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PREPARATION OF FLAME-RETARDANT NATURAL RUBBER BY  
GRAFTING WITH PHOSPHORUS-CONTAINING MONOMERS

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A Thesis Submitted in Partial Fulfillment of the Requirements  
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กราฟต์โคพอลิเมอร์บนยางธรรมชาติของพอลิ(2-เมทาคริลอิลออกซีเอทิลไคไฟนิลฟอสเฟต) และพอลิ(2-เมทาคริลอิลออกซีเอทิลฟีนิลเบนซีนฟอสโฟเนต) ถูกเตรียมโดยกระบวนการกราฟต์แบบซีดเดอิมัลชันพอลิเมอไรเซชัน โดยใช้ควิมีนไฮโดรเปอร์ออกไซด์และเทระเอทิลีนเพนทาเม็นเป็นสารริเริ่มปฏิกิริยาแบบบริดจิ้ง เพื่อปรับปรุงสมบัติการหน่วงไฟของยางธรรมชาติ จากผลการศึกษาปัจจัยที่มีผลต่อประสิทธิภาพการกราฟต์พบว่า คุณภูมิในการทำปฏิกิริยาที่สูงให้ประสิทธิภาพการกราฟต์ที่สูง แต่ความเสถียรของน้ำยางลดลง เมื่อความเข้มข้นของมอนอเมอร์เพิ่มขึ้น พบว่าประสิทธิภาพการกราฟต์ไม่ต่างกันอย่างมีนัยสำคัญ แต่เปอร์เซ็นต์คอนเวอร์ชันลดลงเหลือ 50 เปอร์เซ็นต์ นอกจากนั้นปริมาณสารริเริ่มปฏิกิริยาที่ 0.25 ส่วนเมื่อเทียบกับเนื้อยางให้ประสิทธิภาพการกราฟต์และเปอร์เซ็นต์คอนเวอร์ชันสูงสุด กราฟต์โคพอลิเมอร์ทั้งสองชนิดบนอนุภาคของยางมีลักษณะเป็นคอร์เชลล์ การสลายตัวเมื่อถูกความร้อนของยางกราฟต์แสดงการสลายตัวสองขั้นภายใต้บรรยากาศไนโตรเจน ขั้นแรกเป็นการสลายตัวของสายโซ่โคพอลิเมอร์ และขั้นที่สองเป็นการสลายตัวของสายโซ่ยาง ค่าดัชนีของปริมาณออกซิเจนที่ใช้ในการลุกติดไฟของยางกราฟต์สูงขึ้นเมื่อเพิ่มปริมาณความเข้มข้นของมอนอเมอร์ทั้งสองชนิด นำไปสู่การเพิ่มสมบัติการหน่วงไฟของยางธรรมชาติ สมบัติเชิงกลของฟิล์มของยางกราฟต์มีค่าไม่แตกต่างกันอย่างมีนัยสำคัญเมื่อเทียบกับยางธรรมชาติเนื่องจากปริมาณของกราฟต์โคพอลิเมอร์ที่น้อย

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KEYWORDS: GRAFT COPOLYMERS / NATURAL RUBBER / SEEDED EMULSION POLYMERIZATION / PHOSPHORUS-CONTAINING COMPOUND

KITIKHUN KOKKLIN: PREPARATION OF FLAME-RETARDANT NATURAL RUBBER BY GRAFTING WITH PHOSPHORUS-CONTAINING MONOMERS. THESIS ADVISOR: ASST. PROF. WORAWAN BHANTHUMNAVIN, Ph.D., THESIS CO-ADVISOR: ASST. PROF. VARAWUT TANGPASUTHADOL, Ph.D., 99 pp.

Graft copolymers of natural rubber with poly(2-methacryloyloxyethyl diphenyl phosphate) (NR-g-PMEDP) and poly(2-methacryloyloxyethyl phenyl benzenephosphonate) (NR-g-PMPBP), were prepared by seeded emulsion polymerization using cumene hydroperoxide and tetraethylenepentamine as a redox initiator system to improve flame-retardant properties of NR. The investigation of factors on grafting properties revealed that high reaction temperature afforded high grafting efficiency but the latex stability decreased. When the monomer concentration increased, the grafting efficiency was not significantly different, while the conversion decreased to 50%. In addition, the initiator concentration of 0.25 phr showed the highest grafting efficiency and percent conversion. Both graft copolymers on NR particles showed the core-shell morphologies. Thermal degradation of graft NRs indicated two stage decompositions under N<sub>2</sub> atmosphere. The first stage corresponded to the decomposition of graft copolymers and the second stage exhibited the decomposition of rubber backbone. The limiting oxygen index (LOI) values of graft NRs increased with increasing monomer contents leading to enhancing the flame retardant properties of NRs. Mechanical properties of graft NR films were not significantly different compared with unmodified NR due to the low amount of graft copolymers.

Field of Study : Petrochemistry and Polymer Science Student's Signature : .....

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## LIST OF ABBREVIATIONS

MEDP	: 2-Methacryloyloxyethyl diphenyl phosphate
MPBP	: 2-Methacryloyloxyethyl phenyl benzenephosphate
PMEDP	: Poly(2-methacryloyloxyethyl diphenyl phosphate)
PMPBP	: Poly(2-methacryloyloxyethyl phenyl benzenephosphate)
$\delta$	: Chemical shift
$M_w$	: Weight average molecular weight
$M_n$	: Number average molecular weight
FTIR	: Fourier transform infrared spectroscopy
NMR	: Nuclear magnetic resonance spectroscopy
MS	: Mass spectroscopy
TEM	: Transmission electron microscopy
TGA	: Thermogravimetric analysis
DSC	: Differential scanning calorimetry
$T_g$	: Glass transition temperature
$CDCl_3$	: Deuterated chloroform
ppm	: Parts per million (unit of chemical shift)
Phr	: Parts per hundred of rubber
DRC	: Dry rubber content
CHPO	: Cumene hydroperoxide
TEPA	: Tetraethylenepentamine
GE	: Grafting efficiency
LOI	: Limiting oxygen index

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of the Problem

Natural rubber (NR) obtained from natural resources of *Hevea brasiliensis* tree, known as *cis*-1,4-polyisoprene has been widely used in many industries because of its good mechanical properties. However, the presence of carbon-carbon double bonds in the main-chain of NR leads to low weather and ozone-resistance. Moreover, NR's unsaturated hydrocarbon chain structure exhibits low oil-resistance, ease to burn readily in air and severe flame spread [1]. Consequently, there are limitations which prevents the use of NR in highly demanding applications such as aerotires, power cables, *etc.* [2]. Therefore, an improvement in heat resistance as well as flame retardancy of NR is highly desirable.

In the past few decades it has been shown that phosphorus-based flame retardants are among the best group of compounds used to reduce flammability of polymers [3]. Upon ignition and burning the surface of polymers will be protected by carbonaceous char layers caused by the degradation of phosphorus compounds which can reduce further flame spread and serve as a physical barrier to heat transfer from the flame to the polymer [3]. In addition, these compounds generate less toxic gases while burning compared to other types of flame retarding agents such as the halogen based counterpart [4]. In general, an incorporation of flame retardant compounds as an additive have been used to prepare flame-retardant materials. This also applied to NR. However, high loadings are often required to achieve a significant effect. In addition, high amounts of additives may have undesirable influences on the physical and mechanical properties of NR. Moreover, flame retarding additives may leach out over a long period of time.

An alternative method to introduce flame-retarding property of phosphorus compounds to a polymer is by chemical modification. This can be achieved through copolymerization of unsaturated organophosphorus compounds. Examples include

incorporation of phosphorus compounds to poly(methyl methacrylate) (PMMA) [5-8], polystyrene (PS) [9], fabrics (poly(acrylonitrile), PAN [10] and cotton [11]), and NR [12, 13] to enhance thermal stability and flame-retardant properties of various commercial polymers. This method offers several potential advantages such as that low levels of modification may suffice, that the modifying groups are chemically attached and therefore are less likely to be lost during subsequent service, and that the modification can more readily be molecularly dispersed throughout the polymer [1].

Modification of natural rubber *via* graft copolymerization is one of the efficient techniques to prepare new specialty NR products. This can be achieved by introducing the secondary polymer which is formed from a monomer consisting of carbon-carbon double bond to the rubber chains *via* chemical bonding. For example, grafting of methyl methacrylate (MMA) [14-18] and styrene [19] onto NR were used to increase the surface roughness and reduce the rubber surface's frictions. Moreover, graft copolymerization was useful to improve the polarity and the mechanical properties of NR in the hardness and modulus [19, 20]. As for the initiator system, the hydrophobic initiator, cumene hydroperoxide (CHPO) and hydrophilic amine activator, tetraethylenepentamine (TEPA) have been extensively chosen as couple redox initiator which can promote free radicals onto the interface of NR particles to give high grafting efficiency and low yield of homopolymer content. It is envisaged that CHPO/TEPA would serve as a suitable initiator system [16, 17, 21].

Therefore, the main purpose of this research is to improve inherent flame-retardant properties of NR through graft copolymerization by incorporating phosphorus-containing monomers onto NR main chains. The first part of the work aims at the synthesis of the phosphorus-containing monomers as flame retardant compounds. The second part focuses on the chemical modification of NR by grafting of the synthesized phosphorus monomer onto NR *via* seeded emulsion polymerization using CHPO/TEPA as redox initiator [18]. The thermal characteristics, flame-retardant properties, and mechanical properties of graft copolymers have been investigated.

## 1.2 Research Objectives

The objectives of this research are as follows:

1. To synthesize organophosphorus monomers namely, 2-methacryloyloxy ethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP). Optimum synthetic conditions have been investigated.
2. To prepare graft copolymers of 2-methacryloyloxyethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP) onto natural rubber latex *via* seeded emulsion polymerization using redox initiator, cumene hydroperoxide (CHPO) and tetraethylenepentamine (TEPA). Effects of reaction temperature, monomer concentration, initiator concentration, and amount of reducing agent have been studied.
3. To investigate the thermal properties, flame-retardant properties, and mechanical properties of grafted NR products.

## 1.3 Scope of the investigation

The stepwise investigation was carried out as follows:

1. Literature survey for method to synthesize organophosphorus compounds
2. Literature survey for method of graft copolymerization of NR *via* seeded emulsion polymerization by using redox initiator system
3. Synthesis of organophosphorus compounds:
  - 2-methacryloyloxyethyl diphenyl phosphate (MEDP)
  - 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP)
4. Preparation of grafted copolymers of organophosphorus compounds onto NR latexes particles *via* seeded emulsion polymerization. Parameters to be investigated which may affect the outcome of the reaction in this step are as follow:
  - Effect of reaction temperature (40, 50, 60, and 70°C)
  - Effect of monomer concentration (10, 15, and 20 wt %)

- Effect of initiator concentration (0.25, 0.50, and 1.00 phr)
  - Effect of the amount of the reducing agent
5. Characterization of the morphology of graft copolymers onto NR particles
  6. Characterization of the thermal properties and flame-retardant properties of grafted NR products
  7. Characterization of the mechanical property of grafted NR films
  8. Result interpretation and summary

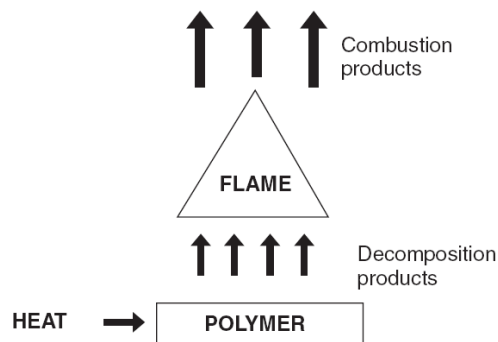


## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Polymer combustion

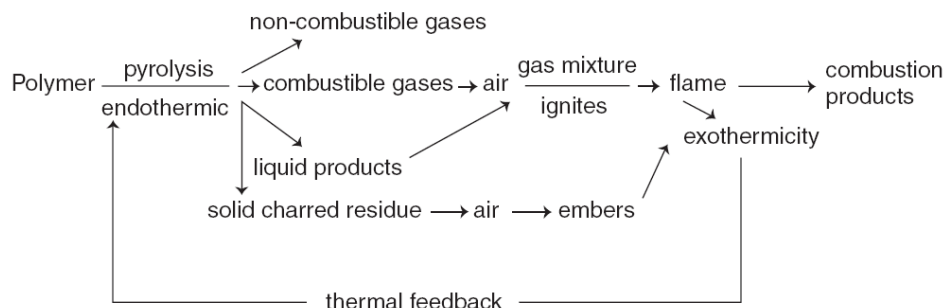
Natural and synthetic polymers, when exposed to a source of sufficient heat, will decompose or 'pyrolyse' evolving flammable volatiles. These mix with the air and, if the temperature is high enough, ignite. Ignition occurs either spontaneously (autoignition) or due to the presence of an external source such as a spark or a flame (flash ignition). If the heat evolved by this ignited flame is sufficient to keep the decomposition rate of the combustible volatiles, i.e. the 'fuel', within the flammability limits for the system, and then a self-sustaining combustion cycle will be established. Figure 2.1 is a representation of this behaviour [22].



**Figure 2.1** Simple representation of polymer combustion processes. (Adapted from reference [22])

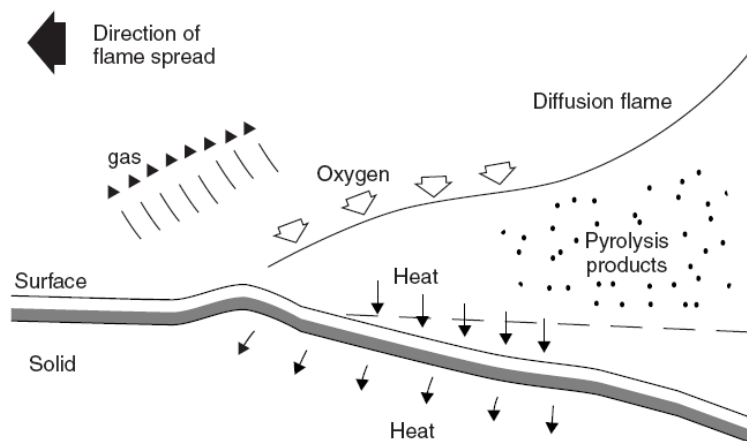
The combustion of polymers is a process comprising a multitude of single steps and basically initiated by endothermic heating and decomposition. The flammable gases formed mix with atmospheric oxygen and ignite, leading to the exothermic processes of flame propagation and heat release. During heating and pyrolysis, endothermic processes take place for overcoming the high bond binding energies between individual atoms (200 to 400 kJ/mole). Ignition initiates the exothermic part of the processes which override the endothermic pyrolytic reaction. Pyrolysis of the polymer is reinforced by thermal feedback (heat release) which fuels the flame at an increasing

level. The flame spreads over the decomposed polymer surface. The diffusion flame is supported by extremely high energy  $H\bullet$  and  $OH\bullet$  radicals which confer a high velocity on the flame front. The schematic of the combustion process is shown in Figure 2.2 [22].



**Figure 2.2** Schematic representation of polymer combustion processes. (Adapted from reference [22])

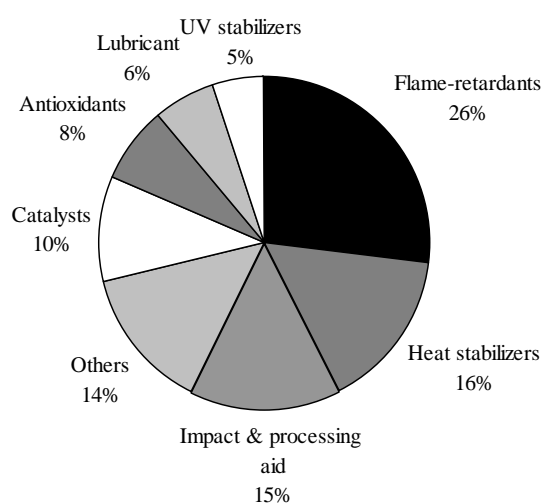
The heat generated *via* the burning process sustains the polymer pyrolysis process as shown by the self-sustaining cycle depicted in Figure 2.2. The rate of pyrolysis will be accelerating leading to an increasing supply of fuel to the flame which then spread over the polymer surface. As a simplified model of the flame chemistry, consider the reactions occurring in a hydrocarbon diffusion flame. The important step is the chain branching step propagated by the highly reactive hydrogen and hydroxy radicals ( $H\bullet$  and  $OH\bullet$ ). These confer a high velocity on the flame front resulting in rapid flame spread. A schematic description of flame spread along a surface is given in Figure 2.3. The diffusion flame advances over the decomposing polymer surface. The extent of the flame spread will also be affected by the heat of combustion of the polymer.



**Figure 2.3** Schematic representation of flame spread.

## 2.2 Type of flame retardants

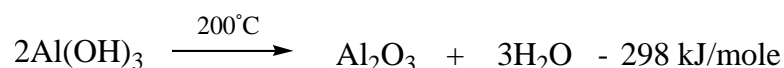
Flame-retardants (FRs), by far the largest group of plastics additives, are playing a major role in the plastic industry by improving life safety. According to Global Business Changes market applications in 1997, the flame retardants were consumed accounting for 27% of plastic additives market (Figure 2.4) [23]. The rapid development of plastic applications in the electronic, building, and automotive industries is very demanding with regard to properties and costs. Type of flame retardants have been designed on inorganic, halogen, and phosphorus compounds.



**Figure 2.4** Worldwide plastic additives [24].

### 2.2.1 Inorganic (Metallic) flame retardant compounds

Inorganic compounds are suitable for use as flame retardants in polymers, since such compounds must be effective in the range of decomposition temperatures of the polymer, mainly between 150 and 400°C. The inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like water, CO<sub>2</sub>, SO<sub>2</sub>, that dilute flammable gases and oxygen to the fire. Currently, aluminium hydroxide (Al(OH)<sub>3</sub>) is the most widely used flame retardant. It starts to break down in the temperature over 200°C.



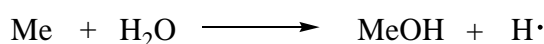
Another flame retardant acting in the same way as aluminium hydroxide is magnesium hydroxide (Mg(OH)<sub>2</sub>), which decomposes at a higher temperature level of

300-330°C. Therefore, it can be used in polymers processed at higher temperature than aluminium hydroxide.

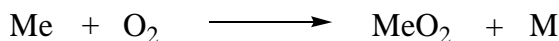


As a result of the endothermic breakdown of aluminium hydroxide and magnesium hydroxide, the polymer is cooled, and thus fewer pyrolysis products are formed. Together with the charring, products of aluminium oxide and magnesium oxide formed on the surface act as an insulating protective layer. In addition, the water vapour liberated has a diluting effect in the gas phase and forms an oxygen displacing protective layer over the condensed phase [25].

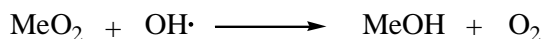
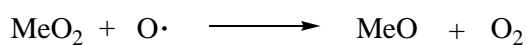
The inhibition action of metal-containing compounds is related to the participation of the compound in the catalyst of destruction of the active centers (atoms and radicals) which are responsible for the development of chain combustion process. Whether heterogeneous or homogeneous mechanisms of active center destruction occur in the presence of metal-containing compounds depends on a large number of factors. Supporters of the homogeneous inhibitor action mechanism for metal-containing compounds assume that the compounds evaporate inside the flame decompose and produce intermediate active forms of the compounds, for instance, hydroxide of metals. Alkali metal hydroxides are easily formed inside a flame when decomposition of metal salts occurs in the presence of water vapour. Inside fuel-rich flames, interaction between alkali metals and water take place according to the equilibrium reaction.



The formation of active intermediate metal-containing particles within a fuel-deficient flame occurs as a result of the direct oxidation of alkali metals, and the metal superoxide is formed.



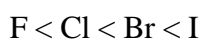
It was assumed that metal superoxides react easily with the active centers of a combustion process, forming more stable and active compounds.



where Me is the metal atoms and M is third particle (for instance, H<sub>2</sub>).

### 2.2.2 Halogen-based flame retardant compounds

There are three types of halogen-containing flame retardants that are used for purposes of reducing combustibility of polymer materials. The derivatives of compounds were aliphatic, cycloaliphatic, and aromatic structures. The nature of halogen atom is varied in each type of structure. The compounds represent either the reactive type of flame retardant or nonreactive type. The effectiveness of flame retardation reactions using halogen containing compounds with similar structures increases in the sequence.



As a function of their structure, the halogen compounds either undergo pyrolysis inside the condensed phase or evaporate and are destroyed in the gaseous phase. The initial pyrolysis reactions of halogen-containing compounds generally lead to the formation of HX and  $RX_n$  but seldom to the formation of  $X_2$ , where X is a halogen atom. The detachment of HX from the aliphatic structure macromolecules is accompanied mostly by the formation of unsaturated systems. The transformation of these systems inside the condensed phase causes the formation of a nonvolatile carbonaceous residue which affects the rate of combustion of the materials [26].

The low-molecular compounds HX,  $RX_n$ , and  $X_2$  enter the gaseous phase and participate in the chain-branching flame reaction of fuel gas oxidation. The relationship between the efficiency of the substances' inhibitor action and the nature of the halogen and the effect of small concentration of additives confirm that the inhibitor mechanism of halogens and their derivatives on the ignition and combustion of model systems has a chemical origin. It was discovered that halogens and their compounds do not affect the oxidation of carbon to carbon dioxide. At the same time, they essentially inhibit the oxidation of CO to  $CO_2$  and the formation of formaldehyde during combustion of methane.

### 2.2.3 Phosphorus-based flame retardant compounds

A variety of phosphorus-base flame retardant compounds including inorganic phosphate, insoluble ammonium phosphate, organophosphorus, chlorophosphate and phosphonate, and red phosphorus compounds is widely used in many materials. The mechanism for flame retardancy varies with the phosphorus compound and the

polymer/polymer type. A phosphorus-containing flame retardant can function in the condensed (polymer) phase, the gas phase, or concurrently in both phase. Phosphorus-containing compounds increase the amount of carbonaceous residue or char formed by one or both of the two mechanisms: redirection of the chemical reactions involved in decomposition in favor of reactions yielding carbon rather than CO or CO<sub>2</sub> and formation of a surface layer of protective char. This layer can shield the polymeric substrate from the flame (heat) and oxygen [3].

