extent which are some chemically treated textile materials. Flame resistant fibres are usually costly when compared with the flame retardants depending on the choice of flame protection of the manufacturer, i.e., the balance between price, safety and other quality requirements such as mechanical durability, comfort, design, etc.

It is substantial to comprehend the process of fire in textile materials and polymers, which is known as pyrolysis to understand the applications and benefits of flame retardants. Pyrolysis is the thermal decomposition of the material. The combustion process in case of fire causes the release of combustible toxic gases until the burning material is all consumed. The flame retardant at this point interrupts the combustion process in different ways.

## 2.2 Common Flame Retardants in the Market

Flame retardants not only are capable of preventing the ignition and spread of the fire but also act as a barrier for other layers of the materials which help to stop the fire propagation through the whole material structure.

Wider array of FRs exists since engineering polymers such as polyamides, polycarbonates, polyurethanes, polyethylene terephthalates have applications in advanced areas and they can be synthesized as thermoplasts, thermosets in foams, elastomers, foils or fibers, etc.

The predominant mechanism of the flame retardants during the combustion process classifies them and is related whether they act in the gaseous phase or in the condensed phase (liquid phase) by a physical effect. Halogen-based flame retardants react in the gaseous phase whilst phosphorus-based flame retardants are generally active in the condensed phase by stopping the reactions that occur in the combustion process.

$Al(OH)_3$ is one of the cheap and effective common FR; however, high loading requirement of it affects the properties of the material (e.g., opacity, tensile strength, coloration) [31]. There are commercially available P-FRs such as APP (ammonium polyphosphate) which retain the respective material properties due to significantly lower loadings [32-34]. Figure 2.1 below shows the structure of ammonium polyphosphate and aluminium hydroxide:

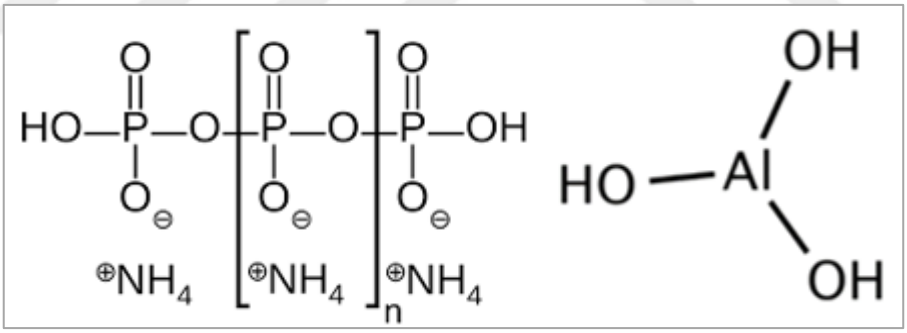



**Figure 2.1** Structures of Ammonium Phosphate(left) and Aluminium Hydroxide(right)

Nanofillers such as metal oxide nanoparticles [35], clays [36], carbon nanotubes [37] can perform as flame retardants due to forming a surface layer that inhibits the supply of polymer to the fire.

Despite the fact that there are many types of flame retardants, flame retardancy mechanisms can be generalized as a) gas phase flame retardants, b) char-forming flame retardants and c) endothermic flame retardants [38, 39].

Gas phase flame retardants (i.e., halogen, phosphorus): The heat released in the gas phase from the combustion process is reduced by the gas phase flame retardants by scavenging free radicals.

Char-forming flame retardants (i.e., intumescents, nanocomposites): Fuel release is prevented through binding up fuel as non-pyrolyzed carbon (char). Char forming flame retardants provide thermal insulation for underlying polymeric material by forming protective char layers.

Endothermic flame retardants (i.e., metal hydroxides, carbonates): A large amount of non-flammable gases as $H_2O$, $CO_2$ are released that reduce the temperature and dilute the flammable gas when endothermic flame retardants are used in the polymeric material that burns in a fire [40].

Although having a wide range of application, many halogen free flame retardants superseded the halogenated ones due to exhibiting a better performance by decreasing the heat and smoke release and limiting the fire propagation.

FRs have turned into a global industry that contains researchers, technologists, and professionals from many fields that are employed by companies, organisations, etc. FRs plays an important role in modern society by decreasing the number of fires and limiting the consequences of fires [41], [42] and in connection with these inorganic compounds as well as organohalogen chemicals, organophosphate esters and less common nitrogen containing compounds have been developed as flame retardants [43], [44]. Electronics in the manufacturing of circuit boards, components and parts used in ovens, casings for home and office electronics, microwaves, dishwashers, refrigerators, and dryers, mobile phone equipment, textile, and paper industries are the fields of applications for halogenated flame retardants [45].

A 'good' FR must have i) cost-effective conservation of the material properties to the greatest possible extent, ii) have the properties with matching polymer processing and pyrolysis characteristics, iii) be environmentally friendly, sustainable and recyclable [1]. Besides that long lasting, non-leaching production of non-toxic gas during flame are important properties for new generation flame retardants.

## 2.3 Phosphorus Containing Flame Retardant Polymers (P-FRs)

Researchers are in quest of halogen free flame retardants such as phosphorus containing flame retardants (P-FRs) since they are the prominent alternatives to their counterparts [39]. Stringent precautions for environment shifted market toward environmentally friendly formulations that prompt the use of halogen free flame retardants [46-48] and nowadays, recyclable FR materials aroused attention because of reducing the environmental impact [49-51]. Environmental considerations rank first besides the significant factors such as efficiency, lower density and light stability for the research and development of P-FRs [52].

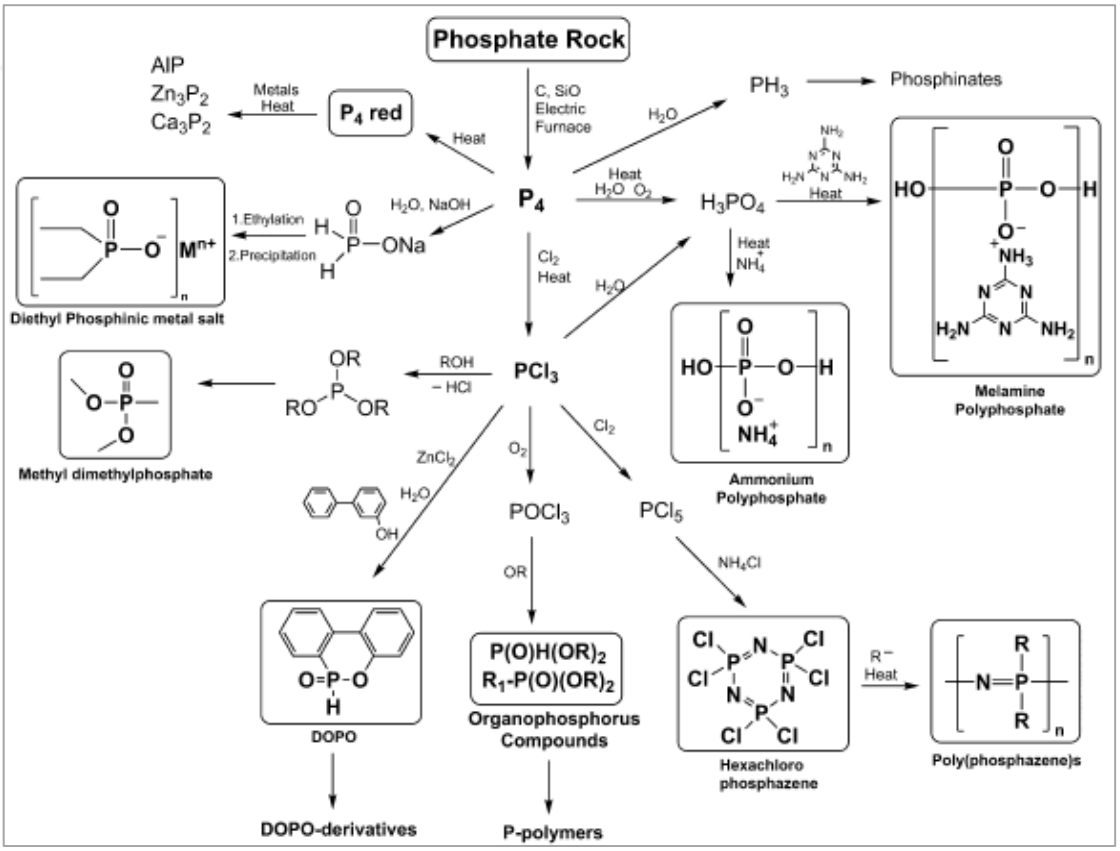



**Figure 2.2** Industrial Pathways to Various P-Based FRs from "Phosphate Rock" [1]

Varied structure from organic to inorganic of P-FRs; varied P content in the P-FRs (e.g., from red P to DOPO); and various oxidation state from 0 to +5 gives P-FRs versatile properties that generate different mechanism both in condensed and gas phase. All these aspects of phosphorus make it unprecedented for tailoring the

properties of FRs as glass transition temperatures ($T_g$), or density by changing the binding pattern (e.g., from alkyl to phenyl groups).

Due to its versatile chemistry, multiple mechanisms and high effectivity at low loadings phosphorus have a substantial role in halogen free flame retardancy (Figure 2.2).

The phosphorus life cycle is required to be considered for FRs and also for agriculture, particularly as there is no other alternative for phosphorus element. Accordingly, preservation of phosphorus chemicals and phosphate fertilizers must be supplied with sustainable phosphate management, recycling strategies and new methods to employ feedstock for future generations.

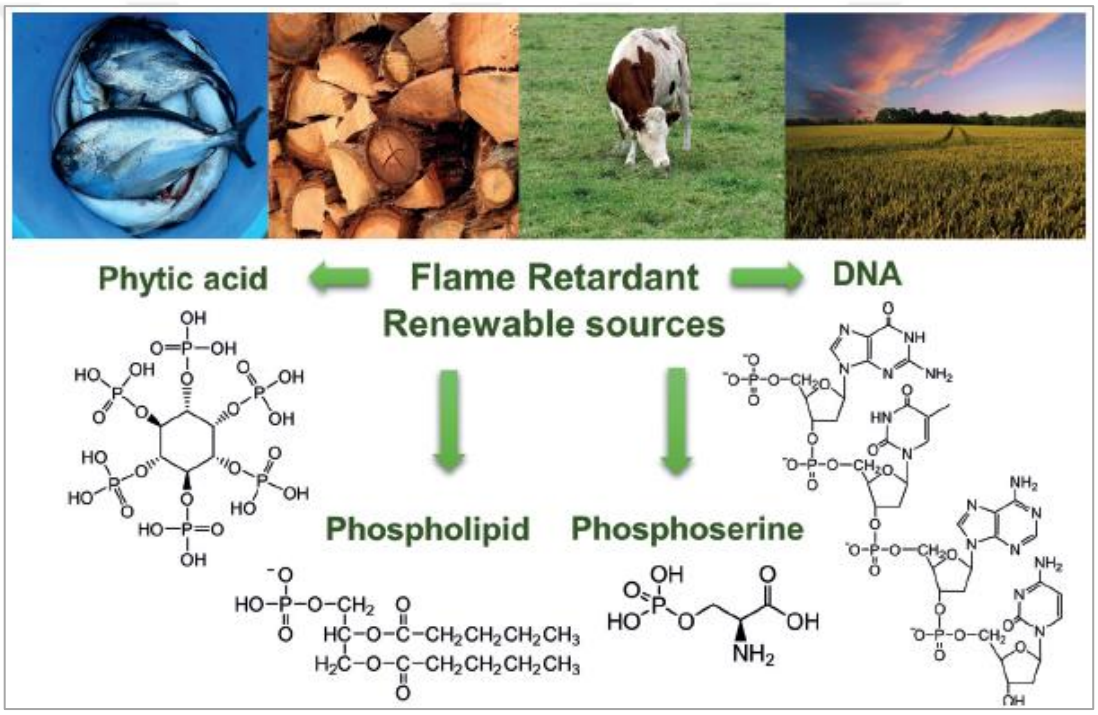



**Figure 2.3** Renewable Sources for Phosphorus Containing Flame Retardants [1]

Isolating P derivatives for the valorization of by-products from the agro or food industry by extracting the phytic acid or biomacromolecules (deoxyribonucleic acid and caseins) can be effective strategies which enable P-FRs to be a part of sustainable phosphorus chemistry (Figure 2.3) where M is usually zinc or aluminum.

The structure property relationship and the interaction between the flame retardant and polymer matrix during thermal decomposition determine the effectivity of the flame retardancy eloquently. The general modes of action for flame retardants are condensed and gas-phase mechanism which successful P-FRs utilize both (Figure 2.3) [53-56].

The decomposition temperature of matrix and FR is crucial for these mechanisms; consequently; pyrolysis specifics and explicit polymer processing should match for the FR in question. Decomposition of premature FR should be avoided in order to ensure chemical interaction during pyrolysis but not during processing, yet the FR decomposition temperature and overlap of the polymer should be maximized [57-59].

Implementation of P-FRs both as additive or reactive components is possible and reactive P-FR components have an inherent flame retardant material property due to its participation in material's constitution. They are mostly used in thermosets like epoxy resins, unsaturated polyesters or polyurethane foams. Functional groups such as alcohols, epoxy, amines, halogens, etc. can be used to equip these FRs, which allow incorporation into polymer matrix during curing [60], [61]. Reactive FRs can be covalently attached to the network which results in having a lower impact on the physical properties of the product in epoxy resins, on the contrary; additive FRs causes decreasing in glass transition temperatures ($T_g$) and are prone to leach. Reactive FRs also decrease the potential wastewater pollution because of its low leaching; however; due to their low price additive FRs are dominant in the market. Reactive FRs have a number of advantages though each matrix requires a novel designed and formulated reactive FRs, whereas additive FRs can be used for different matrices [62-64]. P-FRs can achieve both since these materials have well FR properties and can be both degradable and biocompatible [65].

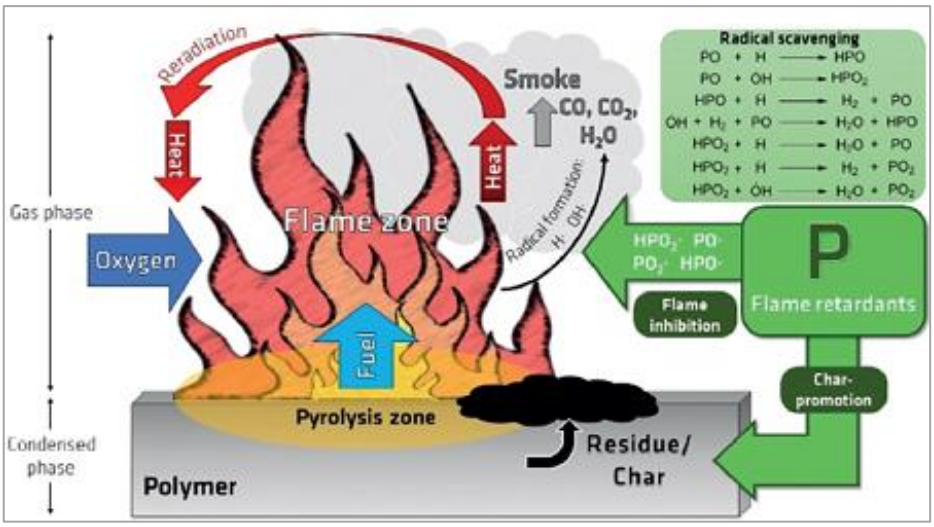



**Figure 2.4** Flaming Combustion of Polymeric Material and the Role of P-FRs [1]

Many P-FRs decompose to form PC radicals which react with OHC radicals and lower their concentration (flame poisoning) [1].

Jeng et al. [66] reported the decrease in the $T_g$ value by the presence of flexible P-O bonds. Additionally, it is stated that introduction of sterically demanding groups such as P-O-$C_6H_4$-O-P could reduce the cross-linking density which causes a lower $T_g$ value. On the other hand, using an FR with a more rigid P-Ph group may result in a less reduced $T_g$ value. Nevertheless, exchanging a P-O bond by a P-C bond influences the FR mechanism.

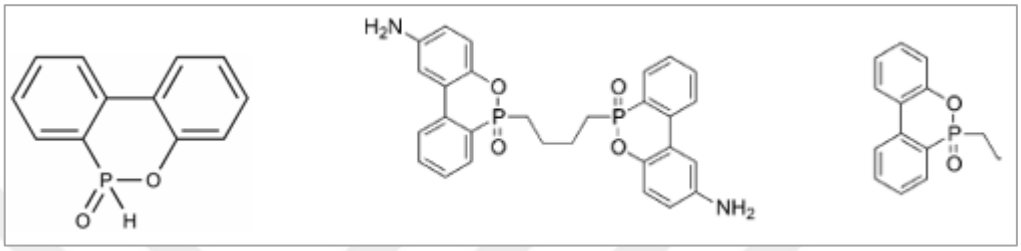
According to most reports, phosphine oxides are more active in the gas phase than the other P-FRs with higher oxidation numbers (i.e., phosphates) despite that they are considered poor char promoters [66-68].

This inference is different than that of Braun et al., who grades phosphate as the worst and the phosphine oxide as the best FR after observing an increase in charring and decrease of flame inhibition for the phosphates that substantially elucidated for the performance of FR in composites. Matrix composites are investigated by Braun et al. and stated that flame inhibition as a main mode of action with minor charring is an exceedingly promising route for flame retardancy [69-71].

There are many phosphorus containing compounds present in the market and DOPO (9,10-dihydro-9-oxa-phosphaphenthrene-10-oxide) is one of the most used compounds that can be derivatized to attach polymer matrix.

DOPO has drawn interest since it has flame retardant efficiency, high thermal stability, highly reactive P-H bond and it was the first efficient halogen free flame retardant for epoxy resins based on novalac [72], [73].

Artner et al. compared two DOPO derivatives (Figure 2.5): one was modified with amine groups and used as an FR hardener in epoxy resins, the other was additive FR with a similar structure [74]. It is revealed that the reactive FR has more potential to be superior compared to the additive FR.