An analysis of the percentage of phosphorus in the residue after combustion of polymer materials shows that phosphorus can remain in the condensed phase, almost completely or partially, or that it can completely vaporize. The latter phenomenon depends not only on the chemical nature and initial concentration of the phosphorus flame retardant but also, to a high degree, on the nature of polymer substrate and the structure of the material. The relationship between the amount of phosphorus remaining in the condensed phase and the nature of the polymer indicates the importance of the nature of the reaction between the polymers and the phosphorus compound. A number of action mechanisms of phosphorus compounds have been described in a survey by Lyons, *et al.* [26]. The function of phosphorus and its compounds as flame retardants is related to the following factors:

- The specific effect of phosphorus compounds on processes in the condensed phase during the combustion of polymer materials. Chemical transformations of polymers occurring at this time tend to increase the yield of nonvolatile char residues and decrease the amount of pyrolysis fuel products.
- The formation of a surface glass or a viscous melted layer of polymetaphosphoric acid. This layer serves as a physical barrier to heat transfer from the flame to the polymer and to diffusion of reagents.
- The inhibition of gaseous phase flame reactions.
- The effect of carbonized polymer pyrolysis product on heterogeneous oxidation.

It has been demonstrated with numerous examples that many phosphorus flame retardants of the reactive and additive types contribute to the formation and increase of yield of nonvolatile carbonized residues during the pyrolysis and combustion of

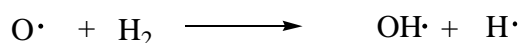
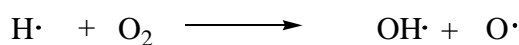
polymers. The detailed mechanism of this effect is not clear, as is the case with the mechanism for the carbonization of polymers [27].

## 2.3 Mechanisms of flame retardancy of polymers

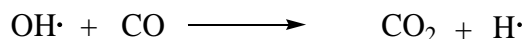
All flame retardants act either in the vapour-phase or the condensed-phase through a chemical and physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition or flame spread. The vapour-phase and condensed-phase processes have been generally considered as the primary, though not the only, effective mechanism of flame retardancy.

### 2.3.1 Vapour-phase or gas-phase mechanisms

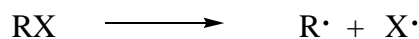
The gas phase activity of the active flame retardant consists in its interference in the combustion train of the polymer. Polymers, like other fuels, produce upon pyrolysis species capable of reaction with atmospheric oxygen and produce the H<sub>2</sub>-O<sub>2</sub> scheme which propagates the fuel combustion by the branching reaction.



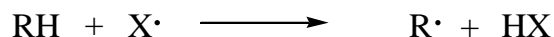
The main exothermic reaction provides most of the energy maintaining the flame. To slow down or stop the combustion, it is imperative to hinder the chain branching reaction.



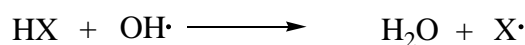
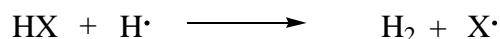
Halogen-containing flame retardants act by interfering with the radical chain mechanism taking place in the vapour phase. The high energy OH• and H• radicals formed by combustible gases are removed by the halogen-containing flame retardant. At first the flame retardant breaks down to radicals, where X is chlorine (Cl) and bromine (Br). The effect in the first instance occur either by releasing of halogen atom, if the flame-retardant molecule does not contain hydrogen, or by releasing a hydrogen halide [28].



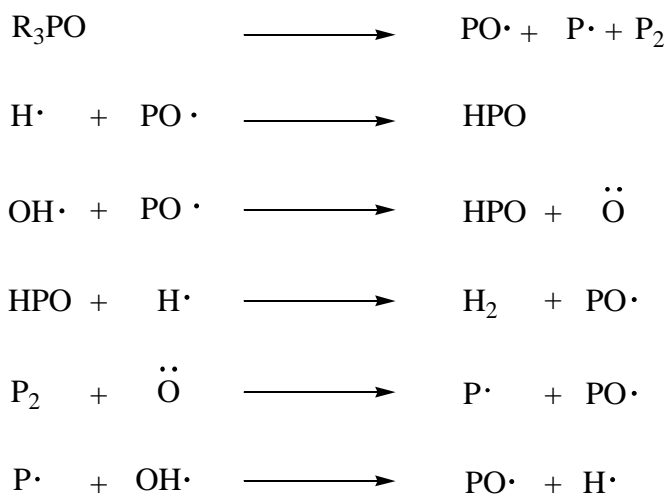
The halogen radical  $X\cdot$  reacts further by undergoing hydrogen abstraction from the substrate  $RH$  to produce hydrogen halide.



The hydrogen halide is believed to be the actual flame inhibitor by affecting the chain branching. It interferes with the radical chain mechanism by reaction with the high energy  $H\cdot$  and  $OH\cdot$  radicals and by replacing them with  $X\cdot$  radicals of lower energy. The actual flame retardant effect is thus produced by  $HX$ .



In the case of the phosphorus compounds, they also exhibit flame by vapour-phase activity. The volatility of phosphorus can be efficient as vapour-phase active inhibitor. This has been demonstrated for example in the case of trialkylphosphate (Scheme 2.1). When phosphorus-containing compounds enter the flame zone during the combustion of polymer they are able to react with active centers of the combustion process and retard the rate of the process. The mechanism of  $R_3PO$  decomposition inside a flame is not clear. The formation of  $P_2$  and  $P\cdot$  indicates a dissociation of the phosphorus compound and the possibility of equilibrium reactions taking place. The salient features of these reactions are the promotion of hydrogen recombination and the scavenging of oxygen radicals by molecule of phosphorus. The volatile phosphorus-containing species can act as a strong vapour-phase active flame inhibiting species [29].



**Scheme 2.1** Vapour-phase flame inhibiting species.



### **2.3.2 Condensed-phase mechanism**

The condensed-phase mechanism postulates a chemical interaction between the flame-retarding agent, which is usually added in substantial amounts, and the polymer. This interaction occurs at temperatures lower than those of the pyrolytic decomposition. Two principal modes of this interaction were suggested as dehydration and cross-linking. When exposed to heat such as ignition, or the combustion flame, the surface temperature of the polymer can rise to a point at which its structure will break down and it will release volatile materials. Physical properties, which can influence this, are thermal conductivity, heat capacity and the ability to melt back away from an ignition source. As part of the degradation mechanism some polymers will also produce carbonaceous char. The behavior of a polymer in a fire risk situation is therefore the result of a combination of many different physical and chemical processes, which take place in the condensed phase. The physics and chemistry of char formation are given in many processes that they affect polymer combustion [22].

#### **2.3.2.1 Bond dissociation**

Thermal decomposition of a polymer is often initiated by dissociation of covalent bonds to form radicals. Bond dissociation energies (BDE) will depend on the nature of the atoms making up the bond and also the precise structural environment in which the bond occurs. Bond dissociation values can often be used to explain why one bond dissociates in preference to another, and are of particular importance for polymers, which degrade by free radical mechanisms.

#### **2.3.2.2 Chemistry of polymer degradation**

The mechanisms of polymer degradation and the temperatures at which they occur will depend very much on the polymer's structure. Mechanisms are usually hypothesized after the analysis of degradation products, and there is still often considerable debate over the precise path taken to reach these structures.

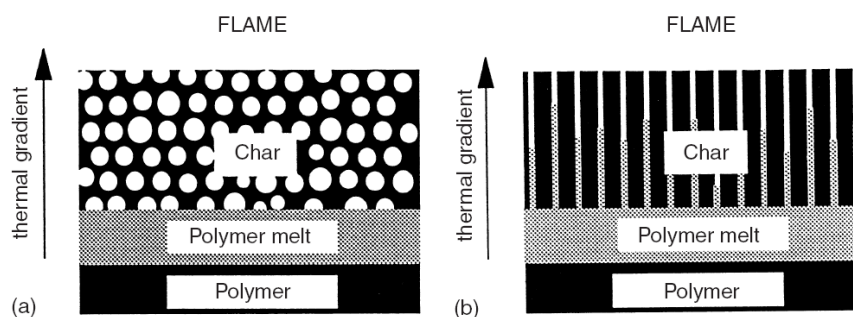
#### **2.3.2.3 Char-forming polymer**

Char formation is probably the most important condensed-phase mechanism for modifying the combustion process. It serves as a barrier to heat and mass flow, and as a means of stabilizing carbon, thus preventing its conversion to combustible gases. The efficiency of a char as a barrier in these processes depends greatly on its chemical and

physical structure. The ability of char formation to prevent sustained ignition will also depend on its rate of formation in relation to other degradation mechanisms, especially the release of combustible gases.

### 2.3.2.4 Char structure

In order to understand the importance of the physical structure of the char on flame-retardant properties, it is useful to describe an ideal and non-ideal char principle as illustrated in Figure 2.5. The ideal char (a) for flame-retardant properties is an intact structure of closed cells containing pocket of gas. The bubbles of gas must become frozen into the expanding and thickening polymer melt, which ultimately solidifies to produce the honey-combed structure. This prevents the flow of volatile liquids or vapours into the flame and provides sufficient thermal gradient to keep the remaining polymer or polymer melt below its decomposition temperature. The non ideal (b) or poor char structure does not contain closed cells but channels or fissures through which gaseous decomposition products or polymer melt can escape. Of these two effects the more important is the movements of liquid products which can be drawn by capillary action into hotter regions where they are more likely decompose.



**Figure 2.5** (a) Ideal and (b) non-ideal of carbonaceous of char residues [22].

## 2.4 Methods of incorporation of phosphorus-based flame retardant into materials

The successful strategies to reduce the flammability of a polymeric material involve interrupting the complex stages of the combustion process at one or more points to reduce the rate and change the mechanism of combustion at that point. From a practical point of view, this is achieved either by the mechanical blending of a suitable flame-retardant compound with the polymeric substrate (i.e. by introducing an additive)

or by the chemical incorporation of the retardant into the polymer molecule by simple copolymerization or by chemical modification of the preformed polymer (*i.e.* using a reactive component). There exist two approaches to achieve flame retardancy in polymers generally known as the physical and chemical means.

#### 2.4.1 Physical modification

Currently, synthetic polymers are usually made more flame retardant by incorporating additives. The conventional additive types of flame retardant have been used by incorporated into polymeric by physical means. This obviously provides the most economical and expeditious way for adding new properties to commercial polymers. Modified natural rubber products have wide commercial applications. The low molecular weight rubber is used for potting compounds, binders for abrasive wheels and as casting moulds. Recently, chemical modification of NR has been carried out by reactions on relatively low molecular weight polymers, including those on liquid natural rubber. In 1994, Derouet *et al.* [2] prepared phosphorus modified epoxidised natural rubber with dibutyl phosphate. The incorporation of phosphorus decreased the flammability behaviors of vulcanized rubber, whereas the phosphorus units affect the crosslinking of NR chain resulting in the decrease of mechanical properties of rubber.

Menon *et al.* [30-32] prepared flame-retardant NR by incorporated polyphosphates as phosphatic plasticizers. This study revealed that the carbonaceous char residues obtained from thermogravimetric analysis and burning of these polymers suggested a condensed-phase mechanism of flame retardancy. The incorporated polyphosphates led to improved thermal stability and superior fire performance. The effect of intumescent flame-retardant (IFR) agent and microencapsulated IFR agent containing 4A zeolite as an additive on the properties NR was studied by Wang *et al.* [33, 34]. They also found that the flame retarding additives can produce carbonaceous char residue which improved thermal stability and flame retarding performance of NR. On the other hand, the high amount of additives can be clearly seen from the fracture surface and thus may lead to the decrease of the tensile properties of the system.

In 2007, Price *et al.* [9] studied the additive polystyrene systems containing incorporated triethylphosphate (TEP) and diethylethylphosphonate (DEEP). The additive was shown to have evolved before polymer decomposition occurred and low

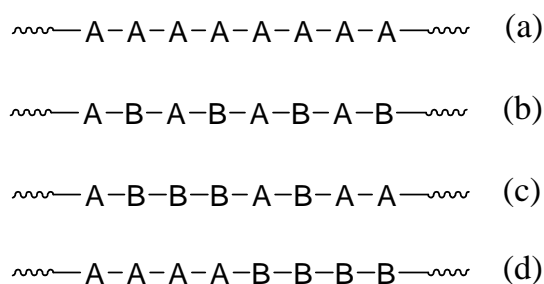
percentage of char residues was observed. Thus the mechanism of flame retardant action of the phosphorus incorporated into the polystyrene was suggested to have occurred in the vapour phase.

## 2.4.2 Chemical modification

In early reports, the application of reactive flame retardants involves either the design of new, intrinsically flame retarding polymers or modification of existing polymers through copolymerization with a flame retarding unit either in the chain or as a pendant group. This leaves modification approach the most favored because covalently incorporating the flame retarding unit in the polymer backbone imparts the flame retardancy permanently, and in most cases the original physical and mechanical properties are maintained. The incorporation of even a few weight percent of the unit into polymer chains can lead to remarkable improvements in the overall flame retardancy of the polymer [35].

### 2.4.2.1 Copolymers

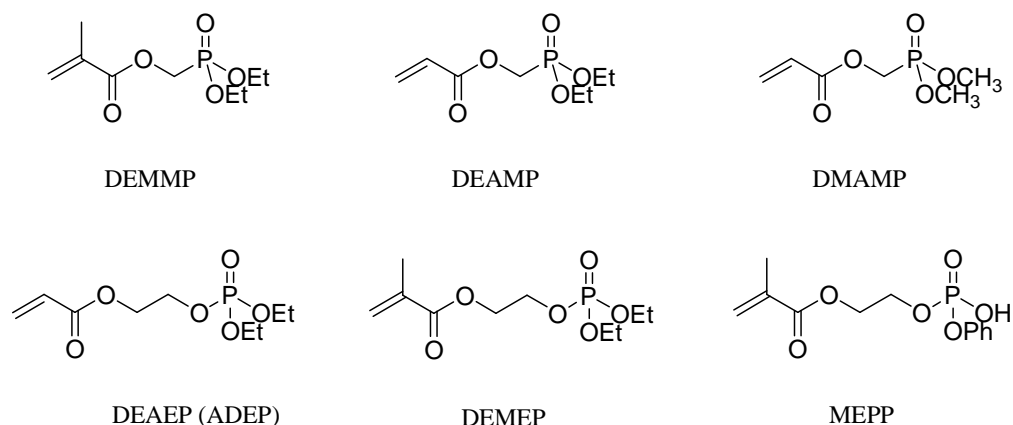
Copolymer is a polymer derived from two or more monomeric species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to methods used to chemically synthesize a copolymer. Since a copolymer consisted of at least two types of constituent units which can be classified based on the arrangement along the chain. Linear copolymers consisted of a single main chain whereas branched copolymers consisted of a single main chain with one or more polymeric side chains. These include the alternating copolymers, random copolymers, and block copolymers were illustrated in Figure 2.6.



**Figure 2.6** Types of polymers: (a) homopolymer, (b) alternating copolymers, (c) random copolymers, and (d) block copolymers.

In 2006, Wang *et al.* [8, 36] reported a method for the synthesis of a new reactive flame retardant compound of 2-methacryloxyethyl phenyl phosphate (MEPP) (Figure 2.7) by esterification of phenyl dichlorophosphate with 2-hydroxyethyl methacrylate, followed by hydrolysis. Copolymers of methyl methacrylate (MMA) and MEPP were prepared by bulk polymerization of MMA in the presence of various amount of MEPP. The increase in the amount of MEPP contents exhibited better thermal stability and more char residue than pristine PMMA. The burning of MMA/MEPP copolymer can be inhibited by as low as 2.17 wt% phosphorus content. In the same year, they reported the preparation of a new flame-retardant polymer of poly(2-methacryloxyethyl phenyl phosphate) (PMEPP) by homopolymerization. PMEPP can effectively inhibit combustion by the action of condensed-phase mechanism and revealed the high LOI values of 34.7. Investigation by Chou [37] revealed that the mechanism for the flame retardancy of this system has been characterized as condensed-phase and volatized products during the thermal degradation of PMEPP and MMA/MEPP. They found that CO, CO<sub>2</sub>, and char residue were produced during burning process which can reduce the concentrations of combustible gases, heat, and oxygen at the polymer surface.

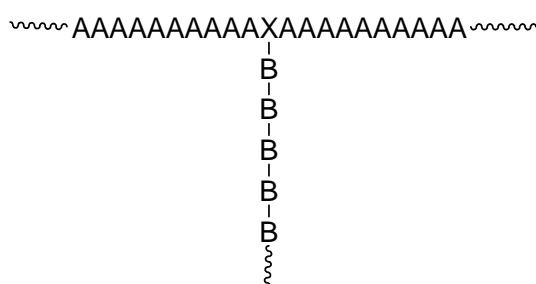
An alternative example of application of organophosphorus-based flame retardants with polymer was reported in a study of the decomposition/pyrolysis of polystyrene copolymers with covalently bonded phosphorus within the polymer structure [9]. The study was performed on both the phosphate and the phosphonate systems, namely, diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl)phosphonate (DEAMP), and diethyl(methacryloyloxymethyl) phosphonate (DEMMP) (Figure 2.7). It was found that the reactive flame retardant copolymers showed lower decomposition temperature than that of polystyrene. Moreover, the increase in the percent char residue exhibited the flame retardancy of materials.



**Figure 2.7** The synthesis of reactive flame-retardant compounds.

### 2.4.2.2 Graft copolymers

Graft copolymerization is one of efficient ways to improve other properties of existing polymers. The side chains of copolymer are formed and attached to macromolecules with different chemical composition. The method of graft copolymerization process can be represented by the following structure in Figure 2.8, where a sequence of monomer units (A) is referred to as the main-chain of polymer. The sequence of units (B) is the side chain of grafted copolymers, and X is the graft sites of polymer backbone which generated a radical on the polymer chain *via* addition or hydrogen abstraction reaction.



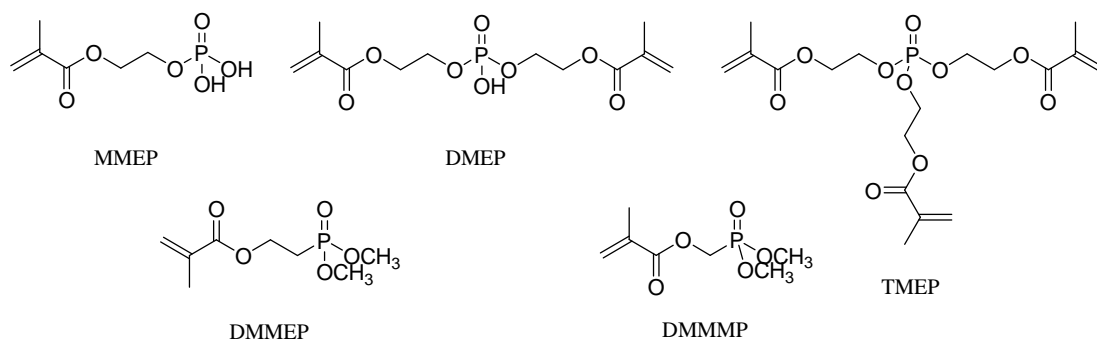
**Figure 2.8** Model of graft copolymers [38].

An example of this method is a report by Tsafack *et al.* [10] where the synthesis of phosphorus-containing acrylate monomers, DEAEP, DEMEP, DEAMP, and dimethyl(acryloyloxymethyl) phosphonate (DMAMP) (Figure 2.7) was carried out. These monomers had been incorporated to polyacrylonitrile (PAN) textiles by plasma-induced graft copolymerization. It was found that the reactive flame retardant copolymers were covalently linked to the surface of the fabric, which assured the resistance of the coating towards washing, even at higher temperatures. Moreover, the

increase in the percent char residue exhibited flame retardancy and reduced the burning rate of materials.

Another example of application of organophosphorus-based agent to fabric was reported by Siriviriyannun *et al.* [11]. The synthesized 2-acryloyloxyethyl diethyl phosphate (ADEP) (Figure 2.7) has been applied to cotton fabric by using admicellar polymerization to enhance flame retardant properties. It was found that the PADEP-coated cotton showed a lower degree of decomposition than untreated cotton. The char residue was produced in a higher amount than that from untreated cotton and improved the flammability after treatment.

Moreover, Jang *et al.* [39] reported the method for the synthesis of the phosphorus-containing acrylate monomers, tris(2-methacryloyloxyethyl)phosphate (TMEP), bis(2-methacryloyloxy)ethyl phosphate (DMEP), and 2-(methacryloyloxyethyl)phosphate (MMEP) from phosphorus oxychloride and 2-hydroxyethyl methacrylate, which can be used as flame retardant monomers for UV-curable systems (Figure 2.9). The flame retardant properties of UV cured films of TMEP, DMEP, and MMEP showed high LOI values of 28.5, 30.3, and 35.1, respectively. The results are related to increase the phosphorus content in monomer films and enhanced the flame retardancy of cured films.



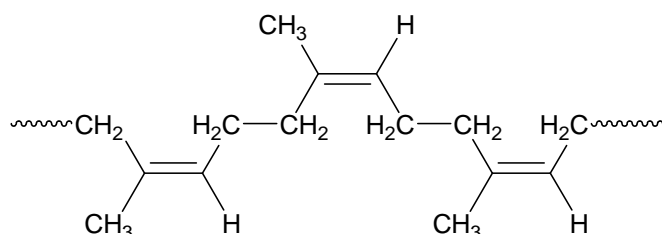
**Figure 2.9** The synthesis of reactive flame-retardant compounds.

Recently, the grafting of organophosphorus compounds, poly(dimethyl (acryloyloxymethyl)phosphonate) (PDMAMP) and poly(dimethyl(methacryloyloxyethyl)phosphonate) (PDMMEP) (Figure 2.9) onto NR latex based on photopolymerization was studied by Derouet *et al.* [12]. The grafting rate increased with increasing monomer concentration. The grafted copolymers can improve the thermal stability of NR. The surface morphology revealed the penetration of UV rays

into the latex particles and grafted copolymers took place into the NR particles. Until 2010, Intharapat *et al.* [13] prepared the grafting of poly(dimethyl(methacryloyloxy methyl)phosphonate) (PDMMP) (Figure 2.9) onto NR (NR-*g*-PDMMP). It was found that the increasing DMMMP contents gave the increase in percentage of grafting rate and showed higher LOI values than NR. In addition, the burning rate of graft copolymers decreased with increasing grafting rates which correlated with increasing in the LOI values.

## 2.5 Natural rubber latex (NRL)

Natural rubber latex (NRL), a white milky fluid, collected by tapping from *Hevea brasiliensis* tree, is a native of the tropical rain forest in Brazil. Most of the world's natural rubber comes today from South-East Asia, mainly Thailand, Malaysia, and Indonesia [40]. In recent years, Thailand has been the world's leader in natural rubber production and exportation. The chemical structure of natural rubber is known as *cis*-1,4-polyisoprene as shown in Figure 2.10. NR has retained a leading place among commodity and engineering elastomers.



**Figure 2.10** Chemical structure of natural rubber (*cis*-1,4-polyisoprene).

The colloidal suspension of natural rubber particles in aqueous phase are known as field latex. Field latex consists of only about 36% dry rubber and 4% non-rubber substances. The non-rubber components include proteins, carbohydrates, liquids, and inorganic salts. Its composition varied according to the clones of rubber, age of rubber tree, and tapping method. The composition of typical field latex is presented in Table 2.1.



**Table 2.1** Compositions of field latexes [41].

<b>Composition</b>	<b>Content (% by weight)</b>
Dry rubber	36.0
Proteinous substance	1.0-1.5
Carbohydrates	1.6
Sugar, Lipids, Resinous substance	1.0-2.5
Inorganic matter	0.5
Water	58.5

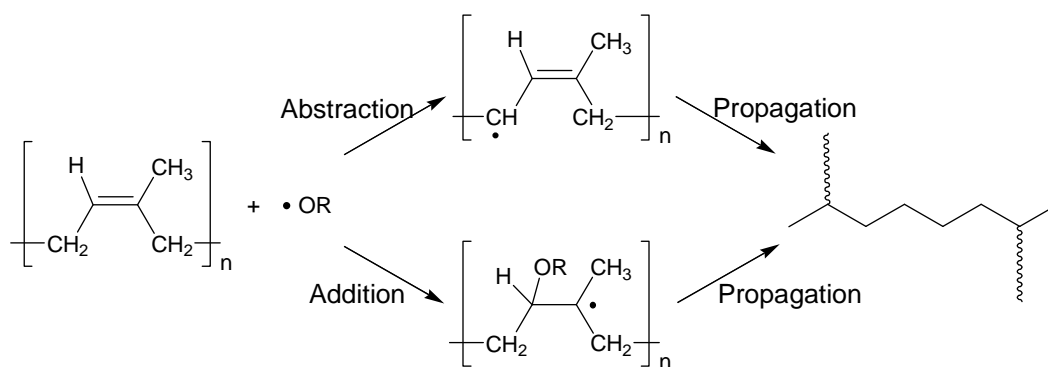
About 10% of natural rubber is not processed into dry rubber but sold as latex. Latex concentrate is usually made by centrifugation-spinning at high speed to separate off a cream of about 60% rubber from a liquid of about 5% rubber, from which dry skim rubber is made. Another concentrate, made by evaporation, evaporated latex concentrate, has higher rubber content and so slightly different properties. Finally, the latex concentrate is mixed with a chemical, such as ammonium alginate, which makes the rubber particles rise to the top of the liquid, like cream, when left to stand for several weeks. All latex concentrates are chemically treated to prevent coagulation.

## **2.6 Graft copolymers from natural rubber**

Graft copolymerization has been used as a method for modifying NR in a latex form. Reactions involving free radicals have been the most widely applied in grafting processes, and such reactions have been used with a wide range of polymers and monomers. Free radical initiators may promote grafting in two different ways when added to a monomer/polymer system. The grafting of secondary polymer onto polyisoprene may be induced in two pathways (Scheme 2.2).

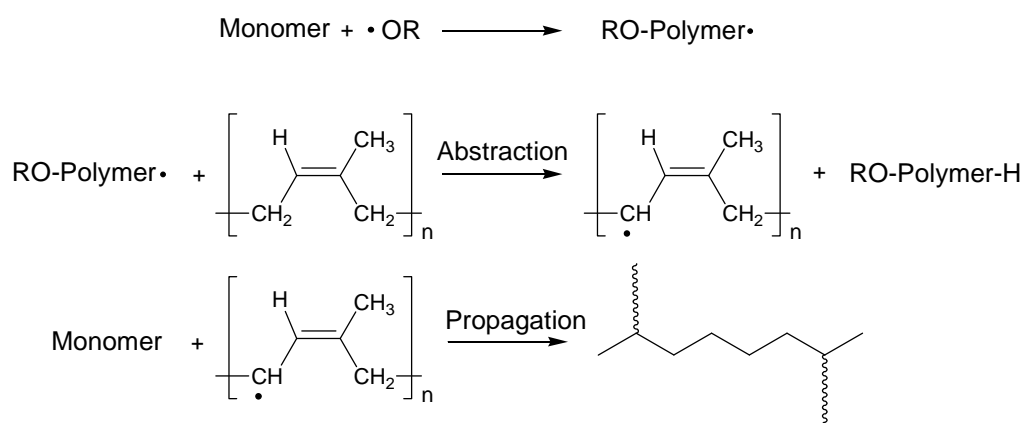
### **Direct attack of rubber by initiator radical:**

The first method is through a grafting site which the initiator-derived radicals either add across the double bond or abstract hydrogen atoms from polyisoprene backbone [16].



### Chain transfer with polymer *via* abstraction:

In the second method, the growing long chain radical (RO-polymer•) undergoes chain transfer with the polymer, probably by hydrogen abstraction, leading to the initiator of a graft [17].



**Scheme 2.2** Graft copolymerization pathways.

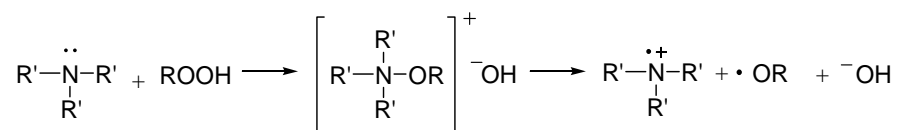
#### 2.6.1 Mechanism of grafting

The following reaction in Scheme 2.3 is proposed for the graft copolymerization of vinyl monomers onto natural rubber by free-radical method [42].

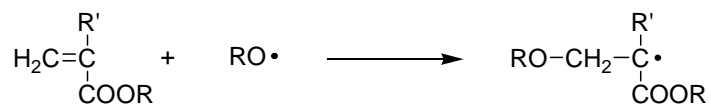
#### Redox initiation:

This type of initiation can produce the radicals by many oxidation-reduction reactions. These can be used to initiate polymerization. In a redox initiation, the hydroperoxide was induced by amine activator decomposition to yield alkoxy radicals (RO•). The alkoxy radical might interact with either the monomer or the rubber molecule to produce macroradical, which initiated grafting sites. It is possible for the  $\alpha$ -

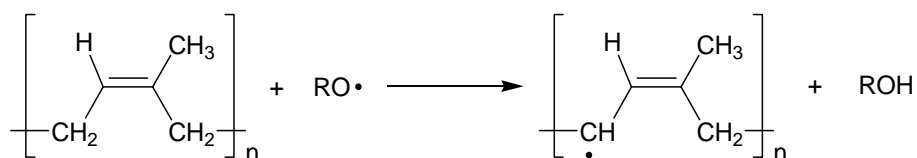
methylene hydrogen atoms in the natural rubber, which are more active, to become the sites of graft copolymerization.



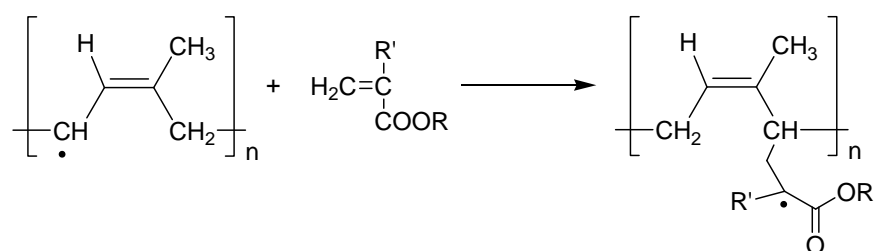
#### Monomer attack:



#### NR attack:



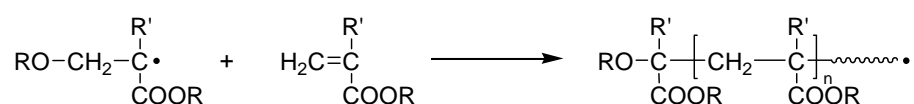
#### Re-initiation:



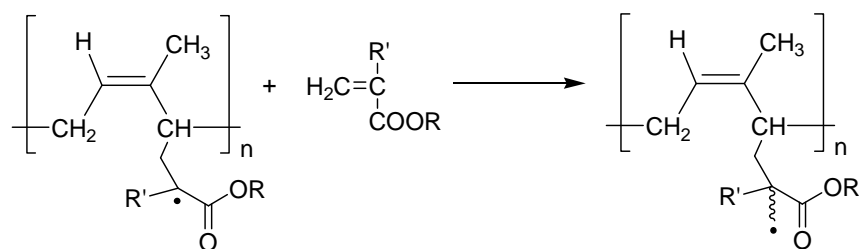
#### Propagation:

The alkoxy radicals (RO•) not only can attack the  $\alpha$ -methylene hydrogen atoms to produce polyisoprene radicals, which initiate monomers to form the graft copolymers, but can also initiate monomers to form free homopolymer radicals.

#### Propagation of free polymerization (homopolymer):



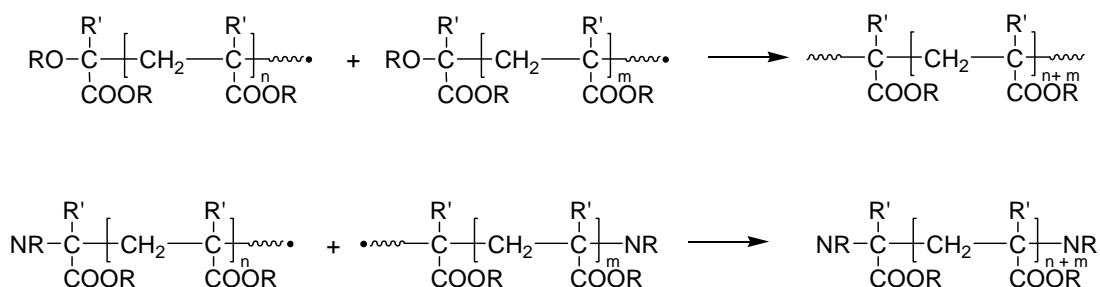
### Propagation of graft polymerization:



### Termination:

Moreover, the free homopolymer radicals can terminate by combination or disproportionation to form free homopolymers. The end product of the graft copolymerization process is composed of graft copolymers and free homopolymer phase in a reaction.

### Combination and disproportionation:



**Scheme 2.3** Mechanism of graft copolymerization of secondary polymer.

The Natural Rubber Research Organizations had investigated processes for grafting polymers to natural rubber using free radical chemistry [43]. Graft copolymer of poly(methyl methacrylate) onto natural rubber under trade name of “Heveaplus-MG”, by a graft copolymerization by *tert*-butylhydroperoxide (*t*-BHPO) has been commercialized since mid 1950s [44]. The chemical modification of NR by grafting with vinyl monomers combines the properties of both NR and the polymer of the monomer grafted. It has gained considerable importance as it leads to polymers with altered and improved properties for the production of new materials. The most promising graft copolymer based on NR, thus far obtained, is that derived from methyl methacrylate (MMA) and styrene (ST) [42]. The graft copolymer may be prepared by

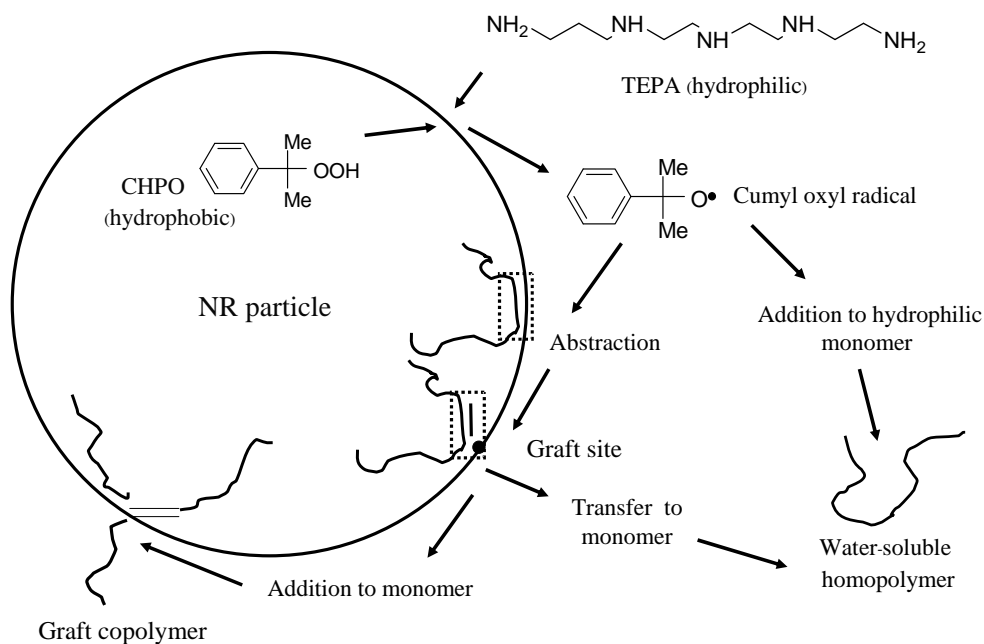
graft copolymerization of NR in latex form, since the NR, an unsaturated elastomer having the existence of double bonds in its chains, can be readily grafted with a variety of monomers, using the well-established technique of seeded emulsion polymerization.

The couple redox initiators have been extensively used to initiate the graft polymerization of secondary polymers at moderate temperature. In 2002, Arayapranee, *et al.* [42] chose the couple redox initiator of cumene hydroperoxide (CHPO)/sodium formaldehyde sufoxylatedihydrate/EDTA-chelated  $\text{Fe}^{2+}$  to prepare the graft copolymerization of MMA and ST onto NR. The hydroperoxide oxidizes the iron (II) ions, thus introducing alkoxy radicals that can be used to initiate polymerization. Moreover, the produced iron (III) ions, in turn, oxidize the reducing agent, being they reduced to iron (II) ions once again.

Recently, the effect of various types of redox initiator systems including CHPO/TEPA, *t*-BHPO/TEPA,  $\text{K}_2\text{S}_2\text{O}_8/\text{K}_2\text{S}_2\text{O}_5$ , and  $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_3$  were studied on the graft copolymers of dimethylaminoethyl methacrylate (DMAEMA), dimethylaminoethyl acrylate (DMAEA) [21], and MMA [16] onto NR by emulsion polymerization. The CHPO/TEPA was found to be the most effective redox initiating system and has been widely applied to prepare graft copolymers of NR and MMA later [14, 17, 18]. It was also found that CHPO/TEPA gave the highest percentage grafting efficiency and lowest yield of homopolymer content of PMMA because the partition ability of CHPO into NR phase is higher than that of *t*-BHPO and  $\text{K}_2\text{S}_2\text{O}_8$ .

### 2.6.2 Core shell mechanism

The couple redox initiator of CHPO/TEPA could be used to prepare NR-based core-shell latex particles. CHPO is soluble in organic phase (NR particles phase and monomer), whereas the amine activator, TEPA, is soluble in aqueous phase. The initiators present in the graft copolymerization of secondary polymers onto NR particles, therefore, seem to be appropriate to create sites of grafting by the abstraction reaction over addition to allylic double bonds acting predominantly at the interface of NR particles as illustrated in Figure 2.11. Therefore, the free radicals are mostly generated only the surface of NR particles. This leads to low conversion of copolymers.



**Figure 2.11** Schematic of the possible grafting reaction by using the bipolar redox initiator (CHPO/TEPA) systems *via* seeded emulsion polymerization [17].

## 2.7 Analytical methods

### 2.7.1 Thermogravimetric analysis (TGA) [45]

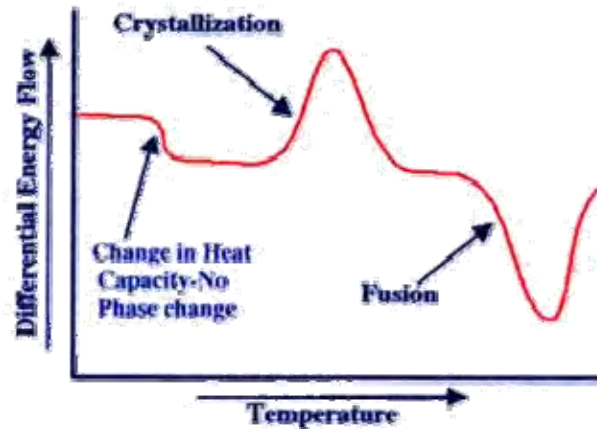
Thermogravimetry technique has been used to study the thermal decomposition of materials and to accumulate kinetic information about such decomposition. A sample is suspended on a sensitive balance that measures the weight as it is exposed to a furnace. Air, nitrogen, or another gas flows around the sample to remove the pyrolysis or combustion products. This technique measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gases. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods. With the use of a derivative computer, the rate of weight loss as a function of time and temperature can also be determined. The computer allows a more accurate determination of peak temperature transitions.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to determine the residues at high temperature.

### **2.7.2 Differential scanning calorimetry (DSC) [46]**

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

DSC can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperature ( $T_g$ ). Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature ( $T_c$ ). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature ( $T_m$ ). The melting process results in an endothermic peak in the DSC curve (Figure 2.12). The ability to determine transition temperature and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems.

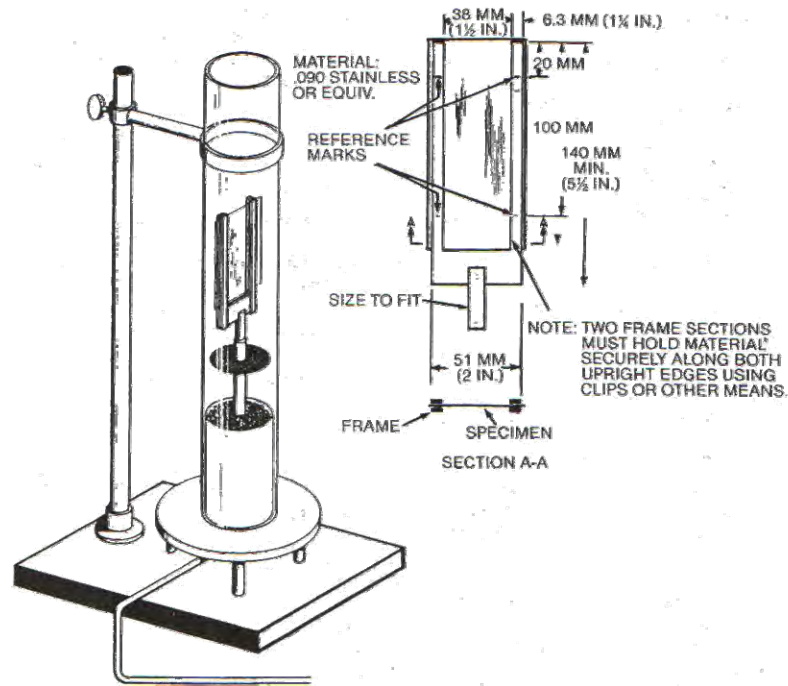


**Figure 2.12** Features of a DSC curve.

### 2.7.3 Limiting oxygen index (LOI) test

This test method measures the minimum oxygen concentration that will support sustained combustion of the material of interest. The test specimen is placed vertically in a mixture of oxygen and nitrogen flowing upward through a transparent chimney. The entire top part of the specimen was ignited with the flame igniter until the flame is sustained at the top of the specimen and then the igniter is removed. As time goes by, if the flame at the specimen extinguished this means that an inadequate amount of oxygen was supplied to the specimen. In this case, an increase in the initial concentration of oxygen should be carried out. The initial concentration of oxygen was selected based on experience of results for similar materials. The oxygen concentration was adjusted until the minimum value for sustained burning is reached. LOI test is especially useful for preliminary flame retardant studies or comparative evaluations. The LOI value usually shows a linear relationship with the concentration of flame retardant added. An LOI value higher than 26 exhibited the self extinguishing material [35].





**Figure 2.13** Limiting oxygen index apparatus.

#### 2.7.4 Tensile properties

The test specimens are stretched in a tensile testing machine and the force required to stretch the sample is measured. Value of stress (force divided by the unstretched cross sectional area of the straight portion of the dumbbell) is recorded at various levels of extension, up to the break point. The extension is measured as percent elongation and is defined as

$$\text{Stress } (\sigma) = \frac{F}{A}$$

where  $\sigma$  is the tensile stress,  $F$  is the tensile force, and  $A$  is the cross-sectional area.

$$\text{Strain } (\%) = \frac{L - L_0}{L_0} \times 100$$

where  $L$  is the stretched length and  $L_0$  is the original length.

Tensile stress before the sample break, show the modulus of the sample. For the rubber chemist, modulus means the tensile value (stress) required for a given elongation. At 300% Modulus is commonly measured at 300% elongation of thin film rubber products. Note that the modulus, as defined here for rubber, is not equivalent to the modulus as understood by an engineer, which is equal to stress over strain.