(a) (b) (c)

**Figure 2.5** DOPO (a), DOPO-Based Hardener (b), Nonreactive Analog (c) [74]

On the contrary, Ciesielski et al. demonstrated that in order to maintain superior mechanical performance using reactive FR is not necessary [75].

It was reported that the most suitable reactive FRs for rigid PU foams are P-containing polyols despite their rare usage in flexible PU foams [76].

Fractions of biomass can be tailored with P-compounds to enhance their FR potential in some cases. According to the Cádiz group, Michael addition, cross-metathesis reaction and cationic polymerization can be used as new approaches to form P-containing triglycerides or fatty acids from vegetable oils. Increased LOI values in the final material were found [77].

Inorganic phosphorus ammonium polyphosphate (APP) based hardener for epoxy resins was investigated by Tan et al. APP was modified with piperazine via cation exchange to be used as hardener. This approach exhibited efficient flame retardancy, homogeneous incorporation without aggregation which results in more improved mechanical features than the dispersion of APP in epoxy resin [78].

Duan et al. used APP in polypropylene in a combination with hyperbranched (hb)-phosphorus/nitrogen containing polymer (see Figure 2.6). Equal parts (10 wt. %)

of polymer and APP formulation exhibited increased LOI values up to 30% against the LOI values of 20% for 20 wt% of the individual compounds which confirms synergism between the hb polymer and the APP. Through the TGA analysis, the protective layer effect was observed due to the existence of charred layers [79].

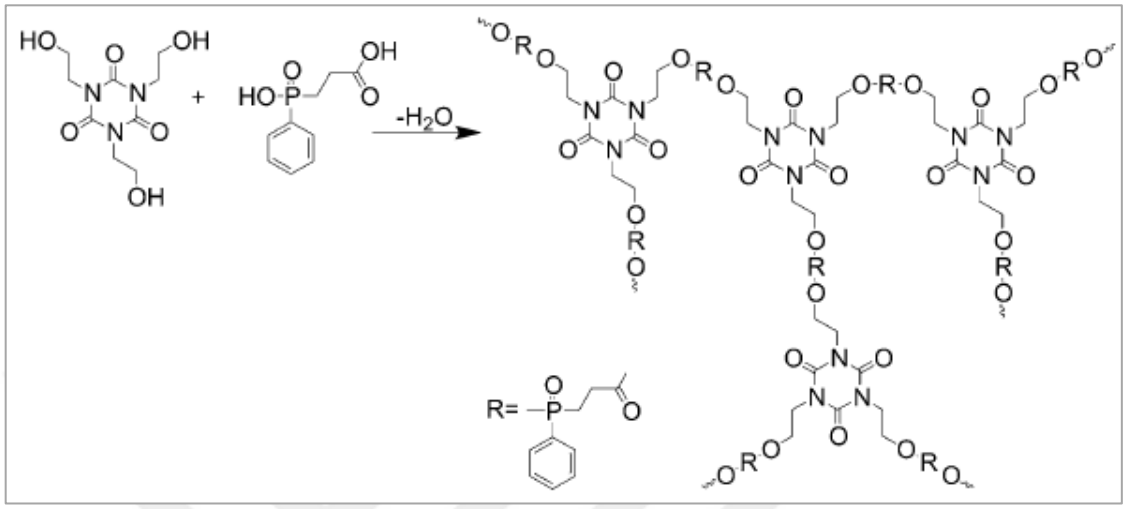



**Figure 2.6** Reaction Scheme of Phosphorus/Nitrogen Containing hb FRs

# 3
# Phospha-Michael Addition

## 3.1 Michael Addition of H-phosphonates (Phospha-Michael Addition)

1,4-conjugate addition, best known as Michael Addition, is a very popular and versatile way of linking electron poor olefins with a range of nucleophiles among synthetic methods. It was first described by Arthur Michael in 1887, as the base catalyzed addition of a resonance stabilized carbanion, such as an enolate (the Michael donor), to an activated α, β-unsaturated carbonyl containing compound (the Michael acceptor) [80].

The scope for Michael Addition has widened since and nowadays it has addition of a wide range of nucleophiles to a conjugated unsaturated compound [81]. Therefore Michael addition offers a whole realm of bond formation possibilities next to its originally described use in the formation of carbon-carbon bonds, and is also widely applied in the formation of oxygen-carbon bonds, [82-84] sulfur-carbon bonds, [85, 86] nitrogen-carbon bonds, and phosphorus-carbon bonds. [87], [88] Phosphorus-carbon bond reaction which is also termed as phospha Michael addition has been applied recently in polymer science [82].

The transformation of the π-bond between the double bond carbon atoms into a σ-bond between the nucleophile and a carbon atom is the same driving force for all types of Michael additions, however; a range of options is possible as reaction mechanism [89]. Figure 3.1 shows someexample for phospha-Michael addition.

The most straightforward and environmentally friendly chemical transformation is the direct addition of the nucleophilic element–hydrogen moiety to unsaturated carbon-carbon bond [90]. P(X)H moiety containing phosphorus reagents are generally considered as poor nucleophiles. Their application is rendered due to their

low reactivity and they require efficient catalysts for reactions that are performed under mild conditions to obtain a reasonable yield and selectivity.

H-phosphonate reactions with different Michael acceptors gained attention on the part of synthetic chemists. When H-phosphonates are added to activated unsaturated systems, it is also referred as the Pudovik reaction [91].

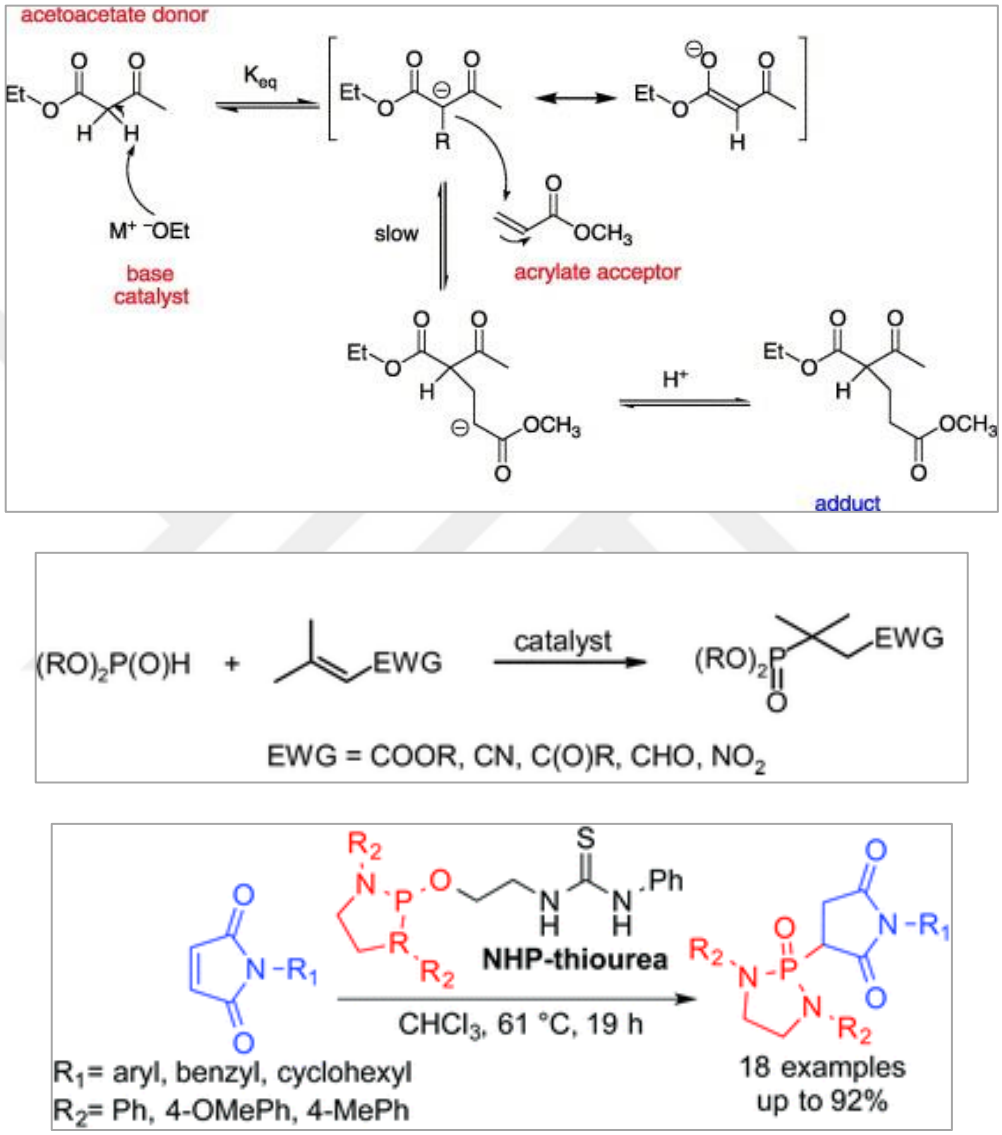



**Figure 3.1** Examples of Phospha-Michael Addition Reactions [81]

The most significant feature of H-phosphonates is that they have two tautomeric forms, which are phosphonate (A) and phosphite (B) as shown in Figure 3.2 [92-95].

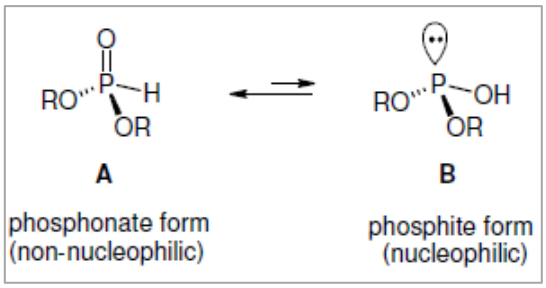



**Figure 3.2** Two tautomeric forms of H-phosphonates

These compounds react readily as nucleophilic species since they possess a lone electron pair on the phosphorus atom of phosphite tautomer.

Nature of the substituents at the phosphorus center, the structure of Michael acceptor and reaction conditions determine the effectiveness of this reaction [96].

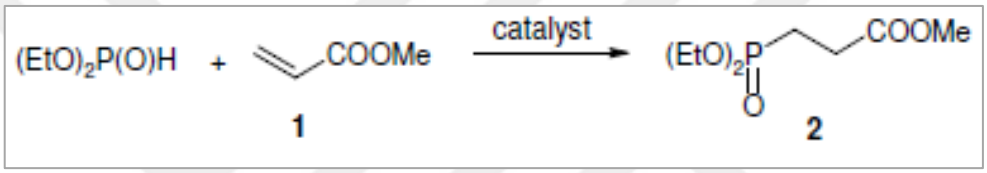



**Figure 3.3** Reaction of Methyl Acrylate with Diethyl Phosphonate [96]

In the presence of strong organic bases such as 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), the addition of dimethyl- or diethyl phosphonates to acrylamide gives a good yield of anti-Markovnikov adduct, on the contrary; when the same conditions are applied to same nucleophiles with acrylonitrile, the reaction is a failure. A catalytic system, including KOH supported on $Al_2O_3$ can be used to promote the reaction in success [97].

The phospha-Michael addition is generally a base-catalyzed process and for this reason, numerous catalysts are under development recently. According to these developments, the most effective catalysts are some inorganic compounds and highly basic nonnucleophilic nitrogen derivatives such as DBU [98], 1,4-diazabicyclo[2.2.2]octane (DABCO) [99], bis(trimethylsilyl)acetamide (BSA) [100], triazabicyclodecene (TBD) [101], aliphatic amines [102, 103], metal oxide [104, 105], alkali metal hydroxides [97], and carbonates [106].

When methyl acrylate (1) is treated with diethyl phosphonate at the presence of $Na_2CO_3$, solid MgO, or polymer-supported sodium carbonate no reaction occurs, yet

the same nucleophile may readily undergo a conjugate addition to ester (2) in the presence of DBU (70% yield) or CaO (80% yield) catalysts at room temperature as shown in Figure 3.3.

Constructing C–P bonds in an atom-economic manner is a readily developing field of synthetic phosphorus chemistry and can be provided by using transition-metal-catalyzed phosphorus-hydrogen (P–H) bond addition to unsaturated compounds. Combination of high selectivity of the catalytic transformation and high atom efficiency of the addition reaction may lead to cost-efficient and environmentally-friendly synthetic procedure, which is in concordance with the requirements of green chemistry [107-113].

P–H bond addition to unsaturated organic molecules; such as alkynes, alkenes, dienes, aldehydes, and imines, etc., can provide the synthesis of various phosphorus compounds. Flame retardants, optical materials and fuel cell membranes are some examples of the practical application of utilized phosphorus compounds [114-121].

## 3.2 Microwave Assisted Phospha-Michael Addition

Y Intense research has been going on atom efficient transformations for past few years [122]. It is known that bis(stannylation) of alkynes, the synthesis of unsymmetrical ketones, and the silylcupration of acetylenes are some of the applications of this technology [123-125].

Atom efficient transformations can be a powerful and practical synthetic approach if the desired reaction can be performed in the absence of solvent. Gaumont et al. reported a microwave assisted addition of diphenylphosphine to alkenes with a Lewis acid ($BH_3$) catalyst [126].

The addition of $HP(O)Ph_2$ to varied alkenes with the products and their yields have been given in Figure 3.4. As can be seen from Figure 3.5; 1 equivalent of $HP(O)Ph_2$ (entry 1) when treated with terminal alkene in the absence of solvent with microwave irradiation high yields of the desired phosphine oxide were obtained. Various alkenes were employed and it was concluded that alkenes with an activating group had the best results and in many cases, the obtained products were isolated with a purity greater than 95% [127].

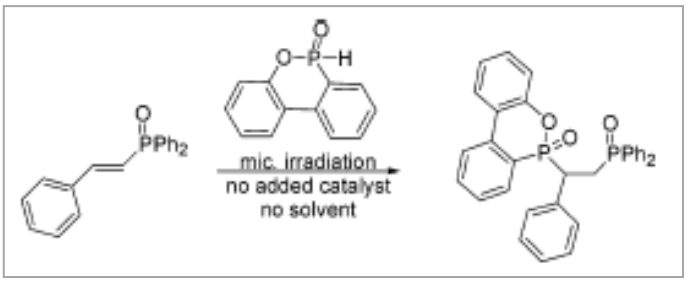



**Figure 3.4** Microwave Assisted Phospha-Michael Addition Reaction Scheme of Phosphine Oxide-DOPO

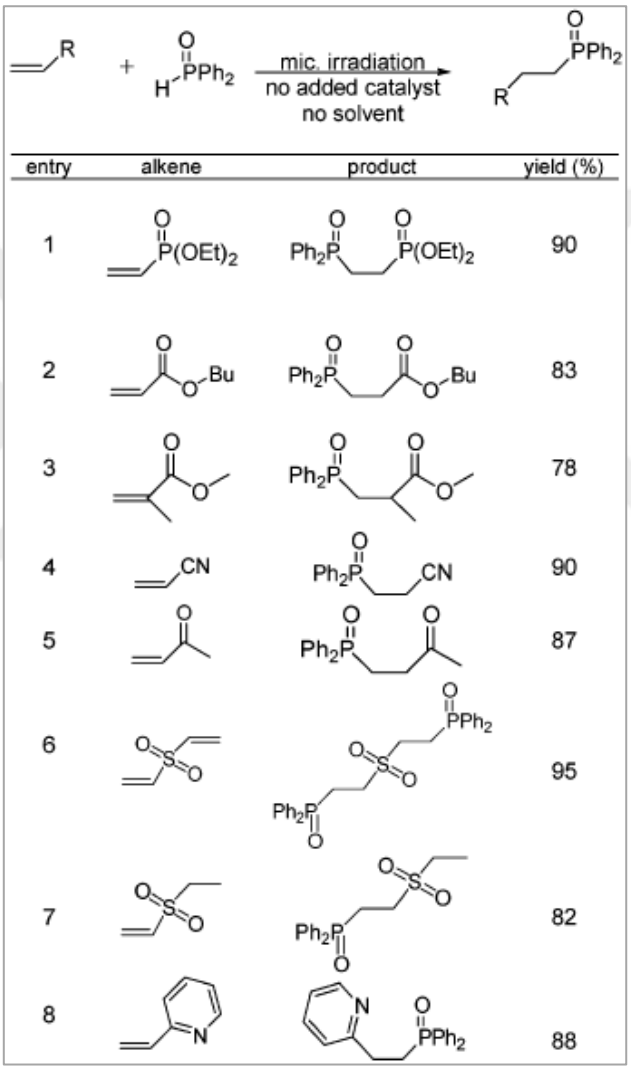



**Figure 3.5** $HP(O)Ph_2$ Addition to Alkenes [127]

# 4
# Kinetics of Polymers

## 4.1 Radical Chain Reaction

Producing polymers from monomers requires at least two functionalities which include coreactive functional groups opening of a double bond, opening of a ring, in the monomers. Carbon carbon double bond in alkenes, carbon oxygen double bond in aldehydes and ketones are the most important significant groups that participate in chain-growth polymerizations.

Alkenes or functionally substituted alkenes are used as monomers to make addition polymers. Addition reactions are the most common and thermodynamically favored chemical transformations of alkenes. Many of these additional reactions are known to proceed through reactive intermediates in a step-by-step fashion, and that is the mechanism that most polymerizations follow. Here is presented a general diagram illustrating these linear macromolecules' assembly, which supports the growth of polymers (Figure 4.1):

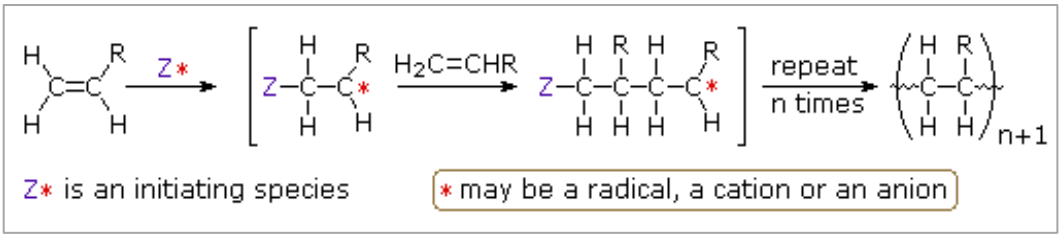



**Figure 4.1** Polymerization of an Alkene Species [128]

The polymerization reaction is usually exothermic by 8 to 20 kcal/mol when a pi-bond in the monomer is converted to a sigma-bond in the polymer.