## CHAPTER III

### METHODS AND MATERIALS

#### 3.1 Chemicals

2-Hydroxyethyl methacrylate (HEMA) (Aldrich, 97%), phenylphosphonic dichloride (PPDC) (Fluka, 95%), phenyl dichlorophosphate (PDCP) (Aldrich, 95%), phenol (Merck), triethylamine (TEA) (Fluka, 98%) were used as received. Tetrahydrofuran (THF; Lab grade), *n*-hexane (commercial grade), and ethyl acetate (commercial grade) were distilled prior to use. High ammonia natural rubber latex (NRL, 0.7% (w/w) NH<sub>4</sub>OH) with 60% dry rubber content was purchased from the Rubber Research Institute of Thailand (Bangkok). The stabilizer oleic acid (Fluka, Lab grade), the latex stabilizer potassium hydroxide (KOH; Fluka), the emulsifier sodium dodecyl sulfate (SDS; Fluka, 99.5%), the couple redox initiator cumene hydroperoxide (CHPO; Fluka, 80%), the amine activator tetraethylenepentamine (TEPA; Fluka, 85%), and petroleum ether (Merck, 98%) were used as received. Ammonia solution (25% (w/v)) was purchased from BDH (England).

#### 3.2 Equipments

##### 3.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton (<sup>1</sup>H) and Carbon (<sup>13</sup>C) NMR spectra were obtained on a Varian mercury plus 400 operating (USA) at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C nuclei. The samples were analyzed in solution of chloroform-D (purity 99%, Aldrich). Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and are relative to that of tetramethylsilane (TMS) or relative to the residual protonated signal of deuterated solvents as a reference. Coupling constants (*J*) are proton-proton coupling unless otherwise noted and are reported in Hertz (Hz). Multiplicities were abbreviated as followed: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, and br = broad. Phosphorus (<sup>31</sup>P) NMR spectra were obtained on a Varian Unity Inova 500 MHz NMR

spectrometer (USA) at the Scientific and Technology Research Equipment Center, Chulalongkorn University.  $^{31}\text{P}$  spectra were obtained by using phosphoric acid as an external standard.

### **3.2.2 Fourier Transform-Infrared (FT-IR) Spectroscopy**

FT-IR spectra were recorded on a Perkin Elmer: spectrum RX-1 with 64 scans at the resolution of  $4\text{ cm}^{-1}$ . All samples were dissolved in dichloromethane and then cast as films on the NaCl cell. The IR spectra were acquired by using the Omnic ESP in a range of  $4000\text{-}500\text{ cm}^{-1}$ .

### **3.2.3 Mass Spectrometry (MS)**

The molecular mass ion determination was conducted in the Electrospray ionization-mass spectrometry (ESI-MS) mode on a Waters Quattro Micromass mass spectrometer (France).

### **3.2.4 Gel Permeation Chromatography (GPC)**

The molecular weight and molecular weight distributions of homopolymers were determined by gel permeation chromatography (GPC) using THF as eluent, on a WATERS gel permeation chromatography system equipped with a WATERS 600 pump and controller, and a WATER 2414 refractive index detector (USA). The flow rate was  $1\text{ cm}^3\text{ min}^{-1}$ . The sample (30 mg) was dissolved in tetrahydrofuran 5 mL and filtered through a membrane filter (45 micron). The molecular weight of homopolymers was reported in Dalton (Da) unit relative to polystyrene standard.

### **3.2.5 Transmission Electron Microscopy (TEM)**

Morphology of NR particles before and after grafting was observed by JEOL transmission electron microscopy (TEM, Model JEM-2100, Japan) at 120 kV. The grafted NR latexes were diluted 400 times by deionized water. A drop of the diluted latex was deposited on a carbon-coated formvar grid. Then, the substrate grid was stained by a drop of chemical staining vapor in a glass-covered dish at room temperature for 24 h and dry overnight in a dessicator. The unsaturated double bonds of

NR were stained with chemical staining vapor. This method was compared with chemical staining using 1% osmium tetroxide ( $\text{OsO}_4$ ) and 1% ruthenium tetroxide ( $\text{RuO}_4$ ).

### **3.2.6 Thermogravimetric Analysis (TGA)**

Thermogravimetric analyses were performed using a Mettler Toledo thermogravimetric analyzer model TGA/SDTA 851 for grafted NR samples were obtained after Soxhlet extraction. Approximately 10 mg of the samples were placed into an aluminum oxide crucible at a heating rate of  $20^\circ\text{Cmin}^{-1}$  under a continuous nitrogen flow rate of  $60\text{ cm}^3\text{min}^{-1}$  and the sample was scanned from  $25\text{-}700^\circ\text{C}$ . Moreover, char yield was determined by TGA from the mass of the residue remaining at  $700^\circ\text{C}$ .

### **3.2.7 Differential Scanning Calorimetry (DSC)**

The glass transition temperature ( $T_g$ ) was determined by Differential scanning calorimeter model Mettler DSC 822 with heating rate of  $10^\circ\text{Cmin}^{-1}$  under a continuous nitrogen flow rate of  $20\text{ cm}^3\text{min}^{-1}$ . The sample was sealed in an aluminum pan and recorded endothermic peak. The sample was quenched to  $-100^\circ\text{C}$  for 5 min, then heat up to  $80^\circ\text{C}$  and kept at this time for 5 min to remove polymer history. The sample was then slowly quenched again to  $-100^\circ\text{C}$  and the second heating scan was recorded.

### **3.2.8 Limiting Oxygen Index (LOI) test**

The minimum oxygen concentration, which can support sustained combustion of the material, was determined with limiting oxygen index (LOI) test according to the ASTM D2863-06a test method. The film sheets obtained before and after Soxhlet extraction were prepared as a test specimen of 52 mm wide, 140 mm long, and about 1 mm thick.

### **3.2.9 Burning rate measurement**

The burning rate of grafted NR film was determined from the time for complete of burning. A specimen of 5 mm wide, 50 mm long, and about 1 mm thick was ignited

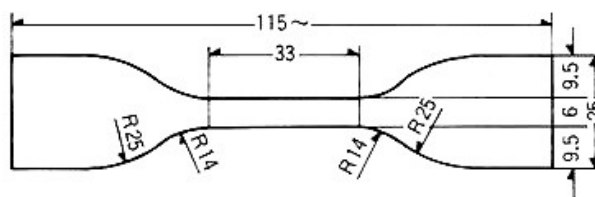
in air, and the burning behavior (in this study, the ignition time was 5 sec) at ambient temperature was calculated according to eq. (4.1).

$$\text{Burning rate (mm/s)} = \frac{40}{t_b} \quad (4.1)$$

where  $t_b$  is the time, in seconds, at which the flame reaches the gauge mark (40 mm).

### 3.2.10 Tensile properties

The tensile properties of grafted NR films were measured following the ASTM D412 test method. The testing was performed on a Universal testing machine (Instron 5569) using dumbbell-shaped specimens. The specimens were cut into the Die C shape with the dimension as shown in Figure 3.1. For each sample, at least 4 specimens were tested with the crosshead speed of 500 mm/min and a full scale force at 1 kN.

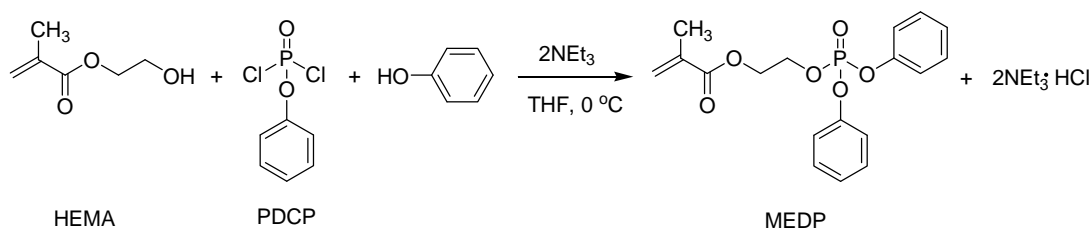


**Figure 3.1** Schematic diagram of tensile test specimen (Die C).

## 3.3 Methods

### 3.3.1 Synthesis of 2-methacryloyloxyethyl diphenyl phosphate (MEDP)

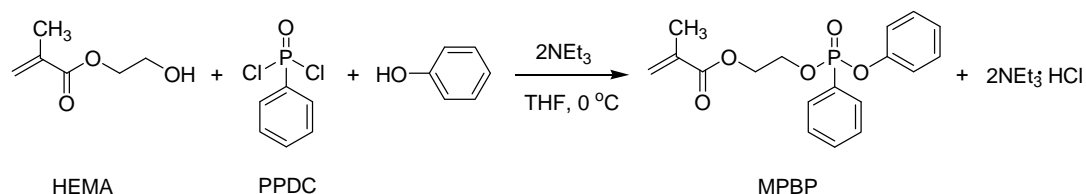
[8]



2-Methacryloyloxyethyl diphenyl phosphate (MEDP) was synthesized by the reaction of phenyl dichlorophosphate (PDCP), 2-hydroxyethyl methacrylate (HEMA) and phenol. PDCP (31.7 g, 0.5 mol) was dissolved in anhydrous tetrahydrofuran (THF)

(120 mL) and the solution was then added to a 1000 mL three-necked round bottom flask equipped with mechanical stirring under an N<sub>2</sub> inert atmosphere. Triethylamine (TEA) (41.7 mL, 1.0 mol) was added to the mixture and cooled down in an ice bath for 30 minutes. The solution of HEMA (19.5 g, 0.5 mol) in anhydrous THF (30 mL) was added dropwise over a period of 30 minutes. After addition of HEMA solution, the mixture was stirred for 2 hours. Phenol (14.1 g, 0.5 mol) in anhydrous THF (30 mL) was added afterwards and the reaction kept at 0 °C for 4 hours. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the reaction was complete, triethylamine hydrochloride salt was filtered off. The filtrate was placed in a rotary evaporator to remove THF and unreacted starting materials. Finally, the crude mixture was purified by using a flash silica gel chromatography column, and eluted with a 7:3 mixture of hexane and ethyl acetate. The product was obtained as light yellowish liquid in 40% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.12-7.42 (m, 10H, aromatic protons), 6.12 (d, 1H, *J* = 6.81 Hz, CH<sub>2</sub>=C(CH<sub>3</sub>-), 5.58 (d, 1H, *J* = 6.95 Hz, CH<sub>2</sub>=C(CH<sub>3</sub>-), 4.30-4.55 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-O-P), 1.93 (s, 3H, CH<sub>2</sub>=C(CH<sub>3</sub>-); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 166.98 (C=O), 135.59 (CH<sub>2</sub>=C-CH<sub>3</sub>), 125.47 (CH<sub>2</sub>=C), 66.68 (O-CH<sub>2</sub>-CH<sub>2</sub>-O-P), 63.04 (O-CH<sub>2</sub>-CH<sub>2</sub>-O-P), 18.22 (CH<sub>2</sub>=C(CH<sub>3</sub>-); <sup>31</sup>P NMR (CDCl<sub>3</sub>, ppm): -10.92 (s); FT-IR (NaCl, cm<sup>-1</sup>): 3063 (C-H stretching, aromatic), 2957 and 2932 (C-H stretching, CH<sub>3</sub> and CH<sub>2</sub>), 1730 (C=O stretching), 1635 (C=C stretching), 1600 and 1493 (C=C stretching, aromatic), 1265 (P=O stretching), 1161 and 975 (P-O-C stretching, aromatic), 1070 and 928 (P-O-C stretching, aliphatic); MS (ESI) *m/z* 363.32 (C<sub>18</sub>H<sub>19</sub>O<sub>5</sub>P+H)<sup>+</sup> [8].

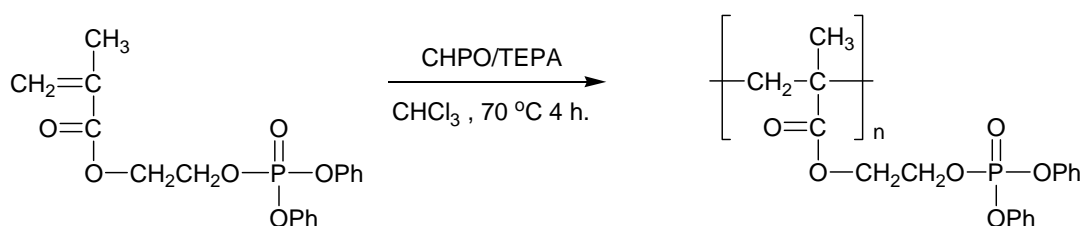
### 3.3.2 Synthesis of 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP) [8]



2-Methacryloyloxyethyl phenyl benzenephosphonate (MPBP) was synthesized *via* the same procedure as described for MEDP by using phenylphosphonic dichloride (PPDC) (29.2 g, 0.5 mol) as a reactant instead of PDCP. The crude mixture was purified by using a flash silica gel chromatography column, which was eluted with a 3:2

mixture of hexane and ethyl acetate. The product was obtained as a light yellowish liquid in 60% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  6.98-7.89 (m, 10H, aromatic protons), 6.01 (s, 1H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ), 5.48 (s, 1H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ), 4.16-4.43 (m, 4H,  $\text{CH}_2-\text{CH}_2-\text{O}-\text{P}$ ), 1.81 (s, 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  166.98 ( $\text{C}=\text{O}$ ), 135.67 ( $\text{CH}_2=\text{C}-\text{CH}_3$ ), 125.01 ( $\text{CH}_2=\text{C}$ ), 64.31 ( $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}$ ), 63.23 ( $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}$ ), 18.20 ( $\text{CH}_2=\text{C}(\text{CH}_3)-$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm): 17.00 (s); FT-IR ( $\text{NaCl}$ ,  $\text{cm}^{-1}$ ): 3063 (C-H stretching, aromatic), 2957 and 2932 (C-H stretching,  $\text{CH}_3$  and  $\text{CH}_2$ ), 1730 ( $\text{C}=\text{O}$  stretching), 1635 (C=C stretching), 1600 and 1493 (C=C stretching, aromatic), 1440 (P-Ph stretching), 1265 (P=O stretching), 1161 and 975 (P-O-C stretching, aromatic), 1070 and 928 (P-O-C stretching, aliphatic); MS (ESI)  $m/z$  347.25 ( $\text{C}_{18}\text{H}_{19}\text{O}_5\text{P}+\text{H}$ ) $^+$  [47].

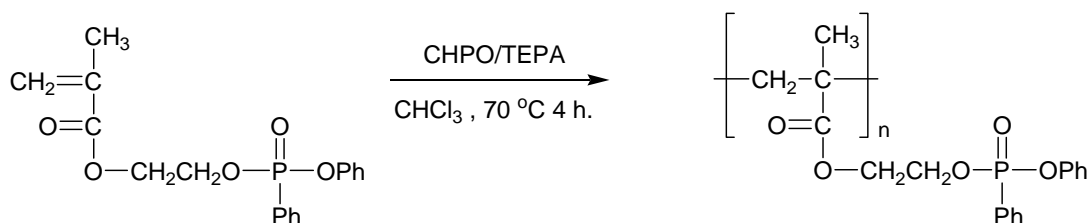
### 3.3.3 Preparation of poly(2-methacryloyloxyethyl diphenyl phosphate) (PMEDP)



The solution polymerization of MEDP was carried out in a 50 mL two-necked round bottom flask equipped with a reflux condenser under nitrogen atmosphere. A solution of MEDP (3.00 g, 8.29 mmol) in chloroform (10 mL) was added to the flask. The reaction mixture was deoxygenated by bubbling nitrogen gas for 30 minutes at room temperature. The mixture was then warmed up to  $70^\circ\text{C}$ . Thereafter, the polymerization occurred when adding an initiator CHPO (0.03 g, 0.20 mmol) and an amine activator TEPA (0.03 g, 0.16 mmol), respectively. The reaction mixture was refluxed at  $70^\circ\text{C}$  for 4 hours. After the completion of polymerization, chloroform was removed from the solution by a rotary evaporator. The polymer was then precipitated by methanol and isolated from unreacted MEDP solution by decantation. PMEDP was dried under vacuum to give a yellowish gum ( $\bar{M}_w$  48100 Da,  $\bar{M}_n$  33500 Da, and PDI = 1.43).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  7.40-7.00 (m, 10H, aromatic protons), 4.52-4.44 (m, 2H,  $\text{CH}_2-\text{CH}_2-\text{O}-\text{P}$ ), 4.43-3.95 (m, 2H,  $\text{CH}_2-\text{O}-\text{P}$ ), 1.73 (s, 3H,  $-\text{CH}_2-\text{C}(\text{CH}_3)-$ ), 1.10-0.78 (br, 2H,  $-\text{CH}_2-\text{C}(\text{CH}_3)-$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm): -10.75 (s); FT-IR ( $\text{NaCl}$ ,

cm<sup>-1</sup>): 3065 (C-H stretching, aromatic), 2952 (C-H stretching, CH<sub>3</sub>), 1732 (C=O stretching), 1600 and 1493 (C=C stretching, aromatic), 1265 (P=O stretching), 1183 and 957 (P-O-C stretching, aromatic), 1070 and 856 (P-O-C stretching, aliphatic).

### 3.3.4 Preparation of poly(2-methacryloyloxyethyl phenyl benzene phosphonate) (PMPBP)



PMPBP was prepared *via* the same procedure as described for PMEDP. PMPBP was obtained as a light yellowish gum ( $\bar{M}_w$  of 64200 Da,  $\bar{M}_n$  39900 Da, and PDI = 1.69). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.83-6.88 (m, 10H, aromatic protons), 4.27-3.89 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-O-P), 3.72-3.62 (m, 2H, CH<sub>2</sub>-O-P), 1.58 (s, 3H, -CH<sub>2</sub>-C(CH<sub>3</sub>-), 0.98-0.69 (br, 2H, -CH<sub>2</sub>-C(CH<sub>3</sub>-); <sup>31</sup>P NMR (CDCl<sub>3</sub>, ppm): 17.30 (s); FT-IR (NaCl, cm<sup>-1</sup>): 3065 (C-H stretching, aromatic), 2952 (C-H stretching, CH<sub>3</sub>), 1732 (C=O stretching), 1600 and 1489 (C=C stretching, aromatic), 1440 (P-C stretching), 1265 (P=O stretching), 1161 and 975 (P-O-C stretching, aromatic), 1070 and 856 (P-O-C stretching, aliphatic).

### 3.3.5 Preparation of grafted NR latexes (GNRL) [18]

The graft copolymers of phosphorus-containing monomers, PMEDP and PMPBP, onto NR latexes were prepared by seeded emulsion polymerization. The high ammonia natural rubber (HANR) latex (60% dry rubber content, DRC) was diluted by 0.7% (v/v) ammonia solution to 30% DRC. Grafting reaction was carried out in a 500 mL round bottom flask under nitrogen atmosphere. The latex was deoxygenated by nitrogen gas for 30 minutes at room temperature. The latex stabilizers potassium hydroxide (10% w/v, 0.25 phr), sodium dodecyl sulfate solution (10% w/v, 1.0 phr), oleic acid (10 phr), and phosphorus-containing monomers, were added, respectively, and the solution was stirred for 15 minutes. The mixture was stirred at room



temperature for 30 minutes so that the latex particles absorb the monomer. Next, the mixture was warmed up to the desired temperature (40-70 °C). The initiator CHPO was added, and the mixture was stirred for 15 minutes. The amine activator TEPA was then added. The bipolar redox initiating system was employed out at 1:1 (CHPO:TEPA) ratio. The reaction was allowed to stir for an additional 1 hour. After the completion of grafting reaction, the GNRL was cast onto a 9 cm diameter petri dish (10 g), and dried at 50 °C for 48 hours before analysis.

### 3.3.6 Preparation of grafted NR films

The graft copolymers of natural rubber latexes were filtered by using a mesh (60 µm, diameter) and cast on an open glass tray (50 g) to obtain GNR films with a thickness of ~0.6-0.8 mm. Thereafter, the GNR films were dried at ambient temperature until transparent films were observed. These films were further dried by heating the films at 50 °C for 48 hours in an oven.

### 3.3.7 Determination of grafting properties of natural rubber

The weight of homopolymers of PMEDP and PMPBP, ungrafted NR (free NR), and grafted NR were determined after a solvent soxhlet extraction method. The ungrafted NR was extracted by light petroleum ether (60-80 °C) for 24 hours, while free homopolymer was extracted by acetone for 24 hours. Calculation for grafting efficiency is shown in eq. (4.2) [18].

$$\% \text{ grafting efficiency} = \frac{\text{The weight of graft copolymers}}{\text{Total weight of polymer formed}} \times 100 \quad (4.2)$$

The percentage of grafted NR was calculated by eq. (4.3).

$$\% \text{ grafted NR} = \left( \frac{b}{a + b + c} \right) \times 100 \quad (4.3)$$

where a, b, c are the weights of the ungrafted NR, grafted NR, and homopolymers, respectively. The percent conversion was determined by the percentage increase in the rubber weight using eq. (4.4).

$$\% \text{ conversion} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad (4.4)$$

### 3.3.8 Determination of degree of grafting

The percent mole and weight of the graft copolymers of NR molecules were calculated based on the copolymer composition using  $^1\text{H}$  NMR technique. This technique was carried out according to the method by Oliveira *et al.* [17] for the determination of copolymer composition. The molar composition of the NR graft copolymers were determined from the assignment of the resonance peaks in the  $^1\text{H}$  NMR spectra. Thus, the composition of each copolymer was determined from the integrated peak area of the corresponding protons.

The results of average molar composition for each copolymer were obtained from the following eq. (4.5). For MEDP and MPBP grafted copolymers,

$$\% \text{ molar composition (C)} = \left[ \frac{\frac{I_{7.0-8.0}}{10}}{I_{5.1} + \frac{I_{7.0-8.0}}{10}} \right] \times 100 \quad (4.5)$$

in which,  $I_{5.1}$  = integrated peak area value of the olefinic proton of NR at 5.1 ppm,  $I_{7.0-8.0}$  = integrated peak area value of the aromatic protons of MEDP and MPBP unit at 7.0-8.0 ppm, and C = % molar of PMEDP and PMPBP in the copolymer.

The percentage weight composition was calculated according to the following eq. (4.6):

$$\% \text{ weight composition} = \left[ \frac{\text{MM} \times \text{C}}{(\text{MM} \times \text{C}) + \text{NR}(100 - \text{C})} \right] \times 100 \quad (4.6)$$

in which, MM = molecular mass of MEDP (362 g/mol) or MPBP (346 g/mol), NR = molecular mass of repeating unit in NR (68 g/mol).

## CHAPTER IV

### RESULTS AND DISCUSSION

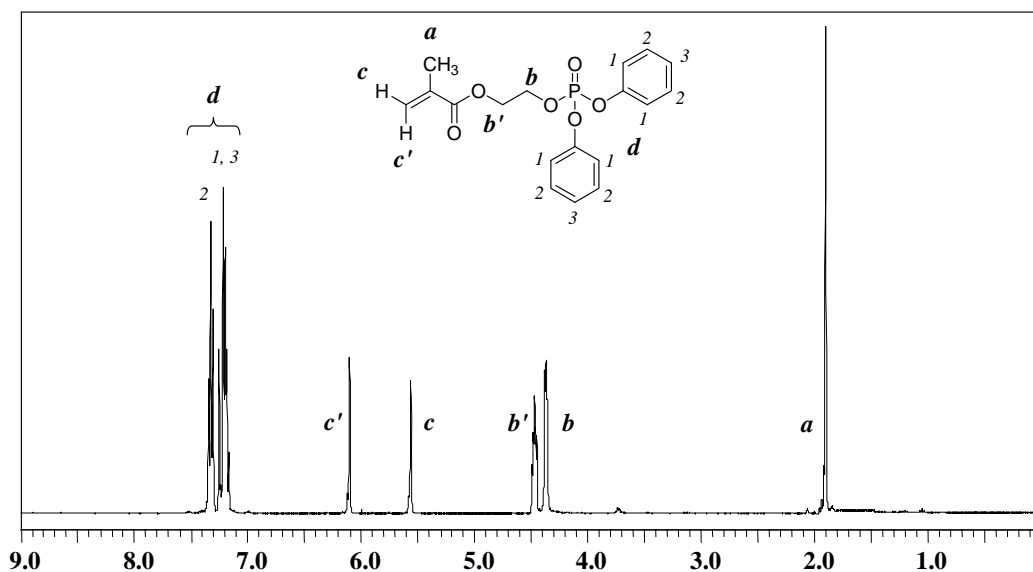
In this chapter, the results have been divided into 4 parts. The first part has been focused on the synthesis and characterization of phosphorus-containing monomers. The second part revealed details on polymerization of both monomers and characterization of both resultant products. The preparation of flame retardant NR by grafting with the phosphorus-containing monomers onto NR latexes *via* seeded emulsion polymerization was elaborated and then investigated the effect of grafting properties in the third part. In the last part, grafted NR products were characterized to determine the particle morphology, thermal properties, flame retardant properties, and mechanical properties on the quality of the NR product.

#### 4.1 Synthesis and characterization of phosphorus-containing compounds

##### 4.1.1 Synthesis and characterization of 2-methacryloyloxyethyl diphenyl phosphate (MEDP)

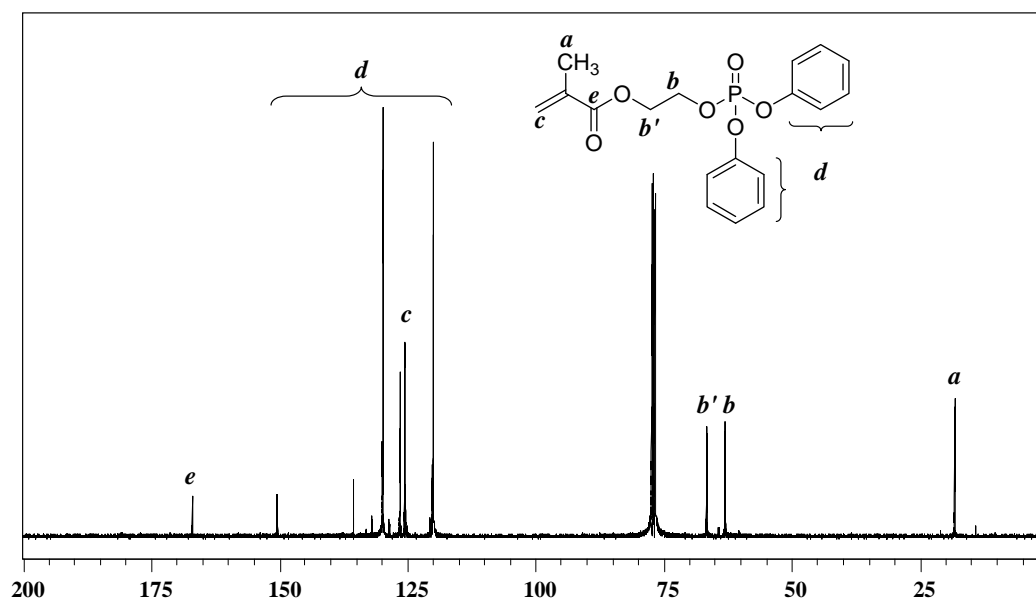
2-Methacryloyloxyethyl diphenyl phosphate, MEDP, was synthesized *via* the 2-step condensation reaction between 2-hydroxyethyl methacrylate (HEMA), phenyl dichlorophosphate (PDCP), and phenol. The reaction was performed in anhydrous tetrahydrofuran (THF) using triethylamine (TEA) as an acid acceptor. The chemical structure of MEDP was verified by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR, FT-IR and MS analyses.

In the  $^1\text{H}$  NMR spectrum of MEDP, illustrated in Figure 4.1, the signals of olefinic vinyl protons were observed as two signals at 5.58 (*c*) and 6.12 (*c*) ppm. The signals of methyl, methylene, and aromatic protons were found at 1.93, 4.30-4.55, and 7.12-7.42 ppm, respectively.



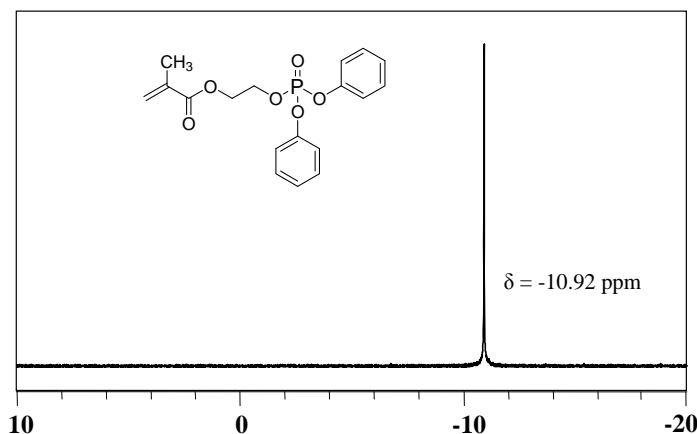
**Figure 4.1**  $^1\text{H}$  NMR spectrum of MEDP

$^{13}\text{C}$  NMR spectrum showed the resonance corresponding to all the carbons of the given structure as shown in Figure 4.2. The carbon signals of methyl group and carbon-carbon double bonds ( $=\text{CH}_2$ ) appeared at 18.2 and 125.5 ppm, respectively. The signal at 167.0 ppm was assigned to the carbonyl group ( $\text{C}=\text{O}$ ). The presence of signal at 66.7 and 63.0 ppm indicated the characteristics of methylene carbons. Signals of aromatic carbons appeared in the region of 120.0-150.4 ppm.



**Figure 4.2**  $^{13}\text{C}$  NMR spectrum of MEDP

The proton decoupled  $^{31}\text{P}$  NMR spectrum exhibited only one signal, corresponding to only one compound with a phosphorus atom in the molecule as shown in Figure 4.3. The phosphorus signal appeared as a single peak at -10.92 ppm. This is a characteristic region for alkyl or aryl phosphates [10].

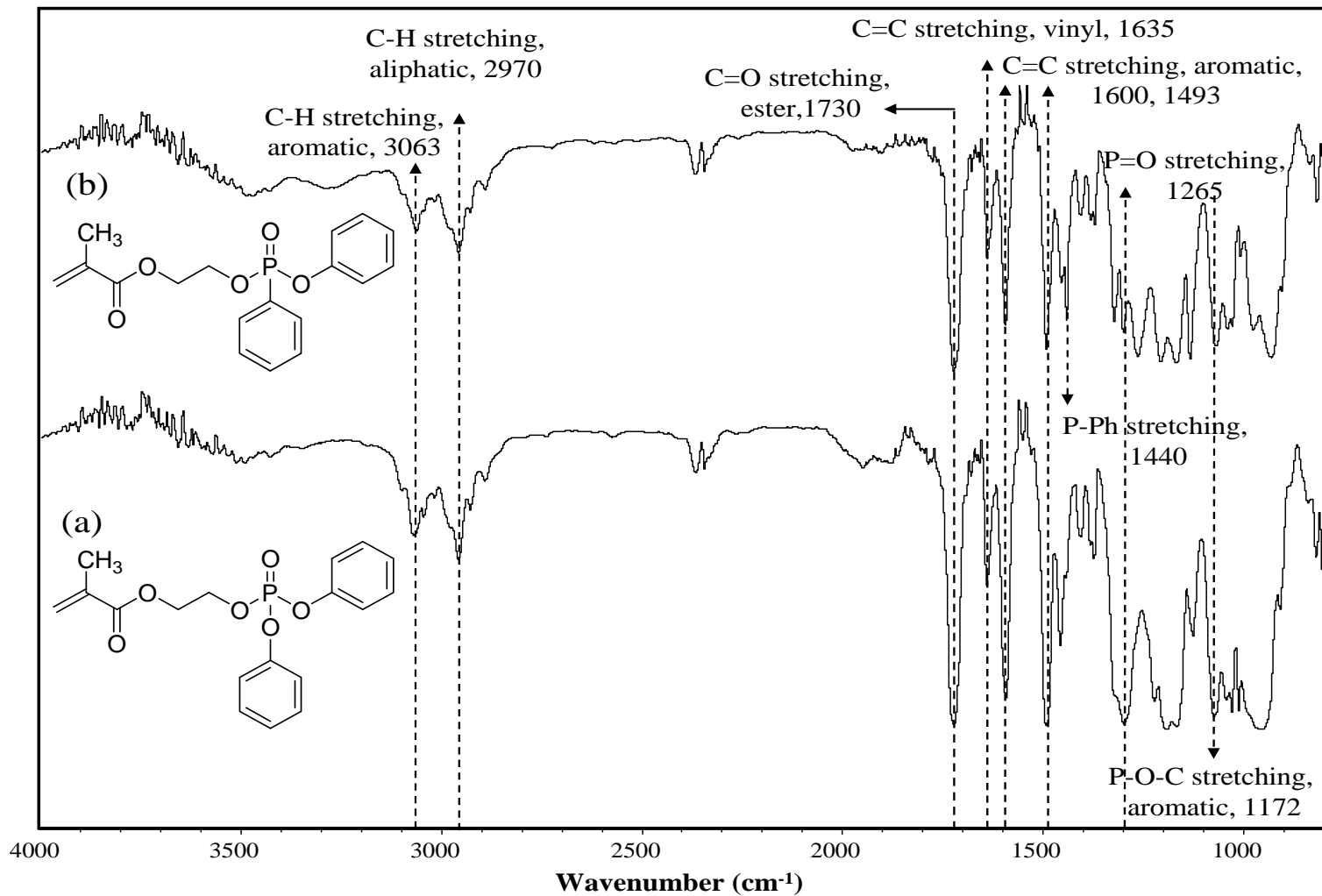


**Figure 4.3**  $^{31}\text{P}$  NMR spectrum of MEDP

The structure of MEDP was also confirmed by FT-IR analysis as shown in Figure 4.4 (a). FT-IR spectrum showed strong absorption bands at  $1730$  and  $1635\text{ cm}^{-1}$  indicating stretching vibrations of carbonyl of ester groups and carbon-carbon double bond of vinyl ( $\text{C}=\text{CH}_2$ ), respectively. The absorption frequencies were found at  $1600$  and  $1493$  correspond to the stretching vibrations of carbon-carbon double bond of aromatics. The absorption band of phosphate structure ( $\text{P}=\text{O}$  stretching) appeared at  $1265\text{ cm}^{-1}$  [8]. In addition, in the mass spectrum the fragmentation ions of MEDP and methacrylate group were found at  $m/z$  363.32 and 113.21, respectively, as shown in Appendix A.1.

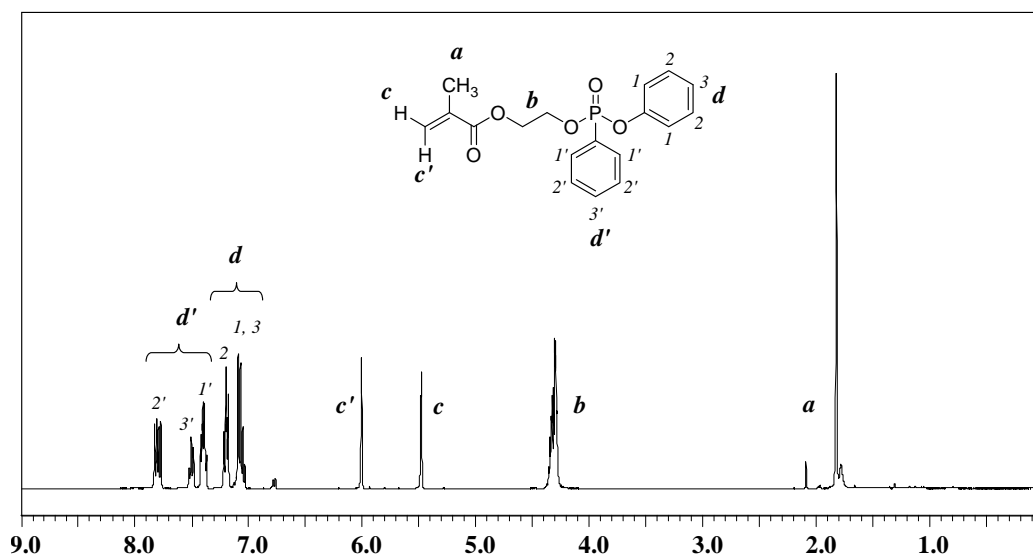
#### 4.1.2 Synthesis and characterization of 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP)

2-Methacryloyloxyethyl phenyl benzenephosphonate, MPBP, was synthesized *via* the 2-step condensation reaction between 2-hydroxyethyl methacrylate (HEMA), phenylphosphonic dichloride (PPDC), and phenol. The reaction was performed using a similar procedure for MEDP synthesis. The chemical structure of MPBP was also verified by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR, FT-IR and MS analyses.



**Figure 4.4** FT-IR spectra of (a) MEDP and (b) MPBP

The  $^1\text{H}$  NMR spectrum of MPBP is illustrated in Figure 4.5. The signals of olefinic vinyl protons were observed as two singlets at 5.48 ( $c$ ) and 6.01 ( $c'$ ) ppm. The signal at 1.81 ppm was attributed to the methyl protons. The signals of methylene protons appeared in the region of 4.16-4.43 ppm. The signals of aromatic protons appeared at 6.98-7.28 ppm corresponding to the phosphate aromatic protons (P-OPh protons,  $d$ ) and 7.32-7.89 ppm corresponding to the phosphonate aromatic protons (P-Ph protons,  $d'$ ).

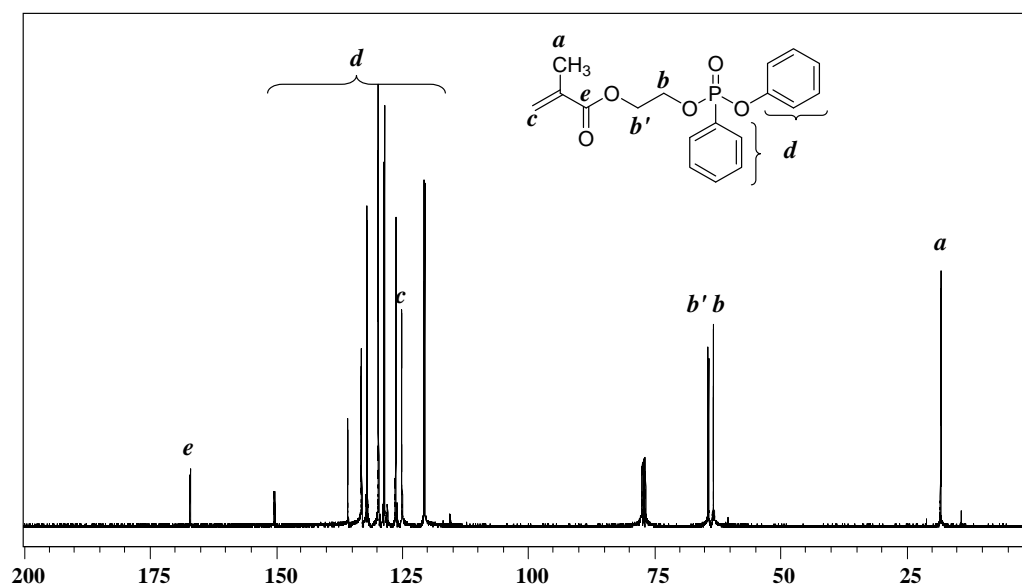


**Figure 4.5**  $^1\text{H}$  NMR spectrum of MPBP

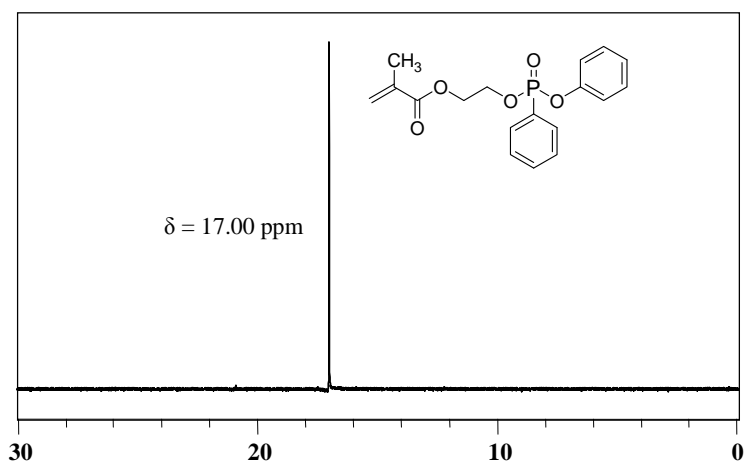
$^{13}\text{C}$  NMR spectrum (Figure 4.6) showed a carbon signal of the methyl group at 18.2 ppm. Olefinic carbon ( $=\text{C}-\text{CH}_3$ ) signal appeared at 135.7 ppm. The signal at 167.0 ppm was assigned to the carbonyl carbon. The signals of aromatic carbons showed up in the region of 120.6 to 150.3 ppm. Also, the presence of the signals at 64.3 and 63.2 ppm indicated the characteristics of methylene carbons.

$^{31}\text{P}$  NMR spectrum of MPBP is shown in Figure 4.7. The phosphorus signal appeared at 17.00 ppm as the only peak. The structure of MPBP was also confirmed by FT-IR analysis as shown in Figure 4.4 (b). All absorption bands matched with the previous result reported by Wang, *et al.* [47]. FT-IR spectrum showed strong absorption characteristics of the  $\text{C}=\text{O}$  stretching of ester groups at  $1730\text{ cm}^{-1}$ . A characteristic peak of carbon-carbon double bond of vinyl ( $\text{C}=\text{CH}_2$ ) was observed at  $1635\text{ cm}^{-1}$ . At 1600 and  $1493\text{ cm}^{-1}$  absorption frequencies of the carbon-carbon double bond of aromatics was strong. The important  $\text{P}=\text{O}$  stretching vibration appeared as a strong peak at  $1265\text{ cm}^{-1}$ . The new absorption peak at  $1440\text{ cm}^{-1}$  was assigned to the  $\text{P}-\text{C}$  stretching of the

phosphorus-aromatic carbon as shown in Figure 4.4 (b). This absorption peak did not appear in FT-IR spectrum of MEDP. The mass spectrum of MPBP exhibited the fragment ions of MPBP and methacrylate groups at  $m/z$  347.25 and 113.03, respectively as shown in Appendix A.2.



**Figure 4.6**  $^{13}\text{C}$  NMR spectrum of MPBP



**Figure 4.7**  $^{31}\text{P}$  NMR spectrum of MPBP

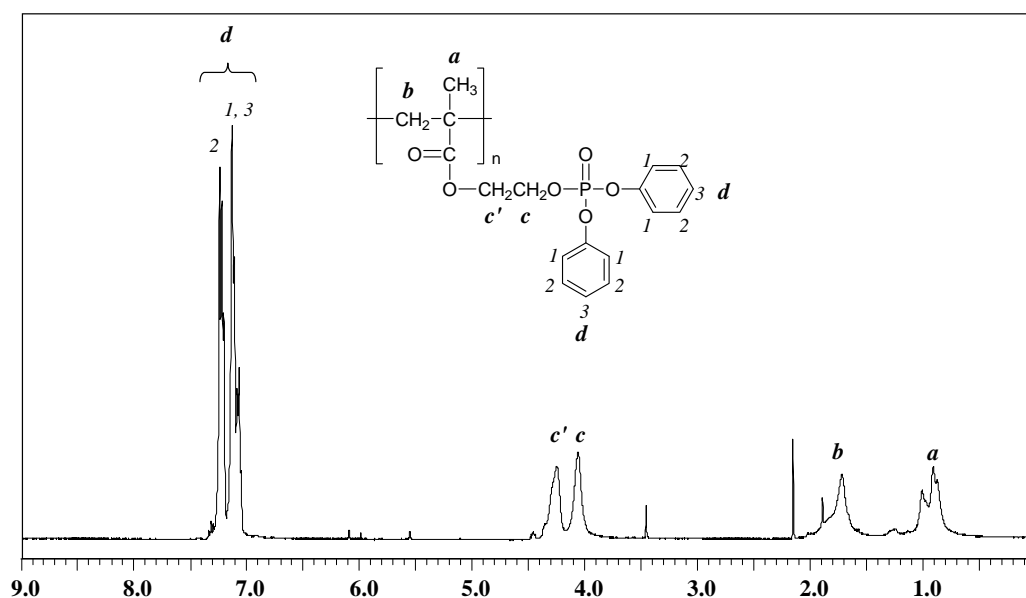


## 4.2 Polymerization and characterization of phosphorus-containing compounds

### 4.2.1 Preparation of poly(2-methacryloyloxyethyl diphenyl phosphate) (PMEDP)

Poly(2-methacryloyloxyethyl diphenyl phosphate) (PMEDP) was synthesized by a solution polymerization of 2-methacryloyloxyethyl diphenyl phosphate (MEDP) initiated with cumene hydroperoxide (CHPO). PMEDP was obtained as a yellowish gum. Its number weight molecular weight ( $\bar{M}_n$ ) and weight average molecular weight ( $\bar{M}_w$ ) that were determined by GPC technique was found to be observed at 33,500 and 48,100 Da, respectively.