Radical polymerization, cationic polymerization, anionic polymerization, and coordination catalytic polymerization are four distinguished polymerization procedures that fit to this general description as in Table 4.1.

**Table 4.1** Propagating Site of Reactivity According to Polymerization Type

| Polymerization Type | Initiator | Propagating Site of Reactivity |
|---|---|---|
| Radical Polymerization | Radical | carbon radical |
| Cationic Polymerization | Acid | carbocation |
| Anionic Polymerization | Nucleophile | carbanion |
| Coordination Catalytic Polymerization | transition metal complex | terminal catalytic complex |

### 4.1.1 Radical Chain Growth Polymerization

As traces of oxygen or other minor impurities can initiate radical polymerization, pure samples of these compounds are often 'stabilized' by small amounts of radical inhibitors to prevent unwanted reactions. When radical polymerization is desired, a radical initiator such as a peroxide or some azo compounds must be used to initiate it.

The formulas of some common initiators and equations are demonstrated radical species formation from these initiators in Figure 4.2.

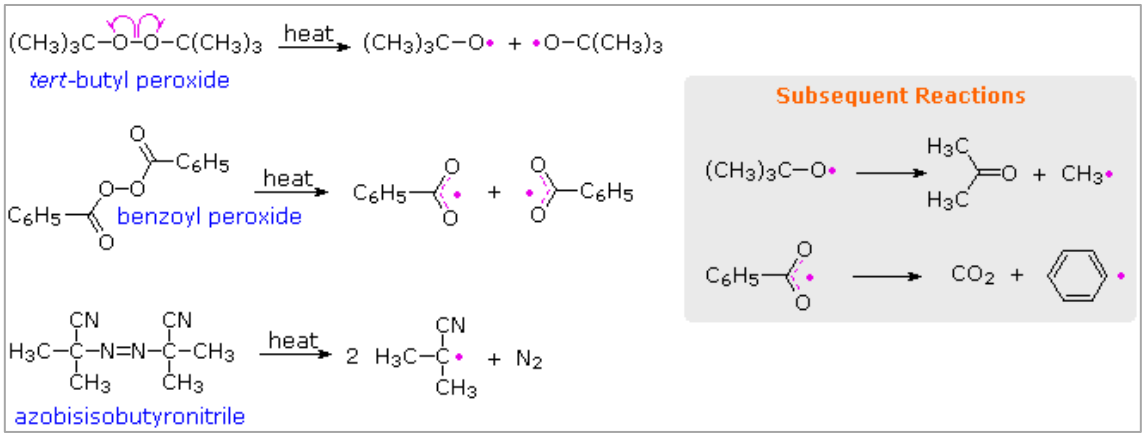



**Figure 4.2** Subsequent reactions of some radical initiators [128]

In most additional polymerizations, the preference for head-to-tail regioselectivity is understandable since carbon radicals are stabilized by many kinds of substituents.

Since radicals tolerate many functional groups and solvents (including water), radical polymerizations in the chemical industry are widely used.

Free radical polymerization consists of three basic steps, i) initiation, ii) propagation, and ii) termination. It is usually faster than in step growth syntheses that use different monomers in any case.

A wide variety of monomers can be polymerized by using small amounts of initiators. An example of this radical polymerization is the conversion of styrene into polystyrene as shown in Figure 4.3.

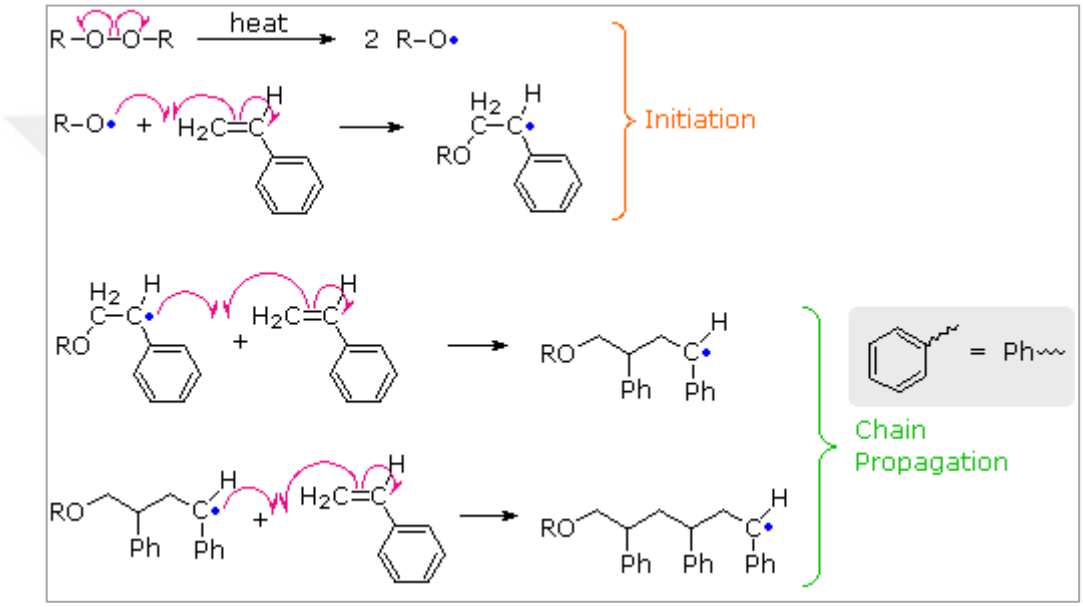



**Figure 4.3** Initiation and Propagation Steps in Radical Polymerization [128]

Despite a radical polymerization is expected to produce some extremely long chain polymers theoretically, the existence of moderately sized chains indicates the chain-terminating reactions in practice. In termination step, reactive radical sites are converted to stable products simultaneously.

Radical combination and disproportionation are the most common termination processes. Rate of the radical-radical termination reactions are very small due to the concentration of radical species being smaller than monomers, solvents and terminated chains, etc. therefore, most growing chains have moderate length prior to termination.

The nature of the monomer that undergoes polymerization varies the relative significance of the termination reactions. Combination is a major process for terminating acrylonitrile and styrene while disproportionation is for methyl methacrylate and vinyl acetate in polymerization [128]. Combination and disproportionation mechanism were shown in Figure 4.4:

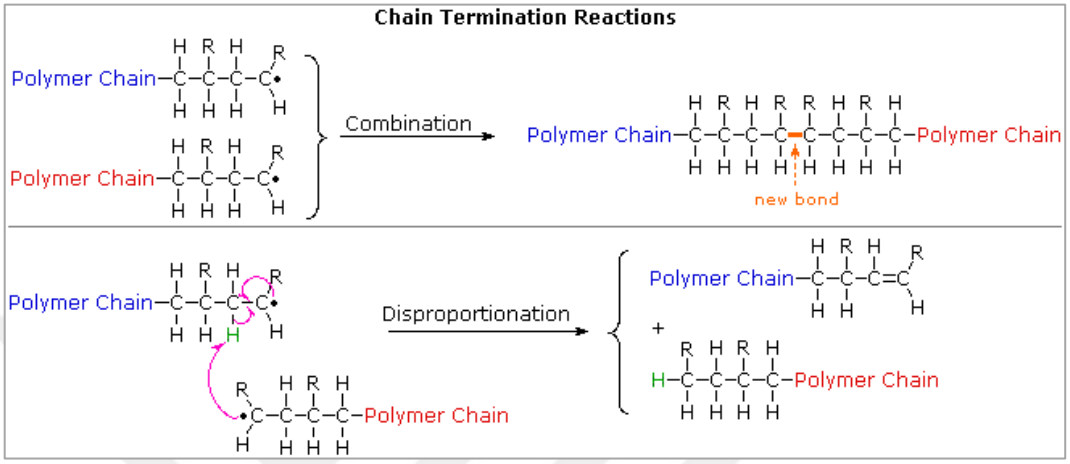



**Figure 4.4** Combination and Disproportionation Chain Termination Reactions [128]

Chain transfer reaction is another reaction to produce linear macromolecules from radical chain-growth polymerizations by an intermolecular or intramolecular hydrogen atom transfer that moves a carbon radical from one location to another.

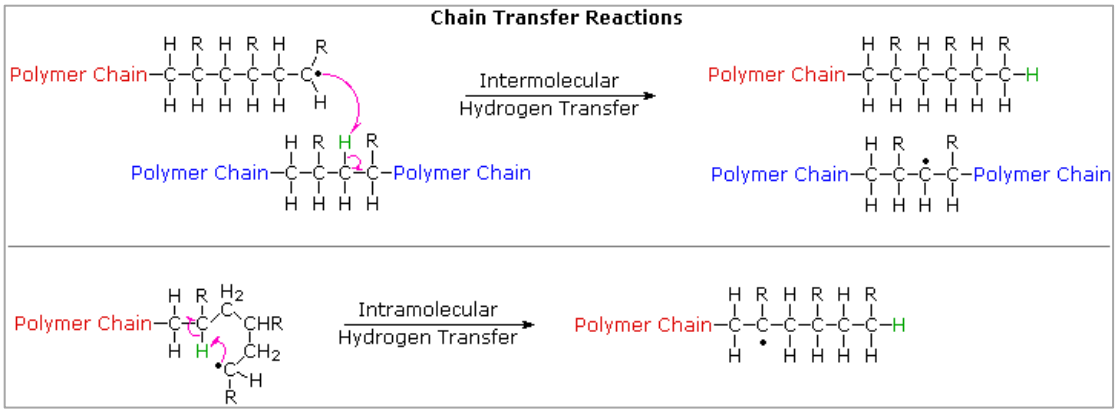



**Figure 4.5** Inter- and Intra-Molecular Chain Transfer Reaction Polymerizations [128]

## 4.2 Copolymerization

A copolymer is a polymer formed when the same polymer chain connects two (or more) different types of monomers. The polymerization reaction to form copolymer is called as copolymerization. Depending on their arrangement in the polymer chain, monomers form random, alternating, block or graft copolymers.

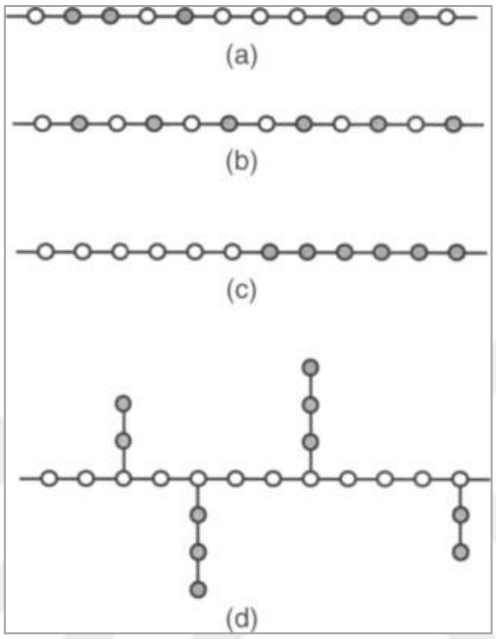



**Figure 4.6** (a) Random Copolymerization (b) Alternating Copolymerization (c) Block Copolymerization (d) Graft Copolymerization Chain Configuration [129]

### 4.2.1 Reactivity Ratio

The reactivity ratio is a measure of tendency of a comonomer to display a preference for insertion into a growing chain where the last inserted unit was the same as the other comonomer. Values are obtained either by kinetic measurement, i.e., by fitting copolymer composition data to a suitable form of copolymer composition equation at several comonomer ratios; or by copolymer microstructural analysis, usually $^{13}C$ NMR determination of monomer sequence distributions.

$$M_1. + M_1 \xrightarrow{k_{11}} -M_1.$$
$$M_1. + M_2 \xrightarrow{k_{12}} -M_2.$$
$$-M_2. + M_2 \xrightarrow{k_{22}} -M_2.$$
$$-M_2. + M_1 \xrightarrow{k_{21}} -M_1. \quad (4.1)$$

According to the Equation (4.1):

$$r_1 = \frac{k_{11}}{k_{12}} \tag{4.2}$$

and

$$r_2 = \frac{k_{22}}{k_{21}} \tag{4.3}$$

The product of the reactivity ratios ($r_1 \cdot r_2$) is usually between zero and one. If $r_1 \cdot r_2$ is approximately one, the last added unit in the chain will not affect the next addition, and according to Bernoullian statistics, the formation of a random copolymer will occur. When this ratio is zero, an alternating copolymer occurs according to the Markovian statistics. Finally, if $r_1 \cdot r_2$ is greater than 1, comonomers tend to give long segments- even homopolymerization, and block copolymer formation predominates [130]. Figure 4.7 shows the copolymer structure according to the reactivity ratio:

| | | | |
|---|---|---|---|
| $r_1 \cdot r_2$ | = | 1 random | EEPEPEPPEP |
| $r_1 \cdot r_2$ | < | 1 alternating | EPEPEPEPEP |
| $r_1 \cdot r_2$ | > | 1 block | EEEEPEPPPE |

**Figure 4.7** Copolymer Structures According to Reactivity Ratios

## 4.3 Finemann-Ross Method

Finemann-Ross Method is used to calculate the reactivity ratio of monomers. Copolymerization (composition) equation is shown below:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right) \tag{4.4}$$

In low compositions, $dM_1/dM_2$ is the concentration ratio of copolymer compound. The above equation can be written in terms of mole fractions, which is called as Finemann-Ross Equation:

$$\frac{1(1-F)}{F} = r_2 - \left(\frac{f^2}{F}\right) r_1 \tag{4.5}$$

Here feed ratios of copolymers are represented as $f_1$ and $f_2$ the while mol fractions of copolymers are represented as $F_1$ and $F_2$.

By using this equation the Finemann-Ross graph can be drawn as shown in Figure 4.8.

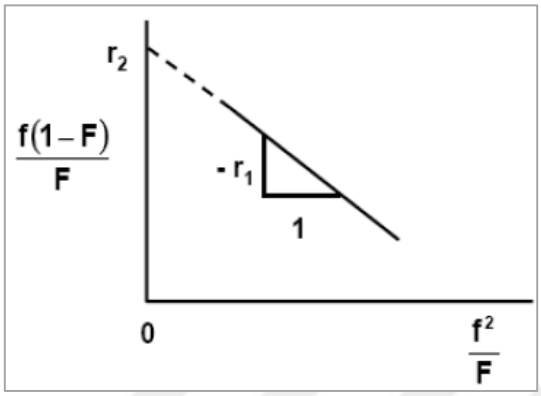



**Figure 4.8** Finemann-Ross Graph

From the Equation 4.1;

$$\frac{[M_1]}{[M_2]} = x \tag{4.6}$$

and

$$\frac{d[M_1]}{d[M_2]} = y \tag{4.7}$$

then;

$$y = x\frac{1 + r_2 x}{r_2 + x} \tag{4.8}$$

so,

$$\frac{x(y-1)}{y} = r_1\frac{x^2}{y} - r_2 \tag{4.9}$$

When the equation is applied to Finemann-Ross Method;

$$G = r_1 F - r_2 \tag{4.10}$$

$$\frac{G}{F} = -r_2 \frac{1}{F} + r_1 \tag{4.11}$$

Figure 4.9 shows the change in copolymer composition against initial monomer composition This method is an obsolete method since the calculation results are mostly based on the last data points calculated. Nowadays, instead of this method, Kelen Tudos and Extended Kelen-Tudos Method (EKT) are generally used.

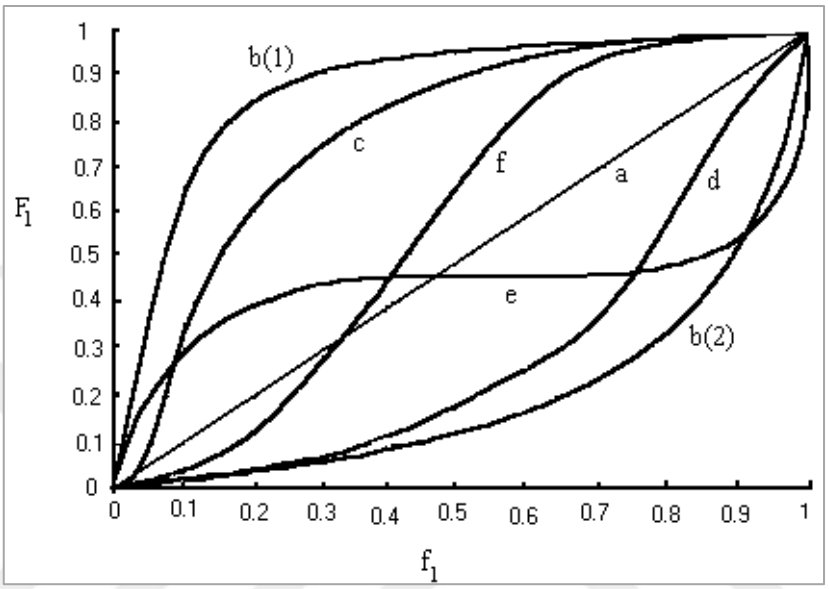



**Figure 4.9** Change in Copolymer Composition against Initial Monomer Composition (a) $r_1=r_2=1$; (b1) $r_1=8$, $r_2=0.125$; (b2) $r_1=0.125$, $r_2=8$ ; (c) $r_1=10$, $r_2=0.9$; (d) $r_1=0.9$, $r_2=10$; (e) $r_1=0.1$, $r_2=0.005$ ; (f) $r_1=20$, $r_2=10$

## 4.4 Kelen-Tudos Method (KT)

F and G are the variables in Finemann-Ross Method represented in Equation (4.10) and Equation (4.11), and α is a variable that can be calculated with the maximum and minimum values of F as shown in Equation 4.12 and also other variables such as η and ξ shown in Equation (4.13):

$$\alpha = \sqrt{F_{min} . F_{max}} \tag{4.12}$$

$$\eta = \frac{G}{\alpha + F} \ , \ \ \xi = \frac{F}{\alpha + F} \tag{4.13}$$

and finally; by using these equations, Kelen and Tudos developed:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{4.14}$$

## 4.5 Extended Kelen-Tudos Method (EKT)

After Kelen-Tudos Method, a new method has been developed that allows high conversion calculations with the name of Extended Kelen-Tudos (EKT) Method. The same equations in KT are applied to this method as well. The linear equation is the same in EKT and z is a variable:

$$z = \frac{1 + r_1 \frac{M_1}{M_2}}{r_2 + \frac{M_1}{M_2}} \tag{4.15}$$

When the copolymerization equation (Equation (4.4)) is integrated;

$$z = \frac{\log(1 - \xi_1)}{\log(1 - \xi_2)} \tag{4.16}$$

Here $\xi_1$ and $\xi_2$ represents partial molar conversions,

$$\xi_1 = 1 - \frac{d[M_1]}{d[M_1{}^0]}, \quad \xi_2 = 1 - \frac{d[M_2]}{d[M_2{}^0]} \tag{4.17}$$

and F and G can be written as:

$$F = \frac{y}{z^2}, \qquad G = \frac{(Y-1)}{z} \tag{4.18}$$

EKT gives accurate and reliable results of conversion for both azeotropic ($r_2$=1-$x_0$ + $x_0$ $r_1$) and ideal copolymer ($r_2$=1/$r_1$). KT allows approximately 5-15% conversion while EKT allows nearly 60% conversion [131-133].

# 5
# Experimental

## 5.1 Materials and Methods

### 5.1.1 Reagents

3-(Acryloyloxy)-2-hydroxypropyl methacrylate (AHM), diphenylphosphine oxide, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), acrylonitrile, azobisisobutyronitrile (AIBN), 2-hydroxyethyl methacrylate (HEMA) and 2,2-Dimethoxy-2-phenylacetophenone (Irgacure 651) from Aldrich Chemical Company were used as received. All other solvents and starting materials were reagent grade and they were used as received.

### 5.1.2 Characterization

Characterization involved TLC plate studies (Camag 254 / 366 nm UV lamp), FT-IR spectroscopy (Perkin-Elmer, FT-IR) and $^{1}H$ (500 MHz), $^{13}C$ (75 MHz) and $^{31}P$ (500 MHz) NMR spectroscopy (Bruker-500 MHz), ICP-OES (Shimadzu ICPE-9000 Plasma Atomic Emission Spectrometer).

## 5.2 Procedure for Synthesis of DK-2 Monomer

Monomer synthesis was performed with AHM (3-(Acryloyloxy)-2-hydroxypropyl methacrylate) (22.3 g, 3 equiv. mol) and diphenylphosphine oxide (7 g, 1 equiv. mol) in the presence of DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) catalyst (10 n/n%) and 20mL $CHCl_3$ at 63°C in a Schlenk tube under inert $N_2$ atmosphere overnight. After 5 hours reaction at 63°C, TLC studies were done by using (3:1, v/v) Hex:THF and (5:2, v/v) EtOAc:Hex solvent mixtures. Product was purified via column chromatography by using (5:2, v/v) EtOAc: Hex as eluent. The product was obtained as yellow liquid in 20% yield and named as DK-2 ($M_w$=402.38 g/mol). The product was stored at -18 °C in the refrigerator after purging with $N_2$ and sealed.

## 5.3 Procedure for Microwave Assisted Synthesis of DK-2 Monomer

Monomer synthesis was performed with AHM (3-(Acryloyloxy)-2-hydroxypropyl methacrylate) (3 equiv. mol) and diphenylphosphine oxide (1 equiv. mol) in a microwave vial without solvent. 1 g (0.00495 mol) diphenylphosphine oxide and 1.0604 g AHM were added into microwave vial and $N_2$ gas was purged into the vial before sealing it. The reaction was carried out for 1 hour at 120°C, 20watt. The product was precipitated in diethyl ether and it was washed with diethyl ether and sonicated (5x5 min); then, dried under $N_2$ gas. It was dissolved in d-$CDCl_3$ for $^1H$ NMR analysis.

## 5.4 Photopolymerization Procedure for DK-2 Monomer and DK-2:HEMA Copolymer

Photopolymerization kinetics of DK-2 as homopolymer and DK-2:HEMA copolymer were investigated using photo-differential scanning calorimetry (photo-DSC) (Q250;TA Instruments Philadelphia, PA) by using 1%(w/w) photoinitiator (2,2-Dimethoxy-2-phenylacetophenone). The chamber of the DSC was purged with nitrogen for removing the air before photopolymerization and purging was continued during the process.

### 5.4.1 Photopolymerization Procedure for DK-2 Homopolymer

Photo-DSC polymerization for commercial HEMA and DK-2 monomer was performed for 5 min at 25°C and 70°C by using 3.67 mg and 3.89 mg DK-2 monomer, respectively. The samples were placed in an uncovered aluminum DSC pan. The heat flow was monitored as a function of time DSC.

### 5.4.2 Photopolymerization Procedure for DK-2: HEMA (1:1) Copolymer

Photo-DSC polymerization for commercial HEMA and DK-2 monomer was performed for 5 min at 25°C and 70°C by using 3.67 mg and 3.89 mg DK-2 monomer, respectively. The samples were placed in an uncovered aluminum DSC pan. The heat flow was monitored as a function of time DSC.

## 5.5 Synthesis of PAN:DK-2 (8:2) Copolymer via Free Radical Polymerization

Copolymers PAN:DK-2(1) (5%), PAN:DK-2(2) (10%), PAN:DK-2(3) (20%), PAN:DK-2(4) (30%), PAN:DK-2(5) (%50) and PAN:DK-2(6) (%90) (wt.% DK-2 monomer) were synthesized by using AIBN.

PAN:DK-2 (5%) were synthesized in the ratio of 8:2 by weight. Acrylonitrile (2g) and DK-2 (0.11g) were dissolved in 8.5 g DMF in a vial with a magnetic stirrer under nitrogen at room temperature. AIBN was dissolved in 2 g DMF and then added to the mixture. The reaction was then kept at 70°C for 5 hours. The obtained copolymers were dried in oven at 80°C. Product was further analysed by $^{1}H$ NMR and GPC techniques.

The same procedure was applied for the other copolymers PAN:DK-2(1) (5%), PAN:DK-2(2) (10%), PAN:DK-2(3) (20%), PAN:DK-2(4) (30%), PAN:DK-2(5) (%50) and PAN:DK-2(6) (%90) (wt.% DK-2 monomer).

FTIR ($cm^{-1}$): 3363.93 (O-H stretch), 2937.21 (alkane stretch), 2242.16 (C=N stretch), 2161.35, 2017.98, 1979.50, 1178 & 1120 (C-O stretch), 1731 (C=O stretch)

## 5.6 Kelen-Tudos/Finemann-Ross Calculation

In order to determine a copolymer's composition; general structure based on the identities of the constituent monomers, their concentrations in the feed and measurement of the relative reactivities of the active centers are required. This can be achieved by using Finemann-Ross and Kelen Tudos calculations. First, from the NMR integration of the copolymers the mol fraction and mol fractions should be calculated.

## 5.7 Microscale Combustion Calorimetry (MCC) Anaysis for PAN:DK-2 (8:2) Copolymers

In order to perform micro-scale combustion calorimetry MCC (Fire Testing Technology, UK) was used according to ASTM D7309. The samples (~5 mg) was heated to 700 °C with a heating rate of 1 °C/s at a flow rate of 80 $cm^3$/min flowing nitrogen. In the nitrogen stream, volatile and anaerobic thermal degradation

products were mixed, before entering the 900 °C combustion furnace at a flow rate of 20 $cm^3$/min containing 20% oxygen and 80% nitrogen. Heat release rate (HRR) in Watts per gram of sample (W/g), Heat release capacity (HRC) in J/g K and total heat release (THR) in kJ/g for PAN:DK-2 samples were obtained. Values herein were reported as the average of four tests.

# 6
# Results&Discussion

## 6.1 Synthesis of DK-2 Monomer

In the presence of DBU catalyst, Phospha-Michael Addition of AHM and diphenylphosphine oxide was performed and DK-2 crude product was obtained. After that, the crude product work up was done by extracting it with chloroform (organic phase) and distilled water (aqueous phase). 10% aq. NaCl brine was used for washing and the organic phase was extracted into an erlenmeyer; then, $Na_2SO_4$ drying agent was added. TLC studies were applied again and after evaporation of the solvent in rotary evaporator column chromatography in silica gel was done using (5:2, v/v) EtOAc:Hex as eluent to purify the crude product. 2.76 g monomer was obtained and monomer yield was determined as 19.79 % after purification. The product was kept in $N_2$ purged a micro glass vial at -18 °C.

$^{1}H$ NMR, $^{13}C$ NMR and $^{31}P$ NMR spectra analyses were done for the product. AHM has two isomers in different ratios presumably because of acrylic acid adding to glycidyl methacrylate and unsymmetrical glycerol substitution (primary hydroxyl group). Small peaks around 3.7 and 5.25 ppm are due to the other isomer formed from 1,2 or 1,3 substitution reactions on glycerol. $^{1}H$ NMR spectra of DK-2 monomer showed the absence of the double bond of methacryl part of AHM, which was at 127.80 and 131.60 ppm. Aromacity of diphenylphosphine oxide was observed at 132.12, 130.74, 128.84 and 128.76.ppm and, phosphorus content of the monomer was approved by the presence of P atom peak at 31.75 ppm in $^{31}P$ NMR.