$^1\text{H}$  NMR spectrum of PMEDP is shown in Figure 4.8. The success of the polymerization process was confirmed by the disappearance of the two singlet signals at 5.58 and 6.12 ppm that were previously assigned to the vinyl protons of the monomer. This evidence implied that MEDP had been polymerized to form PMEDP. The spectrum exhibited broad signals of methyl (*a*), methylene (*b*), and methylene (*c* and *c'*) protons at 0.78-1.10, 1.73, and 3.95-4.52 ppm, respectively. Signals of aromatic protons appeared at 7.00-7.40 ppm as broad multiplets.

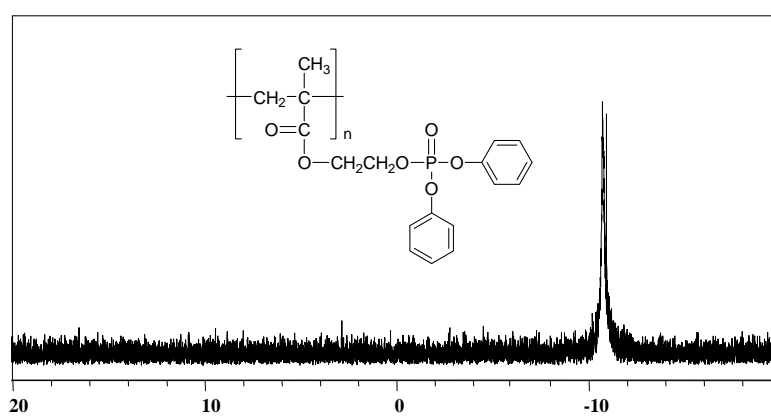


**Figure 4.8**  $^1\text{H}$  NMR spectrum of PMEDP

$^{31}\text{P}$  NMR revealed only one phosphorus signal at -10.75 ppm as a broad peak confirming that there was only one phosphorus species as shown in Figure 4.9. The

structure of PMEDP was also verified by FT-IR analysis as shown in Figure 4.13 (b). Importance absorption peaks were the absorption of the phosphate (O=P) groups at 1265. Moreover, the carbon-carbon double bond of aromatic rings appeared at 1600 and 1493  $\text{cm}^{-1}$ , respectively.

Furthermore, the solubility of PMEDP was investigated to determine an appropriate solvent to be used in a Soxhlet extraction to remove undesired PMEDP from grafted NR (see further discussion later). PMEDP could be dissolved well in acetone while grafted NR did not. Therefore, acetone was chosen as a solvent for soxhlet extraction.

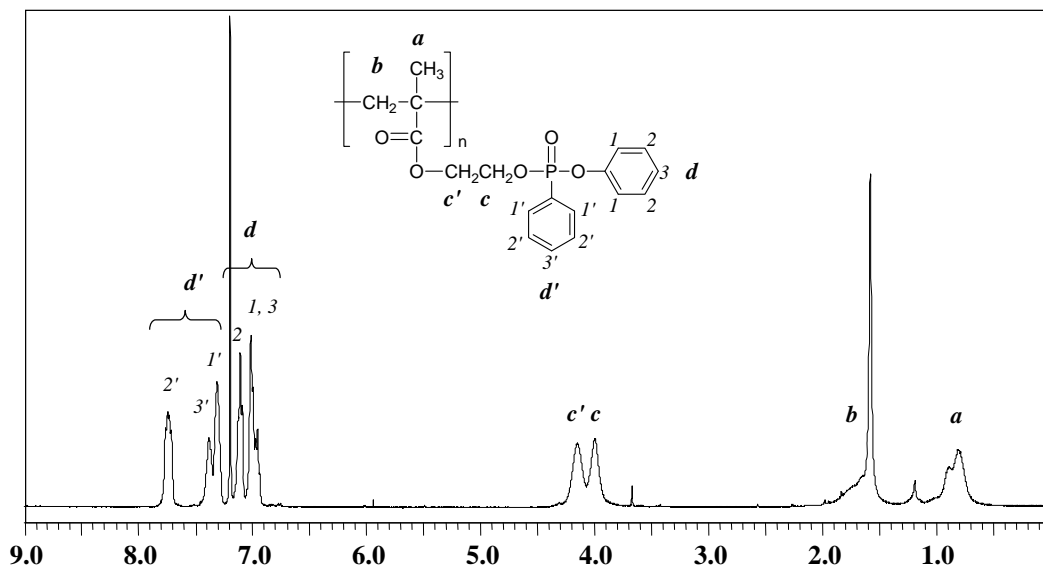


**Figure 4.9**  $^{31}\text{P}$  NMR spectrum of PMEDP

#### 4.2.2 Preparation of poly(2-methacryloyloxyethyl phenyl benzene-phosphonate) (PMPBP)

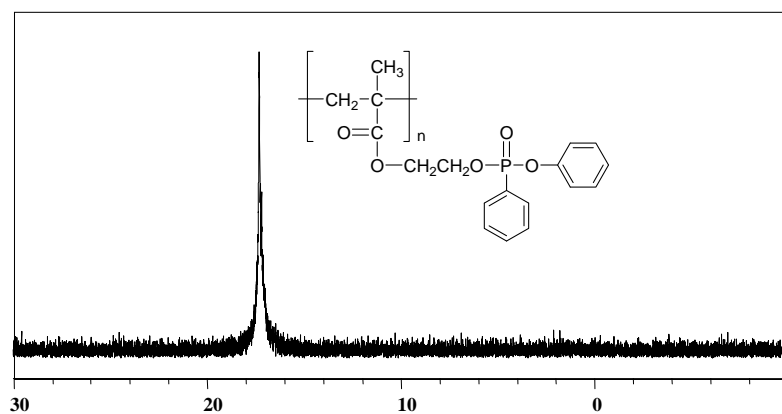
Poly(2-methacryloyloxyethyl phenyl benzene phosphonate) (PMPBP) was also synthesized by the same procedure as that of PMEDP. The product was obtained as a pale yellowish gum. The number weight molecular weight ( $\bar{M}_n$ ) and weight average molecular weight ( $\bar{M}_w$ ) of PMPBP were determined by GPC analysis to be 39,900 and 64,200 Da, respectively.

Figure 4.10 illustrated the  $^1\text{H}$  NMR spectrum of PMPBP. After polymerization, the signal of polymerizable methacrylate monomer unit of MPBP at 5.48 and 6.01 ppm had disappeared, whereas the broad signals of methyl and methylene (*b*) protons appeared at 0.69-0.98 and 1.58 ppm, respectively. The methylene (*c* and *c'*) protons showed up as broad peaks at 3.62-4.27 ppm. Signals of aromatic protons appeared in the region of 6.88-7.83 ppm as broad multiplets.



**Figure 4.10**  $^1\text{H}$  NMR spectra of PMPBP

$^{31}\text{P}$  NMR analysis revealed a spectrum with only one singlet signal at 17.30 ppm as shown in Figure 4.11. This is a chemical shift in a typical range of organophosphonate compounds [10]. In addition, the FT-IR spectrum of PMPBP showed strong absorption peak of the ester carbonyl group at  $1730\text{ cm}^{-1}$ . The important characteristic P=O stretching vibration appeared as a strong peak at  $1265\text{ cm}^{-1}$ . The signals at  $1600$  and  $1493\text{ cm}^{-1}$  were assigned to the absorption peaks of carbon-carbon double bonds of aromatic rings as shown in Figure 4.14 (b). PMPBP was also well soluble in acetone which was further used as a solvent for soxhlet extraction.



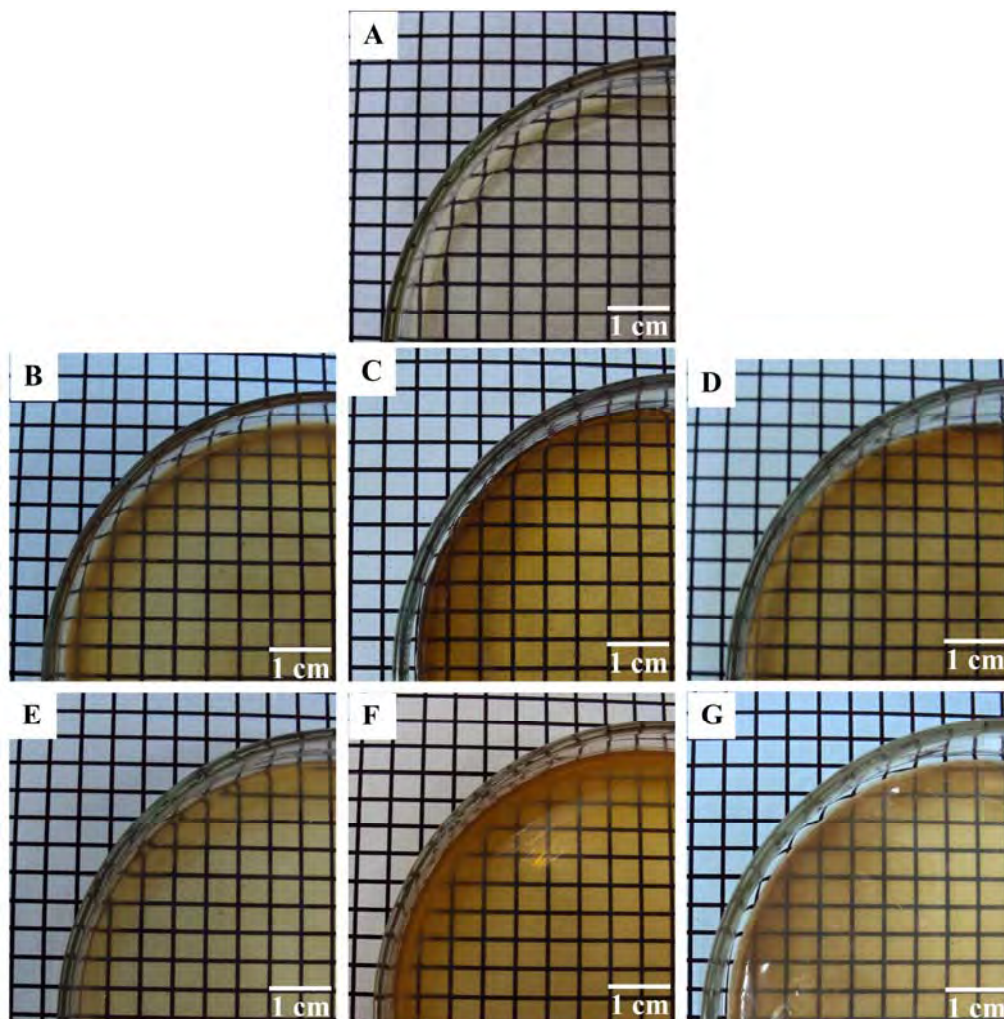
**Figure 4.11**  $^{31}\text{P}$  NMR spectrum of PMPBP

### 4.3 Graft copolymerization and characterization of grafted NR copolymers

Graft copolymerization of MEDP and MPBP was carried out in latex medium *via* seeded emulsion polymerization. Firstly, the high ammonia NR latex with 60% DRC was diluted by 0.7% ammonia solution in order to obtain NR latex having 30% DRC. A potassium hydroxide solution (10% w/v) was added to maintain the basic pH (10-11), hence the latex stability. Sodium dodecyl sulfate (SDS) was then added as an emulsifier with gentle stirring to prevent foaming and to preserve the colloidal stability of the latex. CHPO/TEPA was chosen as the couple redox initiator to generate radicals onto the surface of NR particles to form the copolymer shell around seed particles. This method has been found to give high grafting efficiency and low free homopolymer yield [16, 17]. After the completion of grafting process, the grafted NR latex was dried in an oven at 50°C to yield grafted NR film products. At this stage, the grafted NR products still consisted of free NR, free homopolymer and grafted copolymer. Consequently, the undesired free NR and free homopolymer were extracted out by solvent soxhlet extraction method. The free NR was extracted by petroleum ether for 24 hr. The residue was dried to a constant weight in an oven at 50°C. The dried residue was further extracted in the soxhlet apparatus using acetone for 24 hr in order to remove the free homopolymer. In this research, ungrafted NR was referred to as free NR, ungrafted PMEDP and PMPBP were referred to as free homopolymers. Grafted copolymers were referred to as NR-g-PMEDP and NR-g-PMPBP.

#### 4.3.1 General observation of grafted NR films

The appearance of unmodified NR, MEDP grafted NR, and MPBP grafted NR films at 10, 15, and 20 wt% prepared in this study were shown in Figure 4.12 ((a)-(g)). All samples shown here were without further purification (without Soxhlet extraction). The unmodified NR gave a transparent pale yellowish film. In the grafted NR series, by either MEDP or MPBP, it was clearly observed that as the monomer concentration increased, the grafted NRs became increasingly translucent and more yellowish. Since the grafted NR films were prepared and obtained without further purification, MEDP or MPBP homopolymer which was possibly formed in the reaction mixture would be incorporated in the films. Therefore, the grafted NR films at high concentrations of monomers exhibited more translucent and yellowish than the NR film.



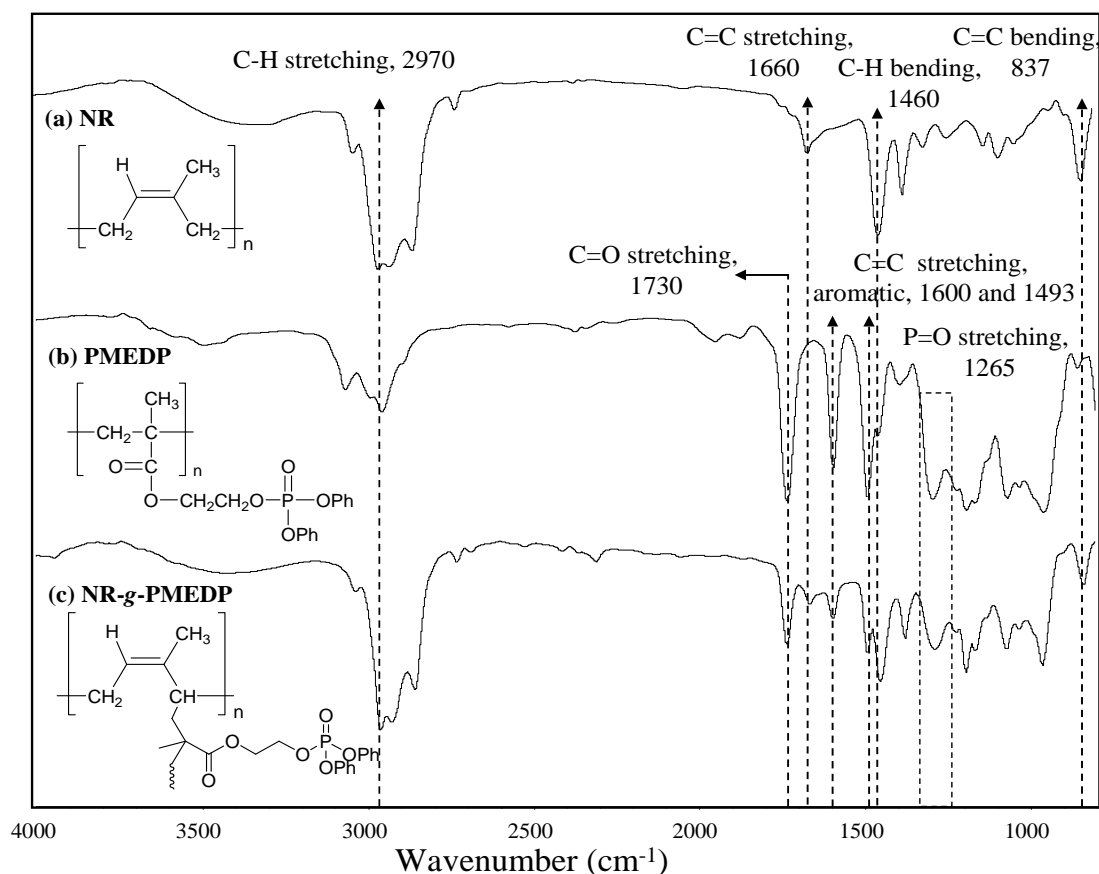
**Figure 4.12** Photographs of (a) NR film, (b) MEDP grafted NR film at 10 wt% MEDP, (c) MEDP grafted NR film at 15 wt% MEDP, (d) MEDP grafted NR film at 20 wt% MEDP, (e) MPBP grafted NR film at 10 wt% MPBP, (f) MPBP grafted NR film at 15 wt% MPBP, and (g) MPBP grafted NR film at 20 wt% MPBP

### 4.3.2 FT-IR analysis

The functional groups of PMEDP and PMPBP grafted NR were characterized by FT-IR technique. Both grafted NR films were purified by Soxhlet extraction to remove all the potentially formed homopolymers (free NR, free PMEDP, and free PMPBP). FT-IR spectra of NR, PMEDP free homopolymer, and NR-g-PMEDP are shown in Figure 4.13.

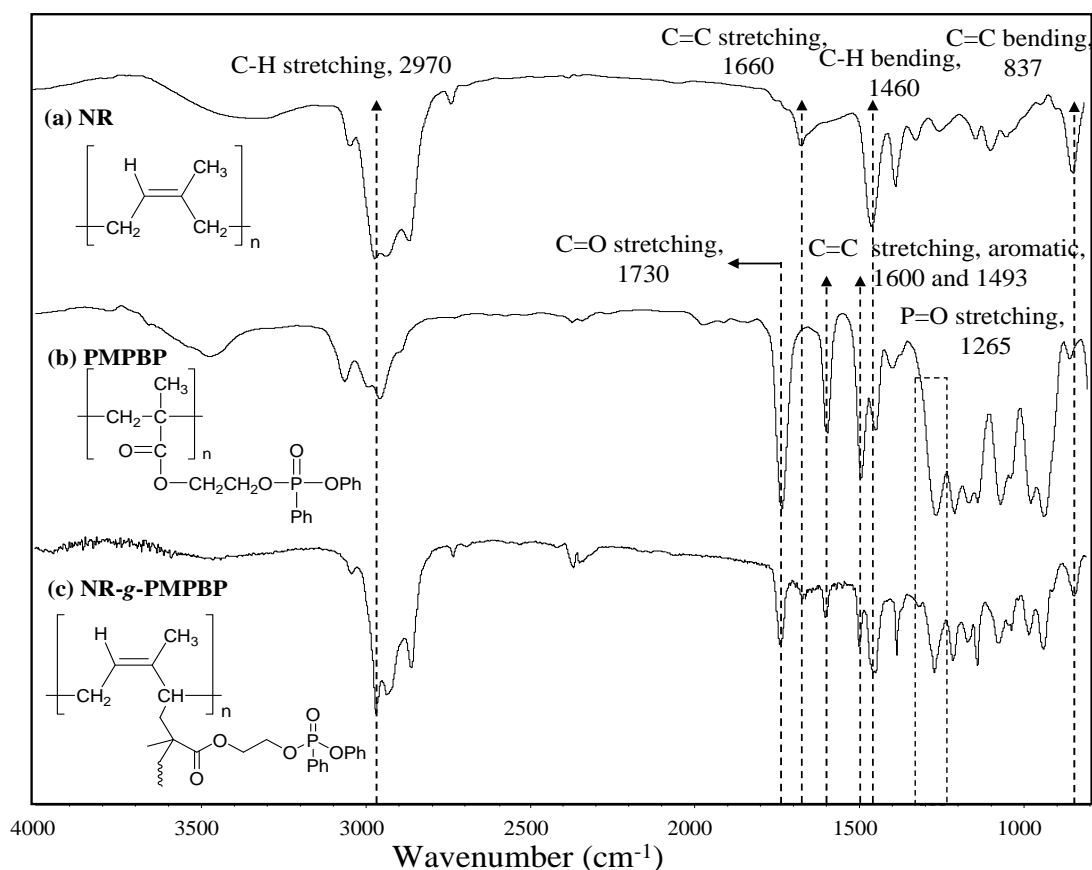
The absorption peaks of the aliphatic C-H stretching at  $2970\text{ cm}^{-1}$ , C=C stretching at  $1660\text{ cm}^{-1}$ ,  $\text{CH}_2$  bending vibration at  $1460\text{ cm}^{-1}$ , and out-of-plane bending vibration of carbon-carbon double bond (C=C) at  $837\text{ cm}^{-1}$  indicated the characteristics

of NR (Figure 4.13(a)) [16]. The absorption peaks of NR-g-PMEDP (Figure 4.13(c)) not only showed the characteristic peaks of NR but also a new absorption peak of the carbonyl group at  $1730\text{ cm}^{-1}$  (C=O stretching). Moreover, the C=C stretching of aromatics at  $1600$  and  $1493\text{ cm}^{-1}$  was also observed. Furthermore, the absorption peak at  $1265\text{ cm}^{-1}$  was attributed to the important phosphate (P=O) stretching vibration. These results indicated that NR-g-PMEDP contained the backbone of NR joined with the PMEDP moiety (Figure 4.13(b)).



**Figure 4.13** FT-IR spectra of (a) NR, (b) PMEDP, and (c) NR-g-PMEDP

FT-IR spectra of NR, PMPBP free homopolymer, and NR-g-PMPBP samples in Figure 4.14 also confirmed the grafting of MPBP. NR-g-PMPBP (Figure 4.14(c)) showed all characteristics peaks of NR and PMPBP. The strong absorption peaks at  $1730\text{ cm}^{-1}$  and  $1265\text{ cm}^{-1}$  were attributed to stretching vibration of carbonyl group (C=O) and P=O stretching vibration of phosphonate group, respectively. These absorptions, consistent with those representing functional groups found in PMEDP (Figure 4.13 (b)) and PMPBP (Figure 4.14 (b)), therefore, confirm the successful incorporation of the phosphorus moiety onto the NR.



**Figure 4.14** FT-IR spectra of (a) NR, (b) PMPBP, and (c) NR-g-PMPBP

### 4.3.3 Grafting conditions

In this section, the study of graft copolymerization conditions including the effect of reaction temperature, monomer concentration, initiator concentration, and amount of reducing agent were investigated. The data obtained from all steps were used to calculate the percentage of grafted NR, free NR, free homopolymer, monomer conversion and grafting efficiency. Grafting efficiency was determined by analyzing the amount of graft copolymer and homopolymer formed during the grafting process. The amounts of free NR and free homopolymer were then calculated based on a weight difference before and after each extraction method. The details of all calculation are shown in section 3.3.7.

#### 4.3.3.1 Effect of reaction temperature

The graft copolymerization of MEDP and MPBP onto NR were studied at a fixed weight ratio of NR to monomer of 90:10, and the initiator concentration at 0.5

phr, with varied reaction temperatures in the range of 40 to 70°C. The grafting results presented here are acquired from one experiment.

In general, the rate of initiator decomposition depends on reaction temperature. When the reaction temperature is increased, more cumyl oxyl radicals are produced. In the case of grafting MEDP onto NR (Table 4.1), the reaction temperature of 70°C resulted in high grafting efficiency of 88.4% and low free homopolymer of PMEDP (1.7%). At high temperature a large amount of cumyl oxyl radicals were produced and reacted with the rubber chain to generate the graft copolymers resulting in the decrease of free NR and free homopolymer. The monomer conversion increased to 87.2% because more radicals were generated to consume the monomer molecules [42].

**Table 4.1** Effect of reaction temperature on grafting performance of MEDP

Reaction temperature (°C)	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMEDP	
40	78.4	83.7	14.0	2.3	82.5
50	87.5	77.4	19.8	2.8	81.1
60	84.5	72.7	24.5	2.8	80.1
70	87.2	79.4	18.9	1.7	88.4

For the case of MPBP grafted onto NR (Table 4.2), it was also found that the grafting efficiency increased up to 85% and free PMPBP decreased to 1.9%. However, the percentage of grafted NR, free NR, and conversion of both monomers were not significantly different.

**Table 4.2** Effect of reaction temperature on grafting performance of MPBP

Reaction temperature (°C)	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMPBP	
40	82.9	81.4	15.2	3.4	75.1
50	82.1	80.2	16.9	2.8	79.4
60	79.8	80.2	17.6	2.3	82.8
70	76.8	78.9	19.2	1.9	85.2



The result of an increase in reaction temperature of 60 and 70°C seemed to work well due to high grafting efficiency and low homopolymerization of both monomers. It was, however, found that at these temperatures, rubber particles would separate from the latex in a solid form during the process. In other words, high temperature affected the latex stability and grafting properties of NR. Moreover, high temperature may affect the crosslink of NR causing the influential effects on grafting properties. Thus, the reaction temperature of 50°C were instead used for the study on the effects of monomer concentration on the reaction outcome because the percentage of grafted NR and percentage of conversion were close to the reaction at high temperature of 60 and 70°C.

#### **4.3.3.2 Effect of monomer concentration**

The effect of monomer concentration on grafting efficiency was studied at a fixed reaction temperature of 50°C which preserved the stability of NR latex, and the initiator concentration of 0.5 phr. The weight ratio of NR:monomer was varied in the range from 90:10 to 75:25 wt%. The grafting properties presented here were based on 3 sets of experiments.

Experiments were carried out to determine the maximum monomer concentration which could be used without disturbing the latex stability at 50°C (Table 4.3). As the concentration of MEDP increased from 10 to 20 wt%, the grafting efficiency slightly increased from 81.1 to 83.6%. The increase in the grafting efficiency might be due to the complexation of rubber with monomers, which was favored by high monomer concentrations. On the other hand, the monomer conversion decreased from 87.5 to 52.5%. The decrease in the percent conversion at high monomer concentration may be caused by two competing processes between grafting and combination of PMEDP macroradicals. When the concentration of PMEDP macroradicals increased, the rate of termination increased faster than the grafting rate with the rubber macroradicals [21]. Moreover, the possible maximum concentration at 50°C was 20 wt% of MEDP. Attempts to increase the amount of MEDP to a concentration higher than 20 wt% at this temperature resulted in the precipitation of the NR out of the colloid latex.

**Table 4.3** Effect of MEDP concentration on grafting performance

Weight Ratio of NR:MEDP	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMEDP	
90:10	87.5 ± 2.3	77.4 ± 2.7	19.8 ± 1.9	2.8 ± 0.8	81.1 ± 5.3
85:15	60.6 ± 1.4	79.8 ± 1.3	17.1 ± 1.7	3.2 ± 0.5	80.3 ± 3.0
80:20	52.5 ± 4.0	75.6 ± 1.8	21.2 ± 2.2	3.2 ± 0.6	83.6 ± 4.5

In the case of MPBP (Table 4.4), as the concentration was raised from 10 to 15 wt%, the percentage of free homopolymer increased from 2.8 to 3.5%, whereas the monomer conversion decreased from 82.1 to 60.1%. The grafting efficiency remained at about 80% which were not significantly different with increasing monomer concentration from 10 to 15 wt%.

Many attempts to increase the MPBP concentration from 15% to 20% at 50 °C failed since the NR started to precipitate out of the latex. In order to obtain MPBP grafted NR at 20 wt% concentration for comparison to that of MEDP grafted NR, effort was made to overcome precipitation problem by carrying out the grafting at room temperature (26-28 °C). It was observed that at room temperature the MPBP concentration of 20 wt% could be carried out to obtain low grafting efficiency of 67% and low conversion of 48%. The low monomer conversion and grafting was a result of performing the reaction at low temperature, causing low radical generation.

**Table 4.4** Effect of MPBP concentration on grafting performance

Weight Ratio of NR:MPBP	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMPBP	
90:10	82.1 ± 9.4	80.2 ± 2.6	16.9 ± 2.0	2.8 ± 0.9	79.4 ± 6.1
85:15	60.1 ± 0.2	81.2 ± 0.1	15.0 ± 1.0	3.5 ± 1.4	77.7 ± 9.0
80:20*	47.7 ± 4.6	77.2 ± 2.2	17.1 ± 2.5	5.7 ± 1.0	67.4 ± 9.4

\*reaction was carried out at room temperature (26-28 °C)

Low grafting efficiency and low conversion at high monomer concentration in both MEDP and MPBP can be ascribed to side reactions competing in the mixture such as combination and disproportionation of PMEDP and PMPBP macroradicals causing high termination rate [21]. Since competing reactions could occur, no further attempt to increase monomer concentration in both cases was carried out. Moreover, it was also believed that when the concentrations of PMEDP and PMPBP increased, the NR latex became increasingly unstable. Consequently, an increasing of monomer concentration from 10 to 20 wt% of both monomers did not help increasing the grafting efficiency and the amount of grafted NR. Although, MEDP and MPBP at 10 wt% exhibited the highest grafting efficiency and percent monomer conversion, they did not show better flame retardant properties compared to those of MEDP and MPBP at 15 and 20 wt% which is discussed in section 4.4.

#### 4.3.3.3 Effect of initiator concentration

As mentioned earlier, the CHPO/TEPA was chosen in part because this system gave the highest grafting efficiency and lowest free homopolymer [16, 17, 21]. The effect of the amounts of initiator on the grafting efficiency of MEDP and MPBP on the NR was studied at a fixed weight ratio of NR to monomer of 90:10, and the reaction temperature of 50°C, with varied initiator concentration in the range of 0.25 to 1.0 parts of rubber (phr) (Tables 4.5 and 4.6). The grafting properties presented here are obtained from one experiment.

**Table 4.5** Effect of initiator concentration on grafting performance of MEDP

Initiator concentration (phr)	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMEDP	
0.25	95.6	78.9	19.7	1.4	91.4
0.50	88.1	76.0	20.9	3.1	78.7
1.00	91.4	81.3	16.8	1.9	87.4

**Table 4.6** Effect of initiator concentration on grafting performance of MPBP

Initiator concentration (phr)	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMPBP	
0.25	89.2	79.1	18.9	2.0	86.9
0.50	87.0	78.8	18.1	3.2	78.0
1.00	81.3	82.7	13.8	3.4	74.6

Generally, an increase in initiator concentration can produce more radicals, i.e. herein the increase number of grafting sites. Indeed, when the initiator concentration increased from 0.25 to 1.0 phr, the percentage of PMEDP grafted NR in each condition was at 76-81% without any correlation with the initiator content (Table 4.5). In the case of PMPBP grafted onto NR (Table 4.6) resulted in a same trend of the percentage of grafted NR at about 79-83%. Interestingly, as the amount of initiator was 1.0 phr, the free NR content of both cases decreased to 16.8% and 13.8%, respectively. This is possibly because the grafting process at high initiator concentration also brought about the crosslinking of NR chains themselves by the radical initiator [21]. Consequently, the crosslinked NR content interfered the removal of free NR content by solvent extraction. Therefore, the grafting efficiency slightly decreased from 91.4 to 87.4% (PMEDP grafted NR) and 86.9 to 74.6% (PMPBP grafted NR) with increasing initiator concentrations. The highest grafting efficiency and monomer conversion were obtained at the initiator amount of 0.25 phr. In addition, the increase in the amount of free homopolymer was observed because the excessive free polymer radicals then reacted with each other to form a greater amount of the free homopolymer rather than grafting on the rubber radicals. Therefore, the formation of the free homopolymer was greatly promoted at high initiator content [21].

The effect of initiator concentration on grafting properties of both cases, when the initiator concentration increased to 1.0 phr, the percentage of grafted NR slightly increased, whereas the amount of free NR decreased resulting that the grafting efficiency decreased. The reason is that the crosslinking of rubber chains and homopolymers are formed readily during the grafting process. In the investigated range, the reaction at the initiator concentration of 0.25 phr provided the highest grafting efficiency and percentages of monomer conversion, whereas the percentage of grafted

NR was not significantly different from the reaction at the initiator concentration of 0.5 and 1.0 phr.

#### 4.3.3.4 Effect of amount of amine activator or reducing agent

The effect of reducing agent TEPA on the outcome of the grafting was investigated in the case of PMPBP grafted NR. These conditions were studied at a fixed weight ratio of NR to monomer of 90:10, the reaction temperature of 50°C, and initiator concentration at 0.5 phr. The grafting results presented here are based on one experiment (Table 4.7).

**Table 4.7** Effect of amount of reducing agent on grafting performance of MPBP

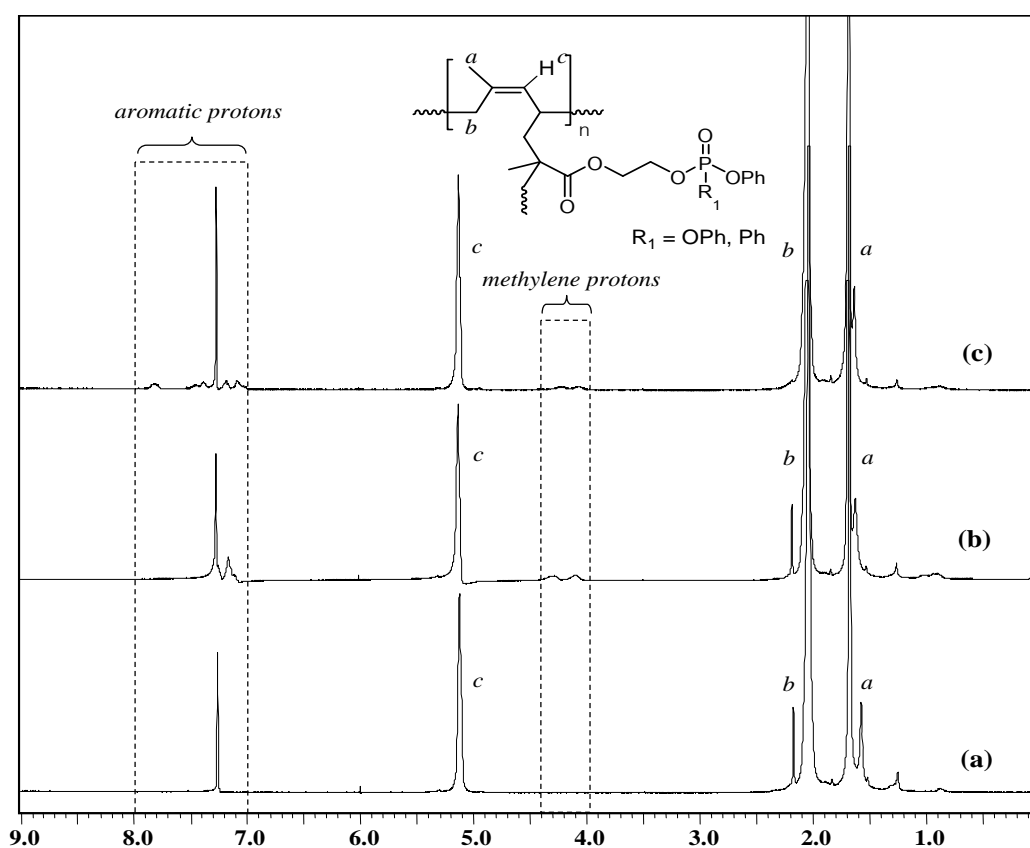
TEPA concentration (phr)	Monomer conversion (%)	Grafted NR (%)	Free homopolymer (%)		Grafting efficiency (%)
			NR	PMPBP	
0.00	84.3	73.1	25.3	1.6	88.5
0.50	87.0	78.8	18.1	3.2	78.0

In the case where TEPA was not added into the reaction mixture, it was found that the percentage of grafted NR decreased from 78.8 to 73.1% and the free PMPBP also decreased from 3.2 to 1.6%. Furthermore, the free NR content was high because without TEPA the radical were generated in a very low amount. CHPO is a thermal initiator, meaning it can decompose to radicals at high temperature generally at 130°C [48]. In latex grafting process, the temperature must not be too high so that the colloid stability of NR latex was preserved. TEPA as a reducing agent was chosen to increase the rate of producing primary radicals and generate radicals of CHPO at moderate temperature (0-50°C) at which precipitation of rubber particles in the latex was avoided [38].

In summary, the investigation of reaction parameters of the grafting process demonstrated that the most suitable temperature was 50°C because at 50°C the latex stability was maintained. The effect of monomer concentrations indicated that the weight ratio of NR to monomer contents of 90:10 wt% gave the highest grafting efficiency and percentage of monomer conversion. The initiator concentration of 0.25 phr was found to give the highest grafting efficiency and monomer conversion. And finally TEPA as a reducing agent was needed to obtain high percentage of grafted NR.

#### 4.3.4 Method evaluation-grafting contents by extraction VS $^1\text{H}$ NMR

After extraction of homopolymers (free NR and free homopolymer), the grafted copolymers were also characterized by  $^1\text{H}$  NMR spectroscopy (Figure 4.15). The characteristic  $^1\text{H}$  NMR spectra of unmodified NR (Figure 4.15(a)) showed a singlet signal at 5.1 ppm corresponding to the olefinic proton ( $=\text{CH}-$ ). The signal at 2.1 ppm was attributed to the methylene protons and the singlet signal of methyl proton appeared at 1.7 ppm [16]. The NR-*g*-PMEDP showed all signals of the unmodified NR. In addition, signals at 7.0-7.3 and 4.0-4.4 ppm corresponding to the signals of aromatic protons and methylene protons of the grafted PMEDP, respectively, were observed. In case of NR-*g*-PMPBP, the signals of aromatic protons appeared in the region of 7.0-8.0 ppm, and the methylene protons were also observed at 4.0-4.4 ppm. These spectra confirmed the existence of PMEDP and PMPBP moiety on the NR particles which were prepared by the seeded emulsion polymerization.



**Figure 4.15**  $^1\text{H}$  NMR spectra of (a) NR, (b) NR-*g*-PMEDP ( $R_1 = \text{OPh}$ ), and (c) NR-*g*-PMPBP ( $R_1 = \text{Ph}$ ) obtained after Soxhlet extraction

To determine the amounts of PMEDP and PMPBP grafted onto the NR particles in terms of mole and weight percentages, the integrated peak areas of aromatic protons and olefinic proton of the grafted copolymers and NR in the  $^1\text{H}$  NMR spectra were used for calculation according to the details in section 3.3.8. The calculated results from  $^1\text{H}$  NMR spectra are presented in Table 4.8, in comparison with the weight percentages of grafted copolymers, which were estimated by extraction method.

**Table 4.8** Copolymers composition data of NR prepared by seeded emulsion polymerization reaction using NR as seed and MEDP or MPBP as grafted monomers.

Graft copolymers	NR/Initial monomer (wt%)	Reaction Temp. ( $^{\circ}\text{C}$ )	Grafting efficiency (%)	Percentage of grafted copolymer		
				Extraction method	$^1\text{H}$ NMR method	
					wt%	mol%
NR-g-PMEDP	90/10	50	81.1	6.8	0.4	2.1
NR-g-PMEDP	85/15	50	80.3	7.2	1.0	5.1
NR-g-PMEDP	80/20	50	83.6	9.5	2.0	9.6
NR-g-PMPBP	90/10	50	79.4	6.0	1.4	6.7
NR-g-PMPBP	85/15	50	77.7	8.0	1.4	6.7
NR-g-PMPBP	80/20	28	67.4	7.6	1.6	7.5

For MEDP grafted NR, when the amount of the employed monomer increased from 10 to 20 wt%, the amount of MEDP in the copolymer increased from 2.1 to 9.6 %. In the case of MPBP grafting, the same trend was observed. When 10 wt% of MPBP was added, the weight composition was 6.7%. At 20 wt% of MPBP, the weight composition increased to 7.5%. Both techniques revealed that the percentage of grafted copolymers showed slightly increased with increasing monomer contents used for the graft copolymerization. However, because of the incomplete conversion and occurrence of homopolymer, the amount of final grafted copolymers was lower than the amount of initial monomer used. As compared to that of extraction method based on the same grafting conditions,  $^1\text{H}$  NMR analysis showed the fewer amounts of grafted copolymers than extraction method. We have to mention the hypothesis that the calculation of

grafting properties by  $^1\text{H}$  NMR was limited because the grafted NR films were swollen, but not completely dissolved by  $\text{CDCl}_3$ , whereas the extraction method could cause the possible crosslinking reactions. Therefore, the extraction technique was chosen because it provided more reliable results than the  $^1\text{H}$  NMR technique.

From the results of the influential effects on grafting properties of both monomers grafted onto NR, the appropriate grafting condition was obtained when the reaction temperature was used at  $50^\circ\text{C}$ , initiator concentration of 0.5 phr in order to increase grafting sites coupled with TEPA as a reducing agent. This optimum grafting condition was therefore used to prepare the NR-*g*-PMEDP and NR-*g*-PMPBP with increasing monomer contents to determine the characteristic properties that will be discussed in Section 4.4.

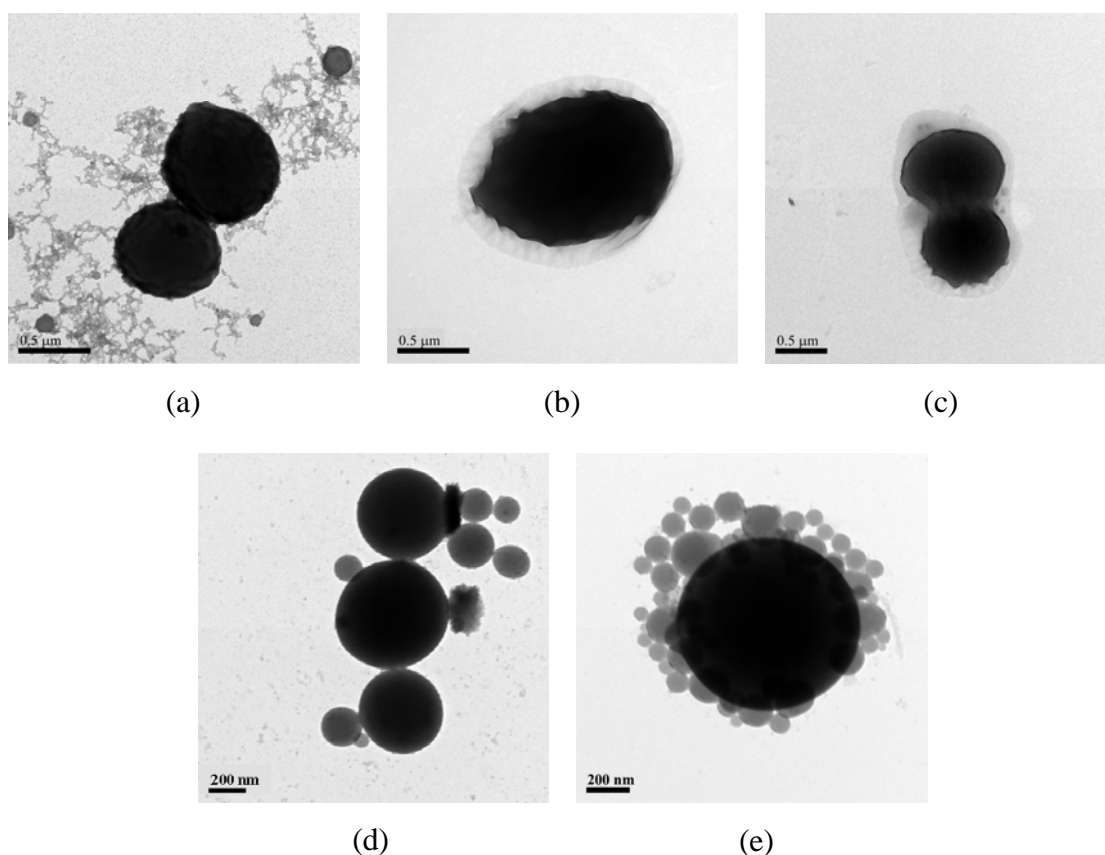
#### **4.4 Characterization of grafted NR products**

##### **4.4.1 Morphology observation by transmission electron microscopy (TEM)**

The grafting of NR latexes was performed in the presence of CHPO/TEPA. Oil-soluble nature of CHPO and water-soluble characteristic of TEPA allowed the generation of radicals at the NR–water interface. This facilitates the polymerization of the secondary polymers at the interface of NR particles, which provided the formation of a shell layer around the core NR particles as core-shell morphology [17]. Transmission electron microscopy (TEM) was employed to investigate the morphology of grafted NR particles obtained from emulsion reactor batch. TEM micrographs of NR latexes, MEDP grafted NR, and MPBP grafted NR stained with either  $\text{RuO}_4$  or  $\text{OsO}_4$  were compared in Figure 4.16.