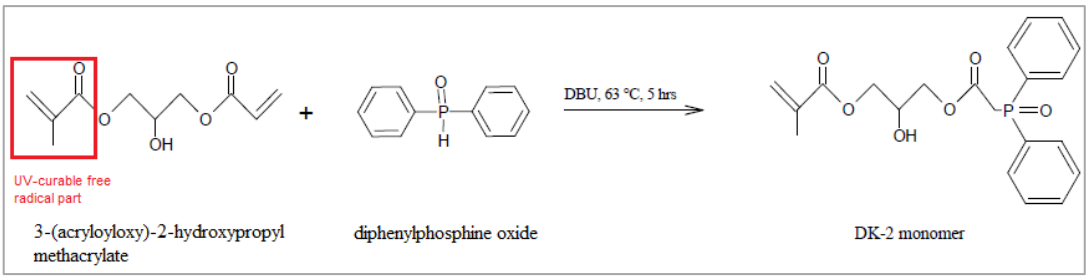



**Figure 6.1** Reaction Scheme of DK-2 Monomer

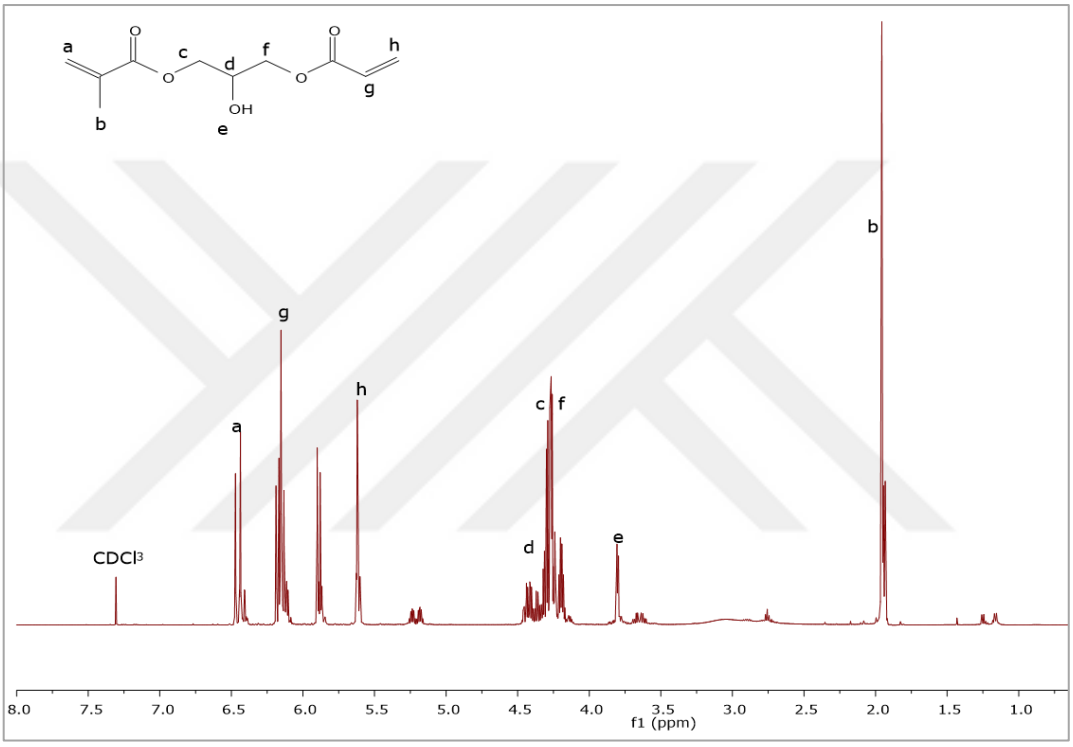



**Figure 6.2** $^{1}$H NMR Spectra of Starting Reagent AHM

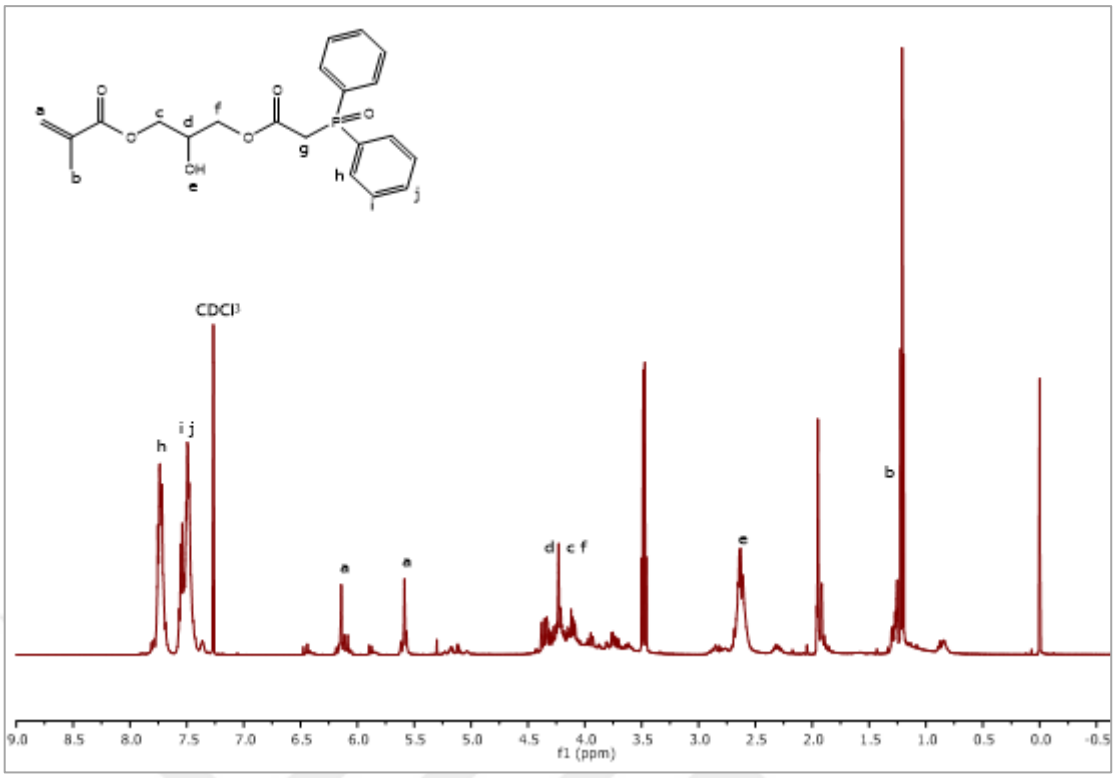



**Figure 6.3** $^{1}$H NMR Spectra of DK-2 Monomer

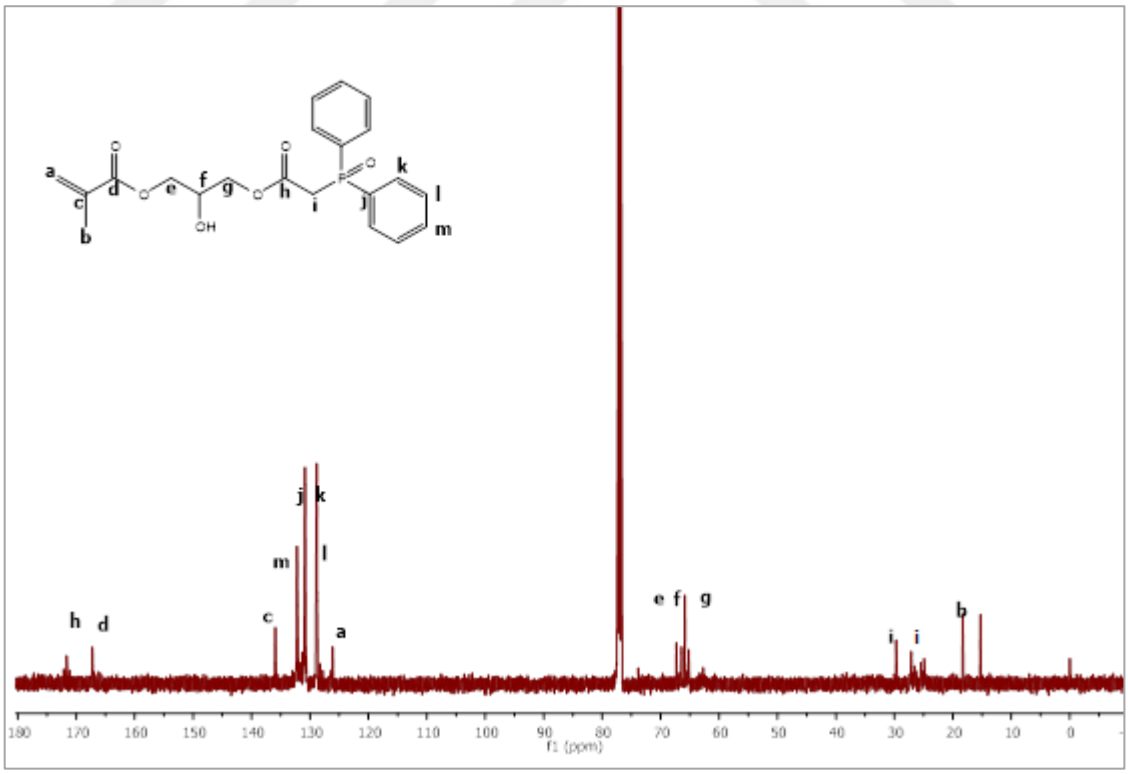



**Figure 6.4** $^{13}$C NMR Spectra of DK-2 Monomer

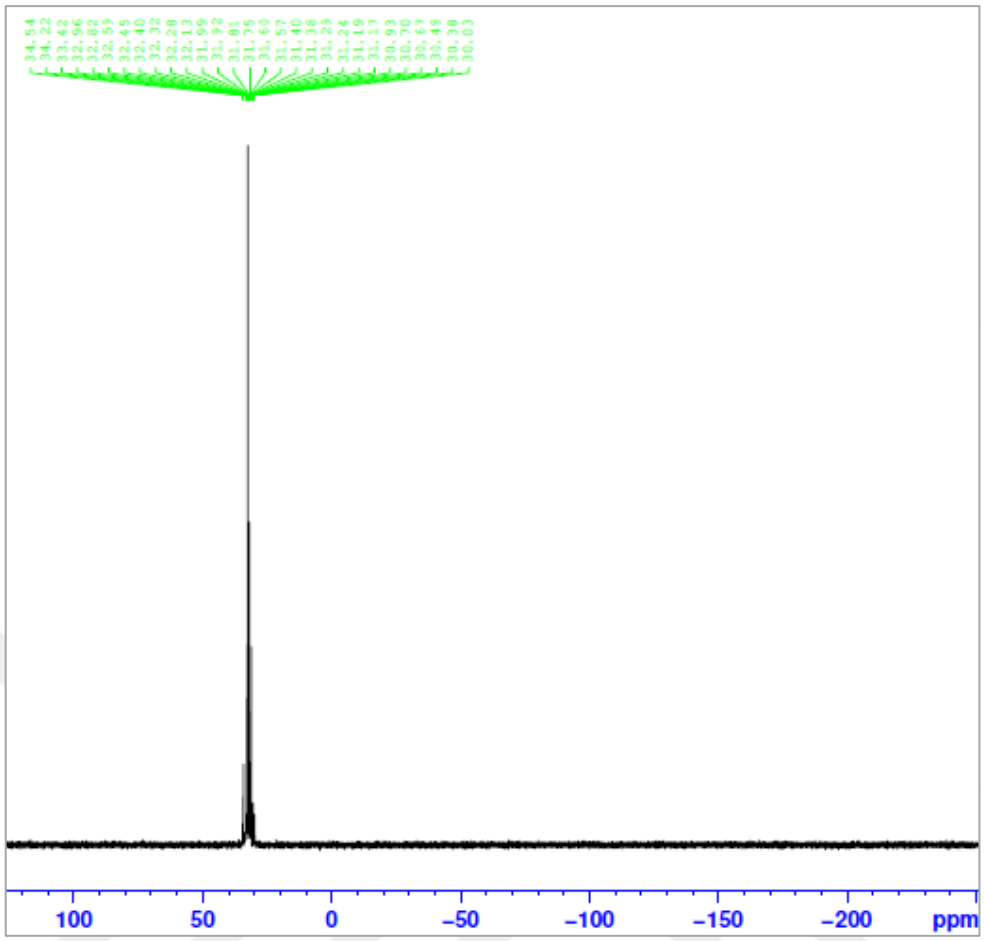



**Figure 6.5** $^{31}$P NMR Spectra of DK-2 Monomer

## 6.2 Synthesis of PAN:DK-2 Copolymer

Copolymers PAN:DK-2 (5%), PAN:DK-2 (10%), PAN:DK-2 (20%), PAN-DK-2 (30%), PAN:DK-2 (%50) and PAN:DK-2 (%90) (wt.% DK-2 monomer) were synthesized. These copolymers were named as PAN:DK-2 (1), PAN:DK-2 (2), PAN:DK-2 (3), PAN:DK-2 (4), PAN:DK-2 (5) and PAN:DK-2 (6), respectively. DMF amount was calculated as 5 times more than the sum of acrylonitrile and DK-2 monomer weight while AIBN amount was determined as 0.3 g against 10 g.

The obtained product was viscous and it was precipitated with deionized water in order to remove unreacted monomer. The obtained copolymer was dried in oven at 80°C. The same procedure was applied for the copolymers in the same manner after calculations were done for the proper amount of reagents and other compounds.

**Table 6.1** Amount of Reagents Used in Copolymerization Reaction

| Copolymer name | Amount of DK-2monomer in rxn (g) | Amount of AN monomer in rxn (g) | Amount of AIBN (g) | Amount of DMF (g) |
|---|---|---|---|---|
| PAN:DK-2 (1) | 0.1053 | 2 | 0.0632 | 10.53 |
| PAN:DK-2 (2) | 0.222 | 2 | 0.0666 | 11.11 |
| PAN:DK-2 (3) | 0.5 | 2 | 0.075 | 12.5 |
| PAN:DK-2 (4) | 0.0872 | 0.2034 | 0.046 | 1.453 |
| PAN:DK-2 (5) | 0.5 | 0.5 | 0.03 | 5 |
| PAN:DK-2 (6) | 0.5 | 0.055 | 0.0167 | 2.775 |

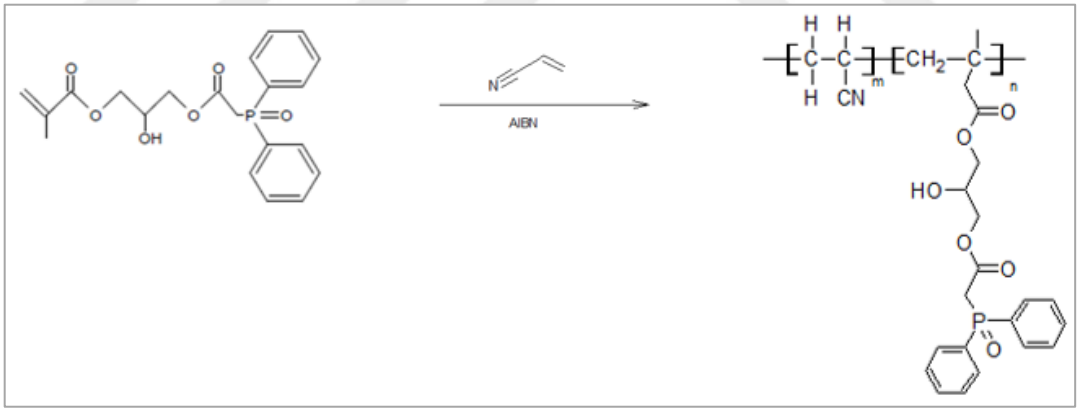



**Figure 6.6** Reaction Scheme of PAN:DK-2 Copolymer

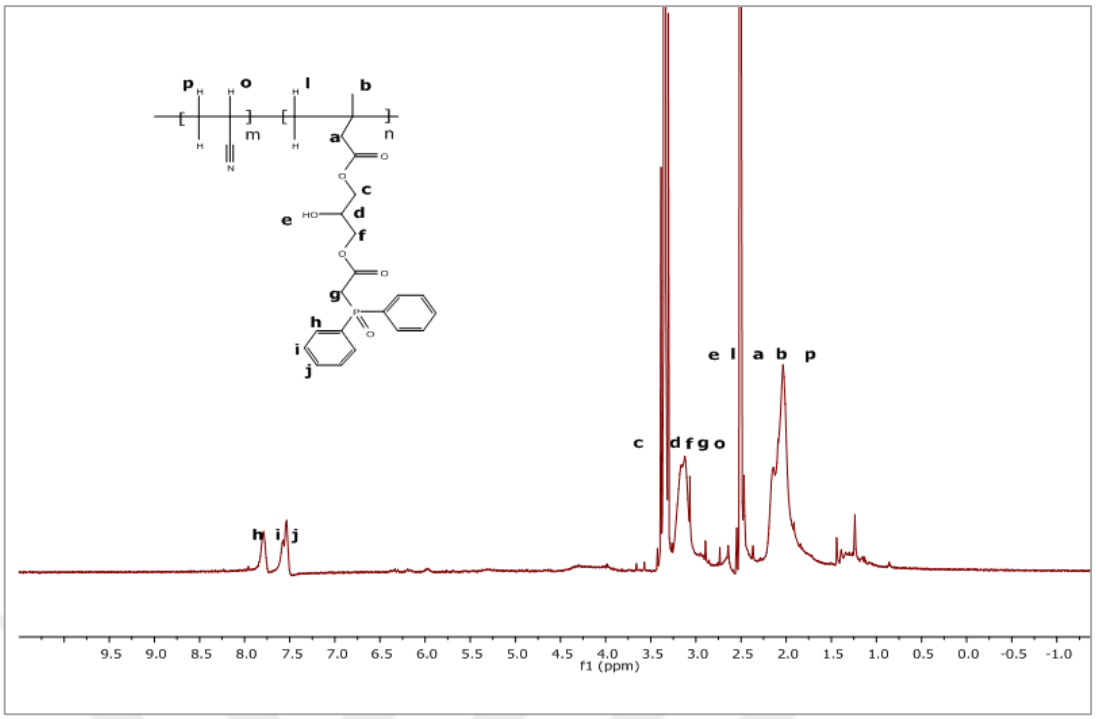



**Figure 6.7** $^{1}$H NMR Spectra of PAN:DK-2 Copolymer

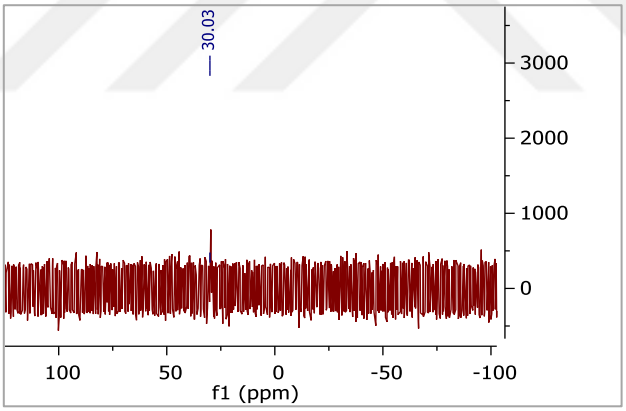



**Figure 6.8** $^{31}$P NMR Spectra of PAN:DK-2 Copolymer

$^{1}$H NMR and $^{31}$P NMR spectra analyses were done for the product. $^{1}$H NMR spectra of PAN: DK-2 monomer showed evidence of polymerization due to the existence of peaks at, 2.47and 2.04 ppm. Aromacity of diphenylphosphine oxide was observed at 4.00, 3.99 and 3.97ppm and phosphorus content of the monomer was approved by the presence of P atom peak at 30.03 ppm in $^{31}$P NMR.

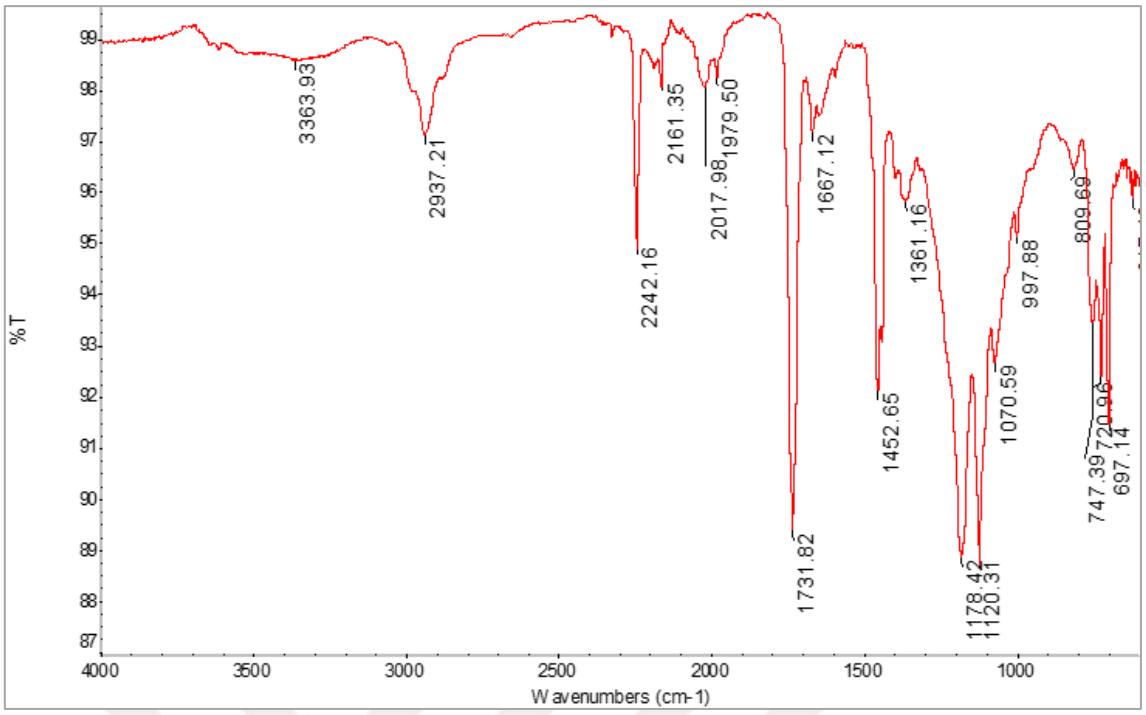



**Figure 6.9** FT-IR Spectra of PAN:DK-2 Copolymer

ICP-OES Analysis was done for PAN:DK-2(1), PAN:DK-2(2) and PAN:DK-2(4) in order to determine the quantity of P element in these copolymers. The results were mentioned in Table 6.2 below:

**Table 6.2** ICP-OES Analysis Values for P Element in PAN:DK-2 Copolymer

| Sample Name | P (mg $L^{-1}$) |
|---|---|
| PAN:DK-2(1) | 3092 ± 123 |
| PAN:DK-2(2) | 4329 ± 172 |
| PAN:DK-2(4) | 9471 ± 376 |

From the values in Table 6.2 it was observed that PAN:DK-2(4) copolymer with highest P loading has the highest ICP-OES value (9471 ± 376 P (mg $L^{-1}$)) than its analogues.

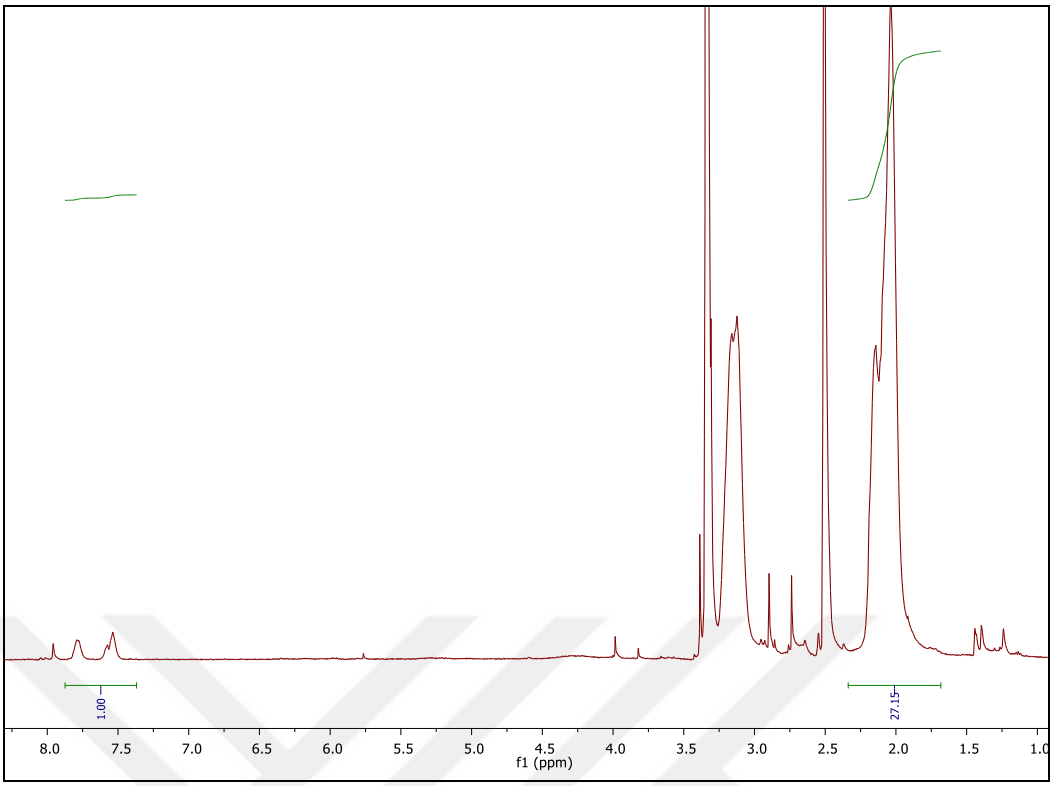



**Figure 6.10** PAN:DK-2 (1) Integrated NMR Data

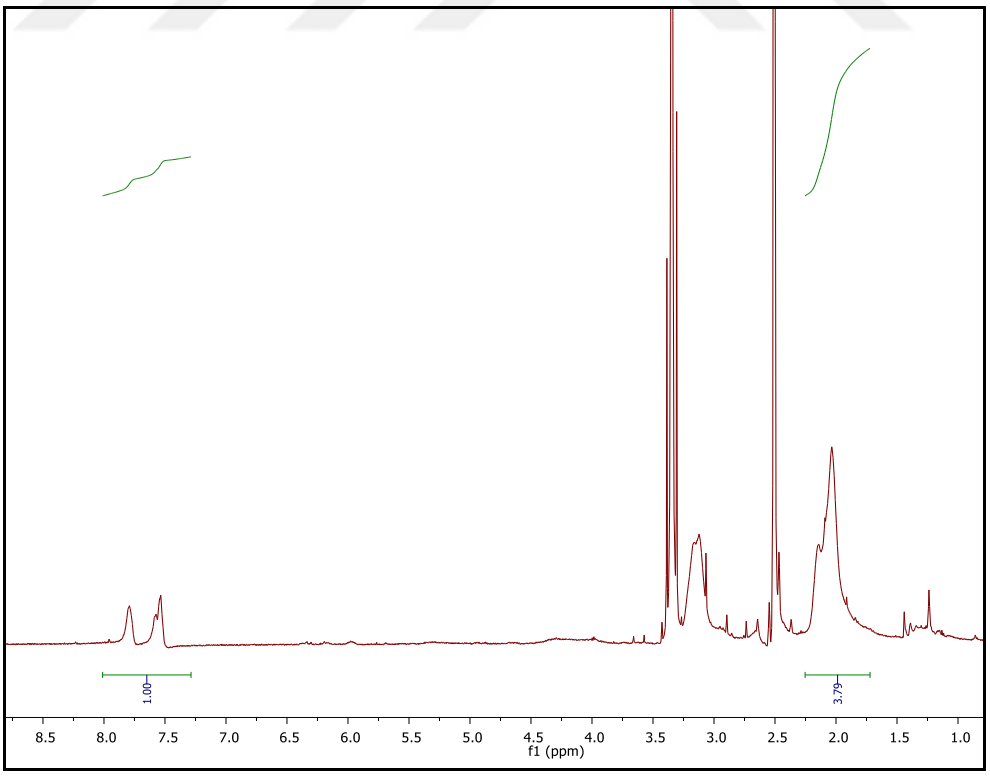



**Figure 6.11** PAN:DK-2 (3) Integrated NMR Data

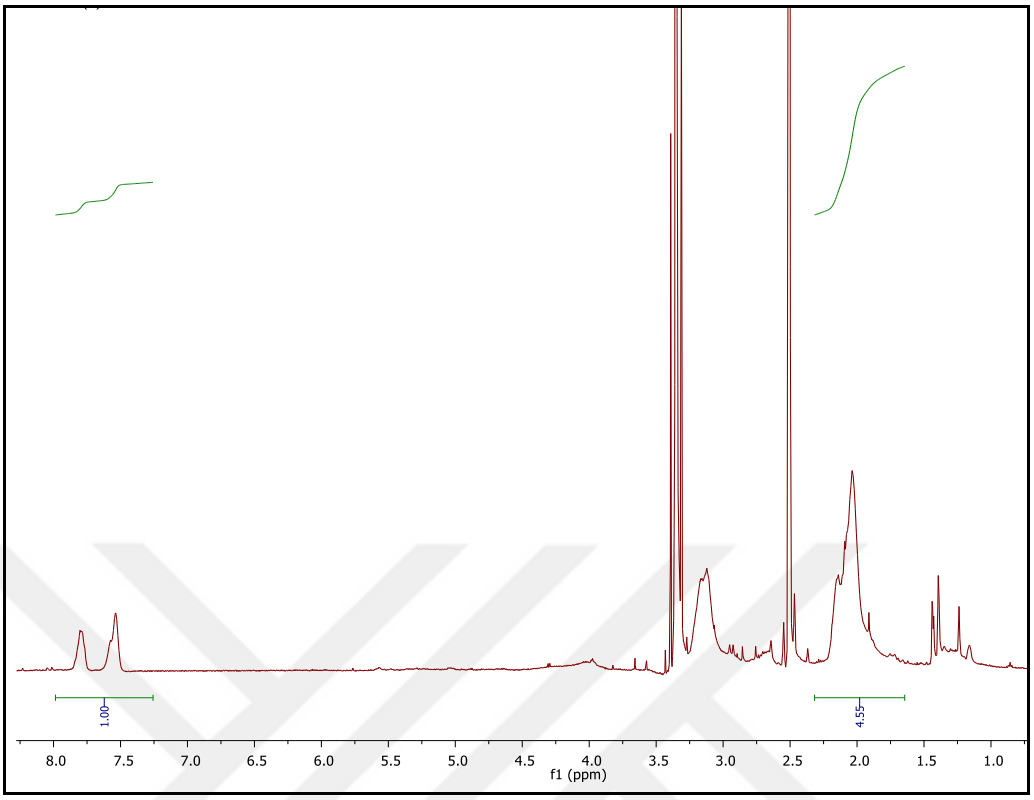



**Figure 6.12** PAN:DK-2 (4) Integrated NMR Data

### 6.2.1 Thermal Properties of PAN:DK-2

TGA analyses were done to determine the char yield of the PAN:DK-2 copolymers. Char yields from TGA values were calculated for PAN:DK-2 (1), PAN:DK-2 (2) and, PAN:DK-2 (4), respectively. According to the Air TGA graph PAN:DK-2 (2) polymer has the highest char yield (57.7%) while PAN:DK-2 (1) polymer has the highest char yield (67%) in $N_2$ TGA graph.

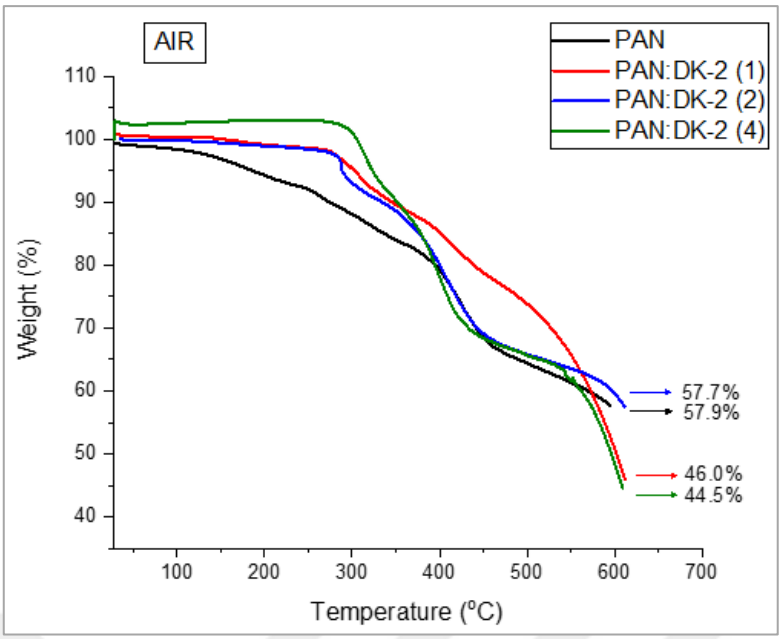



**Figure 6.13** TGA Graph (Air) for PAN, PAN:DK-2 (1), PAN:DK-2 (2), PAN:DK-2 (4) Copolymers

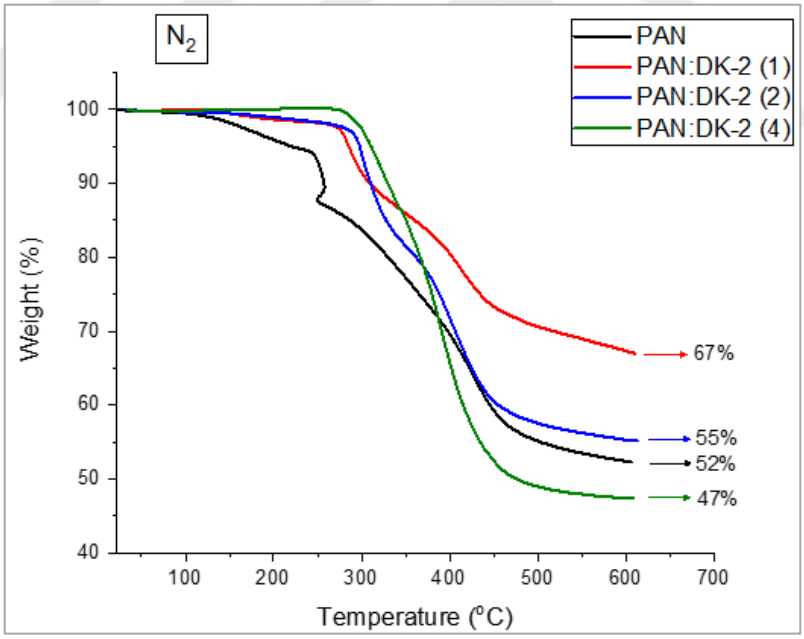



**Figure 6.14** TGA Graph ($N_2$) for PAN, PAN:DK-2 (1), PAN:DK-2 (2), PAN:DK-2 (4) Copolymers

## 6.3 Photopolymerization of DK-2 Monomer and DK-2:HEMA (1:1) Copolymer

Photopolymerization kinetics of DK-2 homopolymer, DK-2:HEMA and PAN: DK-2 copolymers were investigated by using 1% (w/w) photoinitiator IRGACURE 651 (2,2-Dimethoxy-2-phenylacetophenone). First, photopolymerization for homopolymer of DK-2 and then photopolymerization for commercial HEMA and PAN with DK-2 monomer were performed for 5 min at 25 °C and 70 °C. The conversion and polymerization rate was calculated by using the data obtained. The reaction scheme of photopolymerization for HEMA and DK-2 monomer was shown in Figure 6.15.

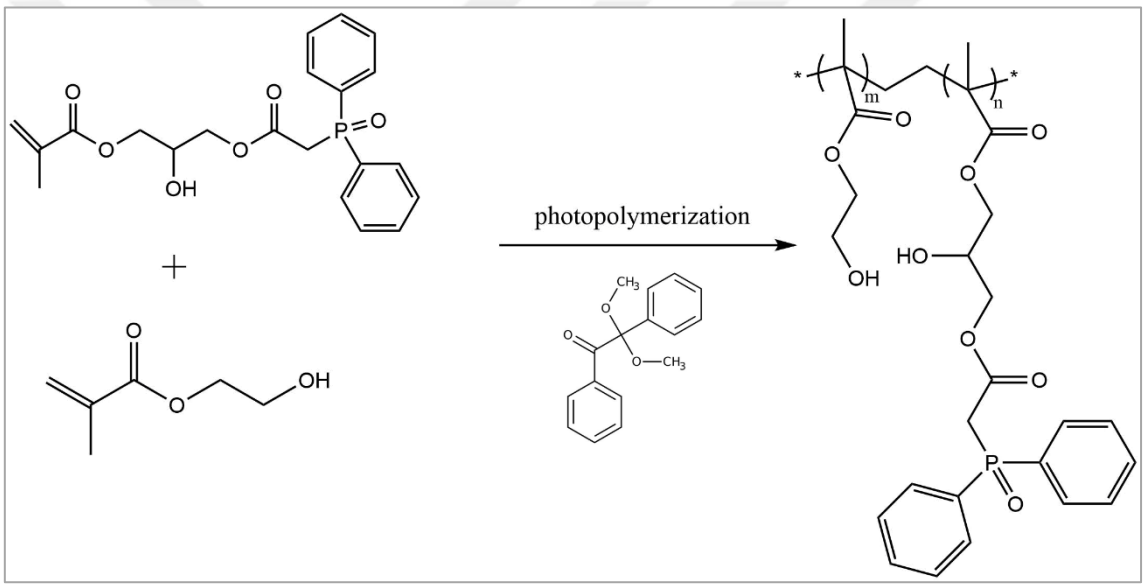



**Figure 6.15** Photopolymerization Reaction Scheme of HEMA and DK-2 Monomer

The rate formula for evaluating of the photopolymerization data was:

$$R_p = \frac{Q/sM}{n\Delta H_p m} \tag{6.1}$$

and the kinetic constants for propagation and termination formula was:

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M](\theta I_0 \epsilon [A])^{1/2}} \tag{6.2}$$

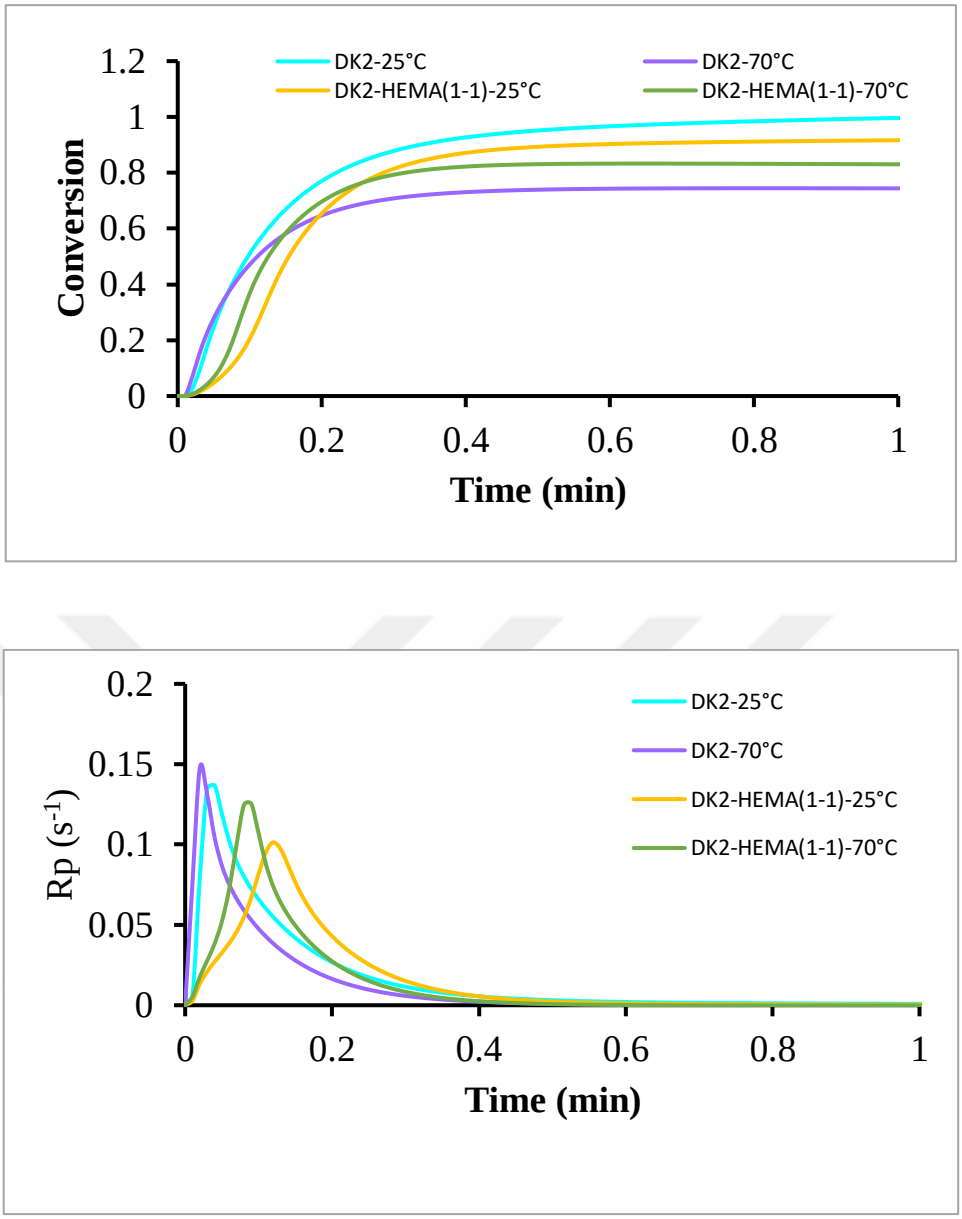



**Figure 6.16** Conversion (top) and Polymerization Rate (bottom) Graphs for DK-2 Homopolymer and DK-2:HEMA Copolymer at 25°C and 70°C