The metal staining at  $\text{C}=\text{C}$  bonds of NR was carried out to improve the contrast between the NR phase and secondary non-NR phase in the composite of latex particles [49]. Core NR particles stained with  $\text{RuO}_4$  appeared darker than those stained with  $\text{OsO}_4$  because  $\text{RuO}_4$  is a stronger oxidizing agent than  $\text{OsO}_4$  [50]. The particle morphology of both grafted NR particles was observed when the samples were stained with 1%  $\text{RuO}_4$ .





**Figure 4.16** TEM micrographs of (a) NR latex particles, (b) NR-g-PMEDP latex at MEDP 10 wt%, and (c) NR-g-PMPBP latex at MPBP 10 wt%. Samples (a)-(c) were stained with 1% RuO<sub>4</sub> vapour. (d) NR-g-PMEDP latex at MEDP 10 wt%, and (e) NR-g-PMPBP latex at MPBP 10 wt%. Figures (d) and (e) were stained with 1% OsO<sub>4</sub> vapour.

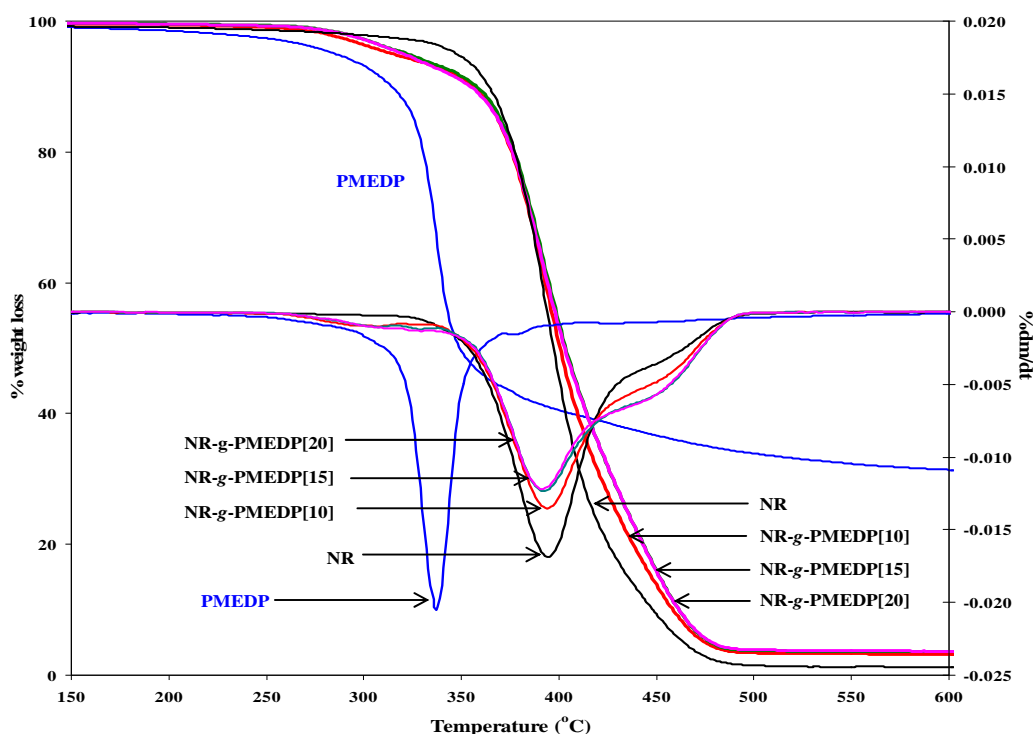
The untreated NR latex particles appeared as dark spheres with clear boundaries as shown in Figure 4.16(a). In the case of grafted NR, representative core-shell morphologies were obtained from the initial monomer weight of 10% as illustrated in Figure 4.16(b) and (c). The core appeared as a dark sphere, whereas the lighter shell layers represent area of the grafted PMEDP (Figure 4.16(b)) and PMPBP (Figure 4.16(c)).

In addition, TEM micrographs of both grafted NR particles stained with 1% OsO<sub>4</sub> also revealed that another possible alternative is an accumulation of homopolymer phase on the NR surface as shown in Figure 4.16(d) and Figure 4.16(e). A highly heterogeneous nature of NR particles was obvious from Figure 4.16(d) and Figure 4.16(e). This is important in seeded emulsion polymerization due to the competitive growth mechanism, which favored the smaller particles. The homopolymer

phase of PMEDP and PMPBP droplet clusters appeared as grayish round particles much smaller than the core NR particles. In this sample set, the grafting condition was performed *via* seeded emulsion polymerization using sodium dodecyl sulfate (SDS) as an emulsifying agent. In this particular case the concentration of SDS may be higher than the critical micelle concentration (CMC). This meant that the extra SDS could gather to form new micelles encapsulating the added monomers and/or the macroradicals of free PMEDP or PMPBP. Therefore, the homopolymers are growing in the micelle of SDS which appeared as small particles.

#### 4.4.2 Thermogravimetric analysis (TGA)

The thermal degradation behavior of unmodified NR, PMEDP free homopolymer, and grafted copolymers was examined by thermogravimetric analysis. Figure 4.17 shows plots thermograms from thermogravimetric analysis (TGA) together with derivative thermogravimetric (DTG) curves of NR, PMEDP, and PMEDP grafted NR under nitrogen atmosphere.

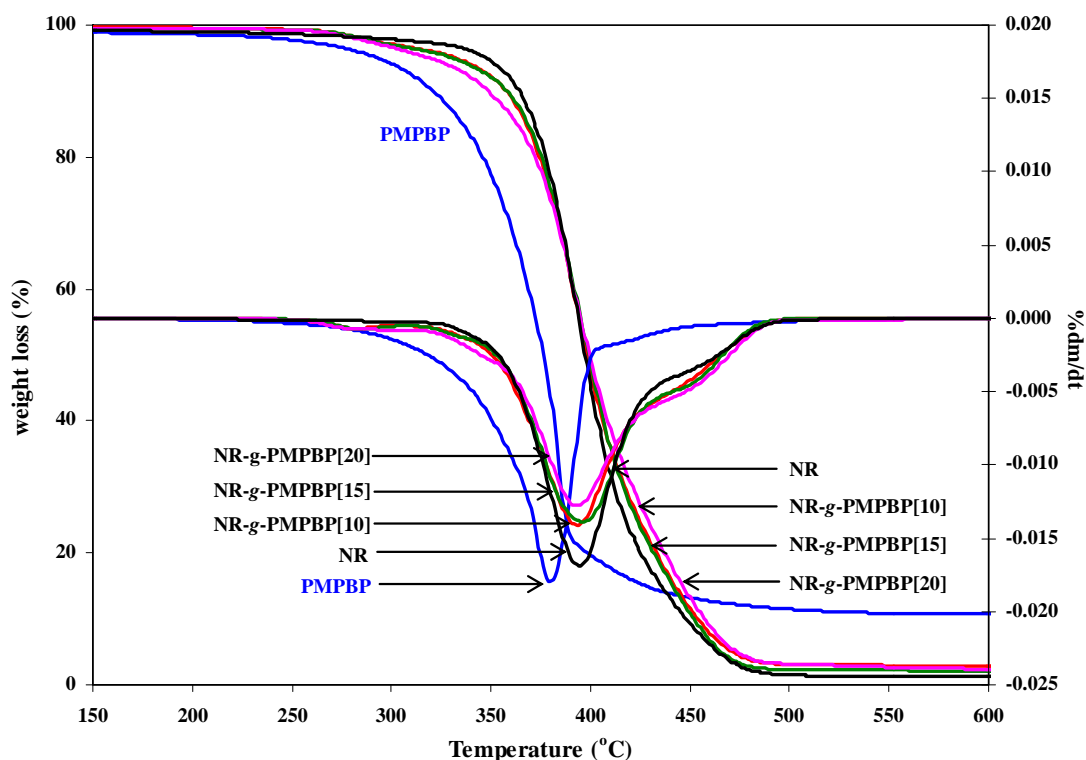


**Figure 4.17** TGA thermograms and derivative thermogravimetric (DTG) thermograms of unmodified NR, PMEDP, NR-g-PMEDP [10] referred as 10 wt% of MEDP, NR-g-PMEDP [15] referred as 15 wt% of MEDP, and NR-g-PMEDP [20] referred as 20 wt% of MEDP

In Figure 4.17, the thermal degradation of PMEDP free homopolymer was observed as a single step process with an onset temperature of 323°C. In the DTG curves, the maximum decomposition temperature ( $T_{max}$ ), determined *via* differentiation of TGA data, was found at 338°C which was in the temperature decomposition range of the least stable P-O-C aromatic and aliphatic structures to eliminate a phosphate complex structures [36, 37]. The residual weight of PMEDP was almost 30% at the temperature above 500°C.

Considering the thermograms of NR-g-PMEDP at 10 to 20 % weight of MEDP contents, two-stage weight loss curves were observed and began to decompose beyond 271°C. The first step was attributed to the degradation of PMEDP functionalized copolymers. The second step decomposition began at 320°C. This corresponded to the degradation of the NR domain [12]. As the initial content of MEDP increased to 20 wt%, an increase in the percentage of char residue from 1.1 (unmodified NR) to 3.7% (NR-g-PMEDP) was observed, according to the slight increase of percentage of grafting efficiency (Table 4.3). This can be related to an increase in the percentage of mass loss in the first step degradation of functionalized PMEDP from 5.3 (10 wt% of MEDP) to 6.8 % (20 wt% of MEDP). Moreover, an increase in the amount of char residue could assist in the coverage of the surface of the burning substances. This resulted in the decrease in the transmission of oxygen, the amount of heat and active gas to the burning surface [37]. These results implied that higher flame retardancy observed in grafted NR was partially attributed to the higher amount of char residue obtained in the system. This can be further supported by the following flammability test (section 4.8).

In the series of MPBP grafted NR, thermograms from TGA together with DTG curves of NR, PMPBP, and PMPBP grafted NR under nitrogen gas are shown in Figure 4.18.



**Figure 4.18** TGA thermograms and derivative thermogravimetric (DTG) thermograms of unmodified NR, PMPBP, NR-g-PMPBP [10] referred as 10 wt% of MPBP, NR-g-PMPBP [15] referred as 15 wt% of MPBP, and NR-g-PMPBP [20] referred as 20 wt% of MPBP

A single stage decomposition was observed for PMPBP free homopolymer. TG and DTG curves of PMPBP free homopolymer exhibited a single step degradation which showed the onset temperature and  $T_{max}$  at 359°C and 380°C, respectively. These were attributed to the scission of the phosphonate side chain beyond 200°C [36, 37]. The residual weight of PMPBP was obtained at 10%. PMPBP grafted NR obtained from all different MPBP contents showed a two-stage decomposition pattern. In the first step, an onset temperature above 260°C was observed indicating that the decomposition of functionalized PMPBP had occurred. The second step, starting at 320°C, reflected the degradation of the NR domain [12]. According to the percentage of grafted PMPBP on NR calculated by  $^1\text{H}$  NMR method, there was no difference between 10 and 15 wt% of initial MPBP contents. Therefore, their residual weights were not significantly different. In the case of 20 wt% of MPBP content, it exhibited the residual weight at 2.4% because this reaction was carried out at room temperature which decreased the grafting efficiency of PMPBP on NR.

When the thermal decomposition behaviors of phosphate (PMEDP) and phosphonate (PMPBP) structures were compared, it could be pointed out that PMEDP showed higher residual weight (30%) than that of PMPBP (11%). The results implied that the case of phosphate (PMEDP) structure can promote crosslinking at a higher extent than the case of phosphonate (PMPBP) structure. The decomposition of phosphonate linkage would easily form the weaker phosphonic acid, therefore, the phosphonate linkage had less ability to promote crosslinking than did the phosphate [9].

Moreover, it was also observed that the degradations of both the phosphate (PMEDP) and the phosphonate (PMPBP) linkages occurred at lower temperatures than that of the NR domain. This phenomenon was attributed to the acceleration of thermal degradation to produce low volatile phosphorus species such as phosphoric acids and rapid surface carbonaceous char formation. Protecting layer is formed on the NR surface and retards further burning (see further discussion).

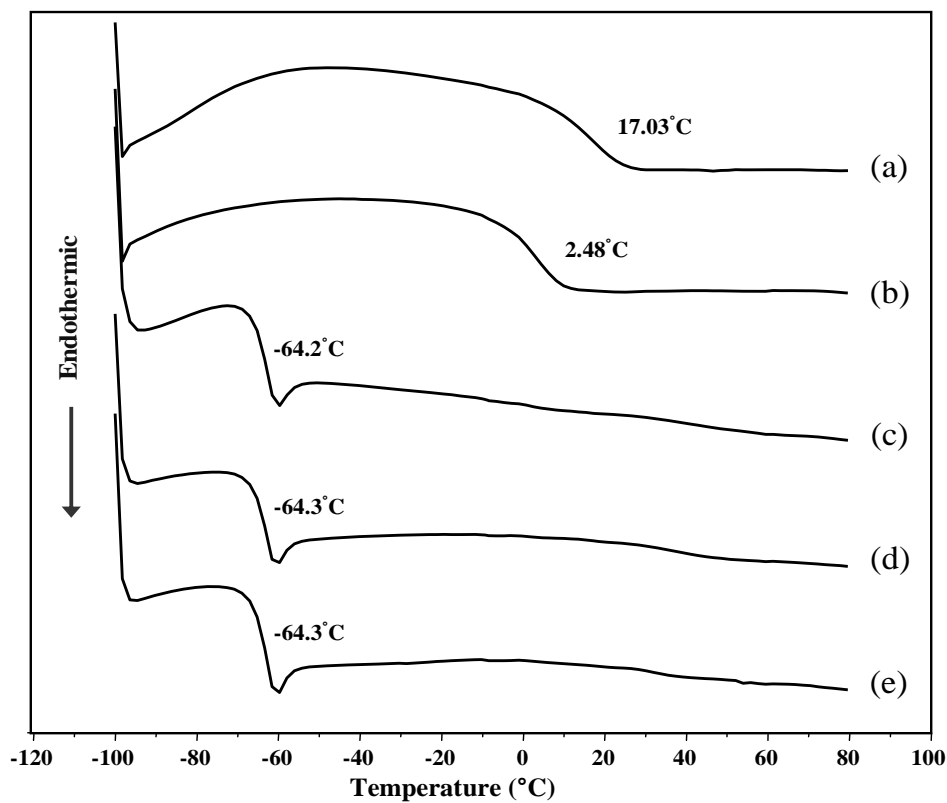
#### 4.4.3 Differential scanning calorimetry (DSC)

In addition to thermogravimetric analysis, thermal properties of free homopolymers (PMEDP and PMPBP) and grafted copolymers were also determined by using differential scanning calorimetry (DSC) and compared with the unmodified NR. Generally, the chemical structure and molecular size of substituents of polymer would affect the glass transition temperature ( $T_g$ ). This can reveal chain mobility of the polymer. The data were summarized in Table 4.9.

**Table 4.9** Glass transition temperature ( $T_g$ ) of unmodified NR and grafted copolymers as measured from Differential Scanning Calorimetric Analysis

Sample designation	Glass transition at onset temperature, $T_g$ ( $^{\circ}$ C)	Glass transition at midpoint temperature, $T_g$ ( $^{\circ}$ C)
PMEDP	7.9	17.0
PMPBP	-4.5	2.5
unmodified NR	-66.0	-64.2
NR-g-PMEDP	-66.0	-64.3
NR-g-PMPBP	-66.0	-64.3

DSC curves of PMEDP and PMPBP grafted copolymers showed differential heat capacities as a function of temperature as depicted in Figure 4.19. The  $T_g$  value of  $17^\circ\text{C}$  was obtained for PMEDP homopolymer. The glass transition at  $2^\circ\text{C}$  indicated  $T_g$  of PMPBP homopolymer. The unmodified NR showed a single glass transition at  $-64^\circ\text{C}$  (midpoint) indicating the  $T_g$  of *cis*-1,4-polyisoprene structure. NR-*g*-PMEDP revealed only a single glass transition at  $-64^\circ\text{C}$  corresponding to the  $T_g$  of grafted NR. In the case of PMPBP grafted NR, the glass transition temperature of NR-*g*-PMPBP was also found at  $-64^\circ\text{C}$ . There might be a few grafted chains in the polymer, which was insufficient to affect the free volume of the backbone. The  $T_g$  of the backbone could initially be the same for the NR itself. Moreover, the low sensitivity detection of the  $T_g$  of the second polymers could be due to the presence of a low amount of grafted copolymers [21].



**Figure 4.19** DSC curves of (a) PMEDP, (b) PMPBP, (c) unmodified NR, (d) NR-*g*-PMEDP, and (e) NR-*g*-PMPBP

#### 4.4.4 Limiting oxygen index (LOI) test

In general, flame retardant properties of materials may be determined by limiting oxygen index (LOI) test which is defined as the minimum concentration of oxygen in oxygen/nitrogen mixtures necessary to burn the sample as evaluated in the LOI values (%). An increasing of LOI value showed the higher level of flame retardancy of material. The data on the LOI values, percent phosphorus contents, and free homopolymer contents of grafted NR films are shown in Table 4.10. The effects of monomer concentration and phosphorus contents on the LOI values are shown in Figure 4.20 and 4.21.

**Table 4.10** Relationship between the LOI values, free homopolymer, and phosphorus contents of unmodified NR, PMEDP, PMPBP, and grafted copolymers obtained before and after Soxhlet

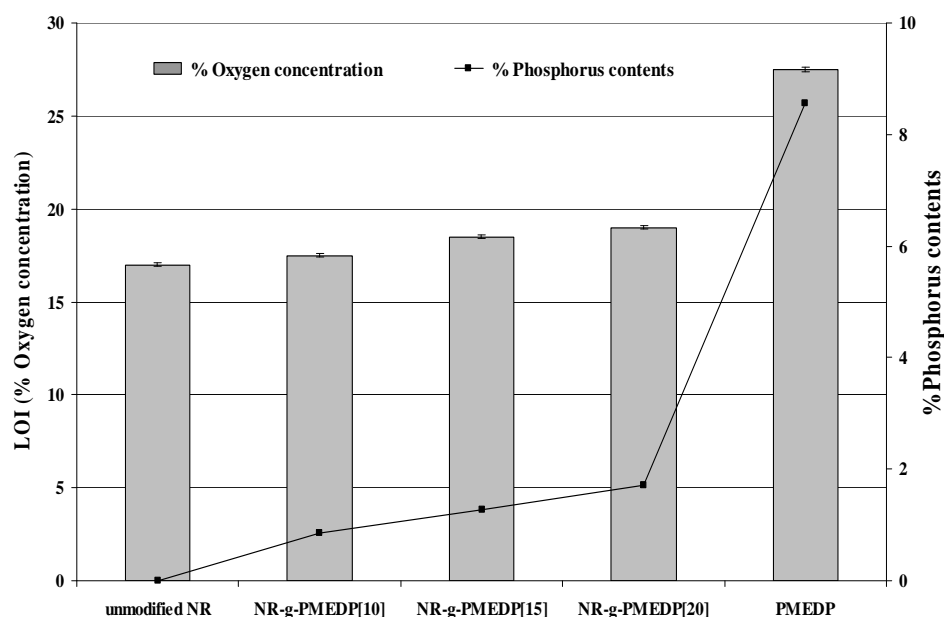
Samples	Free homopolymer (%)	Phosphorus content (%)	LOI values before Soxhlet (%)	LOI values after Soxhlet (%)
unmodified NR	-	-	17.0 ± 0.1	-
NR-g-PMEDP [10]	3.1	0.9	17.5 ± 0.1	17.5 ± 0.1
NR-g-PMEDP [15]	3.2	1.3	18.5 ± 0.1	18.0 ± 0.1
NR-g-PMEDP [20]	3.2	1.7	19.0 ± 0.1	18.5 ± 0.1
PMEDP	-	8.6	27.5 ± 0.1	-
NR-g-PMPBP [10]	3.2	0.9	18.5 ± 0.1	18.5 ± 0.1
NR-g-PMPBP [15]	3.5	1.3	19.5 ± 0.1	19.0 ± 0.1
NR-g-PMPBP [20]*	5.7	1.8	20.5 ± 0.1	20.0 ± 0.1
PMPBP	-	9.0	27.0 ± 0.1	-

The values presented here were averaged from 3 specimens

\*The reaction