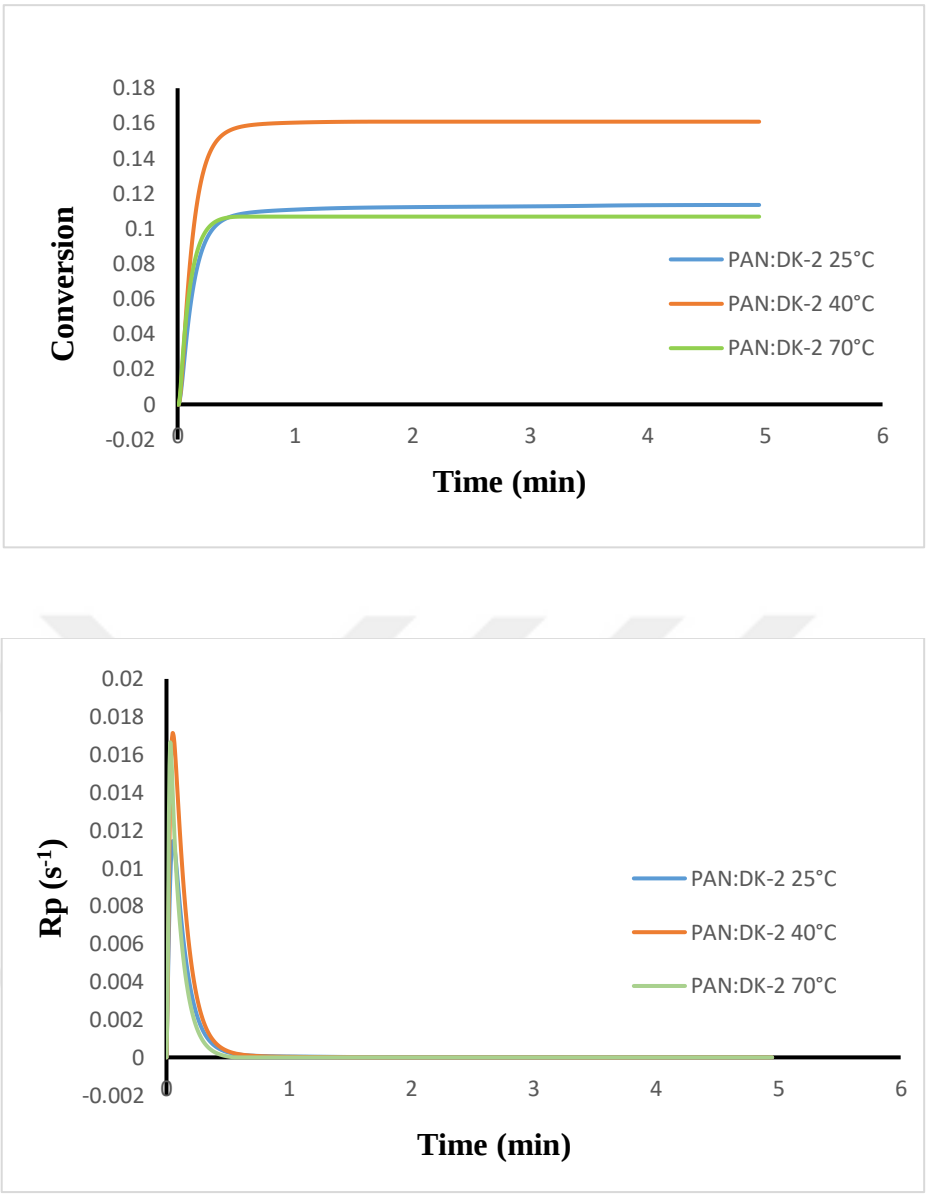



**Figure 6.17** Conversion (top) and Polymerization Rate (bottom) Graphs for PAN: DK-2 Copolymer at 25°C, 40°C and 70°C

AHM contains a centered hydroxyl group and is a mixed methacrylate/acrylate crosslinker which has faster photopolymerization rate than the commercial dimethacrylates. It is known that monoacrylates have slower polymerization rate than methacrylate/acrylates, diacrylates and dimethacrylates; therefore, homopolymer polymerization rate for DK-2 monomer was higher than that of DK-2:HEMA, according to Figure 6.16. However, DK-2:HEMA copolymer exhibited higher conversion than that of DK-2 monomer at 70 °C. The decreased mobility due to the size of the pendant phosphate groups in DK-2 may be the reason for the low

conversion. As for the PAN:DK-2 copolymer conversion and polymerization rate for PAN:DK-2 at 40 °C was greater than the rest of the copolymers of PAN:DK-2 according to Figure 6.17 and PAN:DK-2 at 40 °C and homopolymer have similar conversion value.

## 6.4 Finemann-Ross & Kelen-Tudos Calculation for PAN:DK-2 (8:2) Copolymer

To determine a copolymer's composition; general structure based on the identities of the constituent monomers, their concentrations in the feed and measurement of the relative reactivities of the active centers are required. This can be achieved by using Finemann-Ross and Kelen Tudos calculations.

**Table 6.3** Monomer Feed Ratio and Monomer Mol Fractions

| Initial DK-2 monomer % | $M_1$ | $M_2$ | $m_1$ | $m_2$ | DK-2% | AN% |
|---|---|---|---|---|---|---|
| 5% | 0.5 | 0.95 | 0.1 | 27.15 | 0.4 | 99.6 |
| 20% | 0.20 | 0.80 | 0.1 | 3.79 | 2.6 | 97.4 |
| 30% | 0.30 | 0.70 | 0.1 | 4.55 | 2.2 | 97.8 |

**Table 6.4** Parameters for Kelen-Tudos and Finemann-Ross

| Sample | F= $M_1/M_2$ | f= $m_1/m_2$ | G= $F(1-f)/f$ | H= $F^2/f$ | η= $G/(\alpha+H)$ | ξ= $H/(\alpha+H)$ |
|---|---|---|---|---|---|---|
| 0.4% DK-2 | 0.526 | 0.0037 | 142.408 | 75.1838 | 1.4547 | 0.7680 |
| 2.6% DK-2 | 0.250 | 0.0264 | 0.9736 | 2.8435 | 0.0381 | 0.1113 |
| 2.2% DK-2 | 0.429 | 0.0219 | 19.0901 | 8.3731 | 0.6141 | 0.2694 |

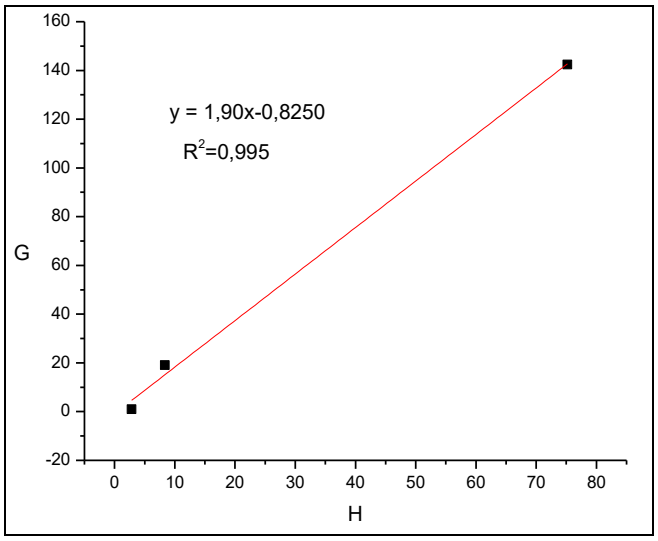



**Figure 6.18** G-H Graph Calculated from F-R Parameters

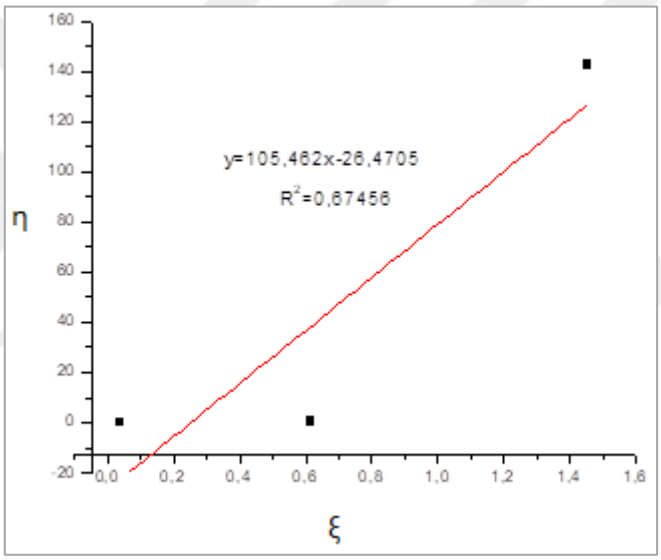



**Figure 6.19** η-ξ Graph Calculated from K-T Parameters

Monomer mol fraction and monomer feed ratio were calculated from NMR integration of the copolymers as shown in Table 6.3 and the parameters for Kelen-Tudos and Finemann-Ross were calculated as well that were demonstrated in Table 6.4. $M_1$ and $M_2$ represents initial mol fraction of DK-2 and AN, while $m_1$ and $m_2$ represents DK-2 and AN feed in copolymers.

$r_1$ and $r_2$ values from F-R graph have been found as 1.90 and 0.82, respectively. $r_1 \cdot r_2$ value is 1.56 which is greater than 1 that can be interpreted as a formation of block copolymer. $r_1$ value is greater than 1 while $r_2$ is smaller than 1 which means copolymer tends to add monomer DK-2 more than it adds AN to the feed.

## 6.5 MCC Analysis for PAN:DK-2 (8:2) Copolymers

In order to measure the rate at which the heat of combustion of fuel gases was released by PAN homopolymer and PAN:DK-2 copolymer samples (in milligram quantities), during controlled pyrolysis in an inert gas stream, micro-scale combustion calorimetry (MCC) analysis was performed. The results of the analyses for PAN:DK-2 copolymers in Table 6.5 demonstrated that the most improved flame retardancy for the copolymers was obtained from PAN:DK-2 (10%) copolymer.

**Table 6.5** MCC Parameters for PAN:DK-2 Polymers

| Parameters | HR Capacity (J/(g·K)) | PHRR (W/g) | Total HR (kJ/g) |
|---|---|---|---|
| PAN | 113.7 | 113.245 | 15.21 |
| PAN:DK-2 (5%) | 129.5 | 121.8 | 16.72 |
| PAN:DK-2 (10%) | 135.25 | 133.85 | 16.13 |
| PAN:DK-2 (20%) | 128 | 124.26 | 17 |
| PAN:DK-2 (30%) | 140.6 | 132.06 | 16.20 |
| PAN:DK-2 (90%) | 457.3 | 458.83 | 22.73 |

## 6.6 Conclusion

In this research, starting reagent AHM was used with diphenylphosphine oxide for synthesizing a phosphorus containing monomer and then this monomer was copolymerized with acrylonitrile to obtain a flame retardant polymer. The copolymerization was done with different monomer ratio in the reaction media; 5%, 10%, 15%, 20%, 30%, 50% and 90%, which were encoded as PAN:DK-2 (1), PAN:DK-2 (2), PAN:DK-2 (3), PAN:DK-2 (4), PAN:DK-2 (5) and PAN:DK-2 (6), respectively.

TGA analyses for these polymers demonstrated that the polymers had a good char yield at 600 °C and PAN:DK-2 (2) had the best yield among them which supports to the contribution of phosphorus containing group to thermal stability of copolymer.

Phosphorus content in the formulation increases the thermal properties of the obtained copolymers.

In photo-DSC graphs, it can be seen that photopolymerization rate of DK-2 homopolymer is faster than DK-2:HEMA copolymer. Phospha-Michael addition to this monomer makes it possible to advance monomers with different reactivities with a variety of additional functional groups. Thus, AHM is suitable to be functionalized because of having an α, β-unsaturated carbonyl group.

Halogen free flame retardants such as P-FRs are alternatives to their halogenated counterparts since the market of the FRs heads towards more and more environmentally friendly solutions due to the precautions for both human health and environmental pollution. Reactive functional phosphorus containing group in DK-2 monomer allows tailoring the properties of FRs that can be derived from it that gives inherent flame retardancy to the materials which can be used in electronics, paper, textile industry, etc.

# References


[1] Velencoso, M. M., et al., Molecular firefighting—how modern phosphorus chemistry can help solve the challenge of flame retardancy. Angewandte Chemie International Edition, 2018. 57(33): p. 10450-10467.

[2] Jang, B., J. Choi, and Technology, Research trend of flame retardant and flame retardant resin. Polymer Science, 2009. 20(1): p. 8-15.

[3] Brushlinsky, N. N., Ahrens M., Sokolov S. V., Wagner P., World Fire Statistics, 2018. Accessed on May 12, 2019. Available: https://www.ctif.org/sites/default/files/2018-06/CTIF_Report23_World_Fire_Statistics_2018_vs_2_0.pdf.

[4] "National National Interagency Coordination Center Incident Management Situation Report," 2019. Accessed on June 3, 2019. Available: https://www.nifc.gov/fireInfo/nfn.htm

[5] Guha-Sapir, D., R. Below, and P. Hoyois, in EM-DAT: International Disaster Database. 2015: Belgium. p. 57-58.

[6] M. Le Bras, D. P., S. Bourbigot, Smoke Development and Suppression, in Flammability Handbook. 2003, J. Troitzsch, Hanser Verlag Pub.: Munich. p. 189–206.

[7] Limiting Oxygen Index, Standard Test Method for Measuring Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics, in ASTM D 2863. 1983.

[8] Babrauskas, V., Development of the Cone Calorimeter—A Bench-Scale Heat Release Rate Apparatus Based on Oxygen Consumption, in Fire and Materials. 1984. p. 81.

[9] UL 94: Test for Flammability of Plastic Materials for Parts in Devices and Appliances, in ANSI/ASTM D-635-77. 1977.

[10] Bourbigot, S. and S. Duquesne, Fire retardant polymers: recent developments and opportunities. Journal of Materials Chemistry, 2007. 17(22): p. 2283-2300.

[11] Arnold, F. E., Mater. Res. Soc. Symp. Proc. 1989.

[12] Xu, L., et al., Research progress of flame retardant polyacrylonitrile and its fiber. 2010. 31: p. 146-152.

[13] Y. L. Ren, et al., Thermal degradation kinetics of poly (O, O-diethyl-O-allylthiophosphate-co-acrylonitrile) in nitrogen. Journal of Applied Polymer Science, 2010. 115(6): p. 3705-3709.

[14] Y. L. Ren, P. Y. Xin, S. U. Qian, B. W. Cheng, D. O., Preparation and Properties of Halogen-Free Fire Retardant Acrylonitrile Copolymer. Chem. J. Chin. 34 2013: p. 2216–2222.

[15] Y. L. Ren, B. W. C., L. Xu, Z. Li, A. Jiang, Y. Lu, , Non-Isothermal Decomposition Kinetics of Novel Fire Retarded Polyacrylonitrile Copolymer in Air. Acta Chim. Sinica 67 2009: p. 2127–2132.

[16] Zhang, J., A. Horrocks, and M. Hall, The flammability of polyacrylonitrile and its copolymers IV. The flame retardant mechanism of ammonium polyphosphate. Fire and Materials, 1994. 18(5): p. 307-312.

[17] Rahaman, M. S. A., A. F. Ismail, and A. Mustafa, A review of heat treatment on polyacrylonitrile fiber. Polymer degradation Stability, 2007. 92(8): p. 1421-1432.

[18] Yaman, N., Preparation and flammability properties of hybrid materials containing phosphorous compounds via sol-gel process. Fibers and Polymers, 2009. 10(4): p. 413-418.

[19] Ren, Y., et al., Flame retardant polyacrylonitrile fabrics prepared by organic-inorganic hybrid silica coating via sol-gel technique. Progress in Organic Coatings, 2017. 112: p. 225-233.

[20] Scott, A. C., The Pre-Quaternary history of fire. Palaeogeography, palaeoclimatology, palaeoecology, 2000. 164(1-4): p. 281-329.

[21] Santín, C. and S. H. Doerr, Fire effects on soils: the human dimension. Philosophical Transactions of the Royal Society B: Biological Sciences, 2016. 371(1696): p. 20150171.

[22] Doerr, S. H. and C. Santín, Global trends in wildfire and its impacts: perceptions versus realities in a changing world. Philosophical Transactions of the Royal Society B: Biological Sciences, 2016. 371(1696): p. 20150345.

[23] "Using Nanotechnology to Minimize Fire Damage," April 10, 2019. Accessed on May 10. Available: https://www.usfa.fema.gov/current_events/041019.html

[24] "What Are Plastics?," 2019. Accessed on June 4, 2019. Available: https://www.plasticseurope.org/en/about-plastics/what-are-plastics

[25] "Flame Retardants Report," 2019. Accessed on April 22, 2019. Available from: https://www.ceresana.com/en/market-studies/chemicals/flame-retardants/ceresana-market-study-flame-retardants.html.

[26] Levchik, S. V., Introduction to flame retardancy and polymer flammability. Flame retardant polymer nanocomposites, 2007: p. 1-29.

[27] Kashiwagi, T., Flame retardant mechanism of the Nanotube-based nanocomposite-final report. NIST GCR, 2007: p. 07-912.

[28] EPA, U., Environmental Profiles of Chemical Flame-retardant Alternatives for Low-Density Polyurethane Foam. 2005.

[29] Visakh, P. and A. Yoshihiko, Flame retardants: Polymer blends, composites and nanocomposites. 2015: Springer.

[30] Kutz, M., Applied plastics engineering handbook: processing and materials. 2011: William Andrew.

[31] Hornsby, P. R., Macromolecular Symposia. Vol. 108. 1996, Chichester. 203–219.

[32] Nalepa, R. and D. Scharf, Hoechst Celanese Corp., 1993; b) L. J. Chyall, HA Hodgen, F. J. Vyverberg, RW Chapman, Pabu Services, Inc., 2005; c) A. Sut, S. Greiser, C. Jäger, B. Schartel. Polymer degradation and stability, 2015. 121: p. 116-125.

[33] Chyall, L. J., et al., Intumescent polymer compositions. 2005, Google Patents.

[34] Sut, A., et al., Interactions in multicomponent flame-retardant polymers: Solid-state NMR identifying the chemistry behind it. Polymer degradation and stability, 2015. 121: p. 116-125.

[35] Friederich, B., et al., Tentative links between thermal diffusivity and fire-retardant properties in poly (methyl methacrylate)–metal oxide nanocomposites. Polymer degradation and stability, 2010. 95(7): p. 1183-1193.

[36] Pavlidou, S. and C. Papaspyrides, A review on polymer–layered silicate nanocomposites. Progress in polymer science, 2008. 33(12): p. 1119-1198.

[37] Kashiwagi, T., et al., Flammability properties of polymer nanocomposites with single-walled carbon nanotubes: effects of nanotube dispersion and concentration. Polymer, 2005. 46(2): p. 471-481.

[38] Bourbigot S., Flammability Handbook: Fire Retardant Plastics. 2003, Munich, Germany: Hanser Publications.

[39] Morgan, A. B. and J. W. Gilman, An overview of flame retardancy of polymeric materials: application, technology, and future directions. Fire and Materials, 2013. 37(4): p. 259-279.

[40] Wang, Q., Polymer nanocomposite: a promising flame retardant. J Mater Sci Nanotechnol, 2013. 1(2): p. e202.

[41] OECD, Risk Reduction Monograph Vol. 3. 1994, Paris.

[42] WHO, Environmental Health Criteria. International Program on Chemical Safety. Vol. 162. 1994, Geneva.

[43] WHO, Environmental Health Criteria. International Program on Chemical Safety. Vol. 192. 1997, Geneva.

[44] WHO, Environmental Health Criteria. International Program on Chemical Safety. Vol. 209. 1998, Geneva.

[45] Baek, Y. J. and J. H. Shin, Risk points of flame retardant textiles by halogen and halogen-free laminating film. Materials Sciences Applications, 2014. 5(11): p. 830.

[46] Papaspyrides, C. D. and P. Kiliaris, Polymer green flame retardants. 2014: Newnes.

[47] Lomakin, S., et al., Novel class of ecofriendly flame retardants based on renewable raw materials. Journal of Characterization and Development of Novel Materials, 2012. 4(1): p. 53.

[48] Zammarano, M., et al., Sustainable flame retardants: bio-derived products as intumescing materials. Fire and Materials, 2011: p. 337-342.

[49] Sommerhuber, P. F., et al., Life cycle assessment of wood-plastic composites: Analysing alternative materials and identifying an environmental sound end-of-life option. Resources, Conservation and Recycling, 2017. 117: p. 235-248.

[50] Hoang, D., et al., Organo-phosphorus flame retardants for unsaturated polyester derived from recycled poly (ethylene terephthalate). Macromolecular Research, 2016. 24(6): p. 537-546.

[51] Schlummer, M., et al., Report: recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE). Waste management research, 2006. 24(6): p. 573-583.

[52] Levchik, S. and E. Weil, Developments in phosphorus flame retardants, in Advances in Fire retardant materials. 2008, Elsevier. p. 41-66.

[53] Lewin, M. and E. D. Weil, Mechanisms and modes of action in flame retardancy of polymers. Fire retardant materials, 2001. 1: p. 31-68.

[54] Rabe, S., Y. Chuenban, and B. Schartel, Exploring the modes of action of phosphorus-based flame retardants in polymeric systems. 2017. 10(5): p. 455.

[55] Schartel, B., Phosphorus-based flame retardancy mechanisms—old hat or a starting point for future development? 2010. 3(10): p. 4710-4745.

[56] Green, J., Mechanisms for flame retardancy and smoke suppression-a review. Journal of Fire Sciences, 1996. 14(6): p. 426-442.

[57] Brauman, S., Phosphorus fire retardance in polymers. 2. Retardant-polymer substrate interactions. Journal of Fire Retardant Chemistry, 1977. 4(1): p. 38-58.

[58] Camino, G., L. Costa, and M. L. Di Cortemiglia, Overview of fire retardant mechanisms. 1991. 33(2): p. 131-154.

[59] Perret, B., K. Pawlowski, and B. Schartel, Fire retardancy mechanisms of arylphosphates in polycarbonate (PC) and PC/acrylonitrile-butadiene-styrene: the key role of decomposition temperature. 2009. 97(3): p. 949-958.

[60] Lu, S. Y. and I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers. Progress in polymer science, 2002. 27(8): p. 1661-1712.

[61] Landrock, A. H., Handbook of plastic foams: types, properties, manufacture and applications. 1995: Elsevier.

[62] Toldy, A., B. Szolnoki, and G. Marosi, Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. 2011. 96(3): p. 371-376.

[63] Szolnoki, B., et al., Comparison of additive and reactive phosphorus-based flame retardants in epoxy resins. Periodica Polytechnica Chemical Engineering, 2013. 57(1-2): p. 85-91.

[64] Levchik, S. V. and E. D. Weil, A review of recent progress in phosphorus-based flame retardants. Journal of fire sciences, 2006. 24(5): p. 345-364.

[65] Steinmann, M., M. Wagner, and F.R. Wurm, Poly (phosphorodiamidate) s by olefin metathesis polymerization with precise degradation. Chemistry–A European Journal, 2016. 22(48): p. 17329-17338.

[66] Jeng, R. J., et al., Flame retardant epoxy polymers using phosphorus-containing polyalkylene amines as curing agents. Journal of applied polymer science, 2001. 82(14): p. 3526-3538.

[67] Hergenrother, P. M., et al., Flame retardant aircraft epoxy resins containing phosphorus. 2005. 46(14): p. 5012-5024.

[68] Monge, S. and G. David, Phosphorus-based polymers: from synthesis to applications. Vol. 11. 2014: Royal Society of Chemistry.

[69] Schartel, B., et al., Pyrolysis of epoxy resins and fire behavior of epoxy resin composites flame-retarded with 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide additives. Journal of Applied Polymer Science, 2007. 104(4): p. 2260-2269.

[70] Braun, U. and B. Schartel, Flame retardancy mechanisms of aluminium phosphinate in combination with melamine cyanurate in glass-fibre-reinforced poly (1, 4-butylene terephthalate). 2008. 293(3): p. 206-217.

[71] Perret, B., et al., A new halogen-free flame retardant based on 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide for epoxy resins and their carbon fiber composites for the automotive and aviation industries. 2011. 296(1): p. 14-30.

[72] Klinkowski, C., L. Zang, and M. Döring, DOPO-based flame retardants: synthesis and flame retardant efficiency in polymers. 2013. 32(3): p. 145-158.

[73] Rakotomalala, M., S. Wagner, and M. Döring, Recent developments in halogen free flame retardants for epoxy resins for electrical and electronic applications. 2010. 3(8): p. 4300-4327.

[74] Artner, J., et al., A novel DOPO-based diamine as hardener and flame retardant for epoxy resin systems. 2008. 293(6): p. 503-514.

[75] Ciesielski, M., A. Schäfer, and M. Döring, Novel efficient DOPO-based flame-retardants for PWB relevant epoxy resins with high glass transition temperatures. Polymers for Advanced Technologies, 2008. 19(6): p. 507-515.

[76] Chen, L., et al., Phosphorus-containing thermotropic liquid crystalline polymers: a class of efficient polymeric flame retardants. Polymer Chemistry, 2014. 5(12): p. 3737-3749.

[77] Sacristán, M., et al., Phosphorus-containing soybean-oil copolymers: Cross-metathesis of fatty acid derivatives as an alternative to phosphorus-containing reactive flame retardants. Journal of Applied Polymer Science, 2011. 122(3): p. 1649-1658.

[78] Tan, Y., et al., Piperazine-modified ammonium polyphosphate as monocomponent flame-retardant hardener for epoxy resin: flame retardance, curing behavior and mechanical property. Polymer Chemistry, 2016. 7(17): p. 3003-3012.

[79] Duan, L., et al., Hyperbranched phosphorus/nitrogen-containing polymer in combination with ammonium polyphosphate as a novel flame retardant system for polypropylene. 2016. 134: p. 179-185.

[80] Michael, A., Prakt, Chem, 1887, 35, 349-356.(b) Michael, A.; Schulthess, OJ Prakt. Chem. 1892, 45, 55-63.(c) Michael, A. Am. 1887. 9: p. 112-124.

[81] Molleti, N., C. Bjornberg, and J.Y. Kang, Phospha-Michael addition reaction of maleimides employing N-heterocyclic phosphine-thiourea as a phosphonylation reagent: synthesis of 1-aryl-2, 5-dioxopyrrolidine-3-yl-phosphonate derivatives. 2016. 14(45): p. 10695-10704.

[82] Mather, B. D., et al., Michael addition reactions in macromolecular design for emerging technologies. Progress in Polymer Science, 2006. 31(5): p. 487-531.

[83] Yoneda, N., et al., Asymmetric oxy-Michael addition to γ-hydroxy-α, β-unsaturated carbonyls using formaldehyde as an oxygen-centered nucleophile. Organic letters, 2014. 16(23): p. 6264-6266.

[84] Thomas, B. E. and P. A. Kollman, An ab initio molecular orbital study of the first step of the catalytic mechanism of thymidylate synthase: the Michael addition of sulfur and oxygen nucleophiles. The Journal of Organic Chemistry, 1995. 60(26): p. 8375-8381.

[85] Hoyle C. E., B., Thiol-ene Click Chemistry. 2010. 49(9): p. 1540-1573.

[86] Nguyen, L. T. T., M. T. Gokmen, and F.E. Du Prez, Kinetic comparison of 13 homogeneous thiol–X reactions. Polymer Chemistry, 2013. 4(22): p. 5527-5536.

[87] Enders, D., et al., The Phospha-Michael addition in organic synthesis. European journal of organic chemistry, 2006. 2006(1): p. 29-49.

[88] Zhao, D., et al., Zinc-Mediated Asymmetric Additions of Dialkylphosphine Oxides to α, β-Unsaturated Ketones and N-Sulfinylimines. The Journal of organic chemistry, 2010. 75(20): p. 6756-6763.

[89] Desmet, G. B., et al., Quantitative first-principles kinetic modeling of the aza-Michael addition to acrylates in polar aprotic solvents. The Journal of organic chemistry, 2016. 81(24): p. 12291-12302.

[90] Zeng, X., Recent advances in catalytic sequential reactions involving hydroelement addition to carbon–carbon multiple bonds. Chemical reviews, 2013. 113(8): p. 6864-6900.

[91] Wang, H., Comprehensive Organic Name Reactions. 2010: Wiley.

[92] Troev, K. D., Chemistry and application of H-phosphonates. 2006: Elsevier.

[93] Kraszewski, A. and J. Stawinski, H-Phosphonates: Versatile synthetic precursors to biologically active phosphorus compounds. Pure Applied Chemistry, 2007. 79(12): p. 2217-2227.

[94] Roy, S. and M. Caruthers, Synthesis of DNA/RNA and their analogs via phosphoramidite and H-phosphonate chemistries. Molecules, 2013. 18(11): p. 14268-14284.

[95] Ma, J. A., Catalytic asymmetric synthesis of α-and β-amino phosphonic acid derivatives. Chemical Society Reviews, 2006. 35(7): p. 630-636.

[96] Rulev, A. Y., Recent advances in Michael addition of H-phosphonates. RSC Advances, 2014. 4(49): p. 26002-26012.

[97] Wozniak, L. A., et al., Stereodefined dinucleoside (3′, 5′)-propionamidophosphonates and β-cyanoethylphosphonates and their incorporation into modified oligonucleotides. Tetrahedron Letters, 2009. 50(22): p. 2620-2623.

[98] Fonvielle, M., S. Mariano, and M. Therisod, New inhibitors of rabbit muscle triose-phosphate isomerase. Bioorganic medicinal chemistry letters, 2005. 15(11): p. 2906-2909.

[99] Xang, L., Phosphorus, Sulfur and Silicon. 2009. 184.

[100] Badkar, P. A., N. P. Rath, and C.D. Spilling, Asymmetric Synthesis of 2-Alkyl-3-phosphonopropanoic Acids via P− C Bond Formation and Hydrogenation. Organic letters, 2007. 9(18): p. 3619-3622.

[101] Jiang, Z., et al., P–C Bond formation via direct and three-component conjugate addition catalyzed by 1, 5, 7-triazabicyclo [4.4. 0] dec-5-ene (TBD). Tetrahedron Letters, 2007. 48(1): p. 51-54.

[102] M. A. Kulkarni, V. R. P., U. V. Desai and P. P. Wadgaonkar, C. R. Chemie, 2012. 15.

[103] Birnbaum, J. C., et al., Synthesis of carbamoylphosphonate silanes for the selective sequestration of actinides. Chemical Communications, 2002(13): p. 1374-1375.

[104] Martínez-Castro, E., et al., A green procedure for the regio-and chemoselective hydrophosphonylation of unsaturated systems using CaO under solventless conditions. Green Chemistry, 2010. 12(7): p. 1171-1174.

[105] Tedeschi, L. and D. Enders, Asymmetric Synthesis of β-Phosphono Malonates via Fe2O3-Mediated Phospha-Michael Addition to Knoevenagel Acceptors. Organic letters, 2001. 3(22): p. 3515-3517.

[106] Samarat, A., et al., A new synthesis of (±)-homosarkomycin ethyl ester. Tetrahedron Letters, 2001. 42(7): p. 1273-1274.

[107] Alonso, F., I. P. Beletskaya, and M. Yus, Transition-metal-catalyzed addition of heteroatom− hydrogen bonds to alkynes. Chemical reviews, 2004. 104(6): p. 3079-3160.

[108] Beletskaya, I. and M. Kazankova, Catalytic methods for building up phosphorus-carbon bond. Russian journal of organic chemistry, 2002. 38(10): p. 1391-1430.

[109] Tanaka, M., Homogeneous catalysis for HP bond addition reactions, in New Aspects in Phosphorus Chemistry IV. 2004, Springer. p. 25-54.

[110] Coudray, L. and J. L. Montchamp, Recent Developments in the Addition of Phosphinylidene-Containing Compounds to Unactivated Unsaturated Hydrocarbons: Phosphorus–Carbon Bond Formation by Hydrophosphinylation and Related Processes. European journal of organic chemistry, 2008. 2008(21): p. 3601-3613.

[111] Merino, P., E. Marques-Lopez, and R.P. Herrera, Catalytic enantioselective hydrophosphonylation of aldehydes and imines. 2008. 350(9): p. 1195-1208.

[112] Baillie, C. and J. Xiao, Catalytic synthesis of phosphines and related compounds. Current Organic Chemistry, 2003. 7(5): p. 477-514.

[113] Delacroix, O. and A. Gaumont, Hydrophosphination of unactivated alkenes, dienes and alkynes: a versatile and valuable approach for the synthesis of phosphines. Current Organic Chemistry, 2005. 9(18): p. 1851-1882.

[114] Bock, T., H. Möhwald, and R. Mülhaupt, Arylphosphonic Acid-Functionalized Polyelectrolytes as Fuel Cell Membrane Material. 2007. 208(13): p. 1324-1340.

[115] Ogawa, T., N. Usuki, and N. Ono, A new synthesis of π-electron conjugated phosphonates and phosphonic bis (diethylamides) and their SHG activities. Journal of the Chemical Society, Perkin Transactions 1, 1998(17): p. 2953-2958.

[116] Zakeeruddin, S., et al., Molecular engineering of photosensitizers for nanocrystalline solar cells: synthesis and characterization of Ru dyes based on phosphonated terpyridines. Inorganic Chemistry, 1997. 36(25): p. 5937-5946.

[117] Belfield, K. D., C. Chinna, and K. J. Schafer, New NLO stilbene derivatives bearing phosphonate ester electron-withdrawing groups. Tetrahedron letters, 1997. 38(35): p. 6131-6134.

[118] Welch, C. M., E. J. Gonzales, and J. D. Guthrie, Derivatives of unsaturated phosphonic acids. The Journal of Organic Chemistry, 1961. 26(9): p. 3270-3273.

[119] W. F. J, and H. Paxton, Preparation and polymerization of addition compounds of unsaturated tertiary phosphine oxides. Journal of Polymer Science Part A: General Papers, 1965. 3(10): p. 3427-3437.

[120] Welch, F. and H. Paxton, Preparation and polymerization of propenyldiphenylphosphine oxide isomers. Journal of Polymer Science Part A: General Papers, 1965. 3(10): p. 3439-3449.

[121] Levchik, S. V. and E. D. Weil, Flame retardancy of thermoplastic polyesters—a review of the recent literature. Polymer International, 2005. 54(1): p. 11-35.

[122] Trost, B. M., On inventing reactions for atom economy. Accounts of chemical research, 2002. 35(9): p. 695-705.

[123] Mancuso, J. and M. Lautens, Mild procedure for the catalytic bis (stannylation) of alkynes with hexaalkylditins. Organic letters, 2003. 5(10): p. 1653-1655.

[124] Lee, P. H., S. W. Lee, and K. Lee, Pd-catalyzed carbonylative cross-coupling reactions by triorganoindiums: Highly efficient transfer of organic groups attached to indium under atmospheric pressure. Organic letters, 2003. 5(7): p. 1103-1106.

[125] Liepins, V., A. S. E. Karlström, and J. E. Bäckvall, Allylic phosphates and allylic phosphinates as electrophiles in efficient silylcupration reactions of acetylenes. The Journal of organic chemistry, 2002. 67(7): p. 2136-2143.

[126] Mimeau, D. and A. C. Gaumont, Regio-and stereoselective hydrophosphination reactions of alkynes with phosphine− boranes: access to stereodefined vinylphosphine derivatives. The Journal of organic chemistry, 2003. 68(18): p. 7016-7022.

[127] Stockland, R.A., et al., Microwave-Assisted Regioselective Addition of P(O)−H Bonds to Alkenes without Added Solvent or Catalyst. Organic Letters, 2005. 7(5): p. 851-853.

[128] "Free Radical Polymerization," 2015. Accessed on May 5. Available: https://chem.libretexts.org/Courses/Purdue/Purdue_Chem_26100%3A_Organic_Chemistry_I_(Wenthold)/Chapter_08%3A_Reactions_of_Alkenes/8.7.%09Polymerization/Free_Radical_Polymerization

[129] Bovey, F.A. and P.A. Mirau, NMR of Polymers. 1996: Academic Press.

[130] Tait, P. J. T. and I. G. Berry, 4 - Monoalkene Polymerization: Copolymerization, in Comprehensive Polymer Science and Supplements, G. Allen and J. C. Bevington, Editors. 1989, Pergamon: Amsterdam. p. 575-584.

[131] Fineman, M. and S.D. Ross, Linear method for determining monomer reactivity ratios in copolymerization. 1950. 5(2): p. 299.

[132] Kelen, T. and F. Tudos, Analysis of the linear methods for determining copolymerization reactivity ratios. I. A new improved linear graphic method. Journal of Macromolecular Science—Chemistry, 1975. 9(1): p. 1-27.

[133] Kelen, T., et al., Analysis of the linear methods for determining copolymerization reactivity ratios. IV. A comprehensive and critical reexamination of carbocationic copolymerization data. Journal of Polymer Science: Polymer Chemistry Edition, 1977. 15(12): p. 3047-3074.

# Publications from the Thesis

**Contact Information:** dlk.kcmz@gmail.com

**Conference Papers**

**1**. Synthesis and Characterisation of UV-Curable Phosphorus Containing Flame Retardant Polymer, 16th European Workshop on Phosphorus Chemistry, 24-26 April, 2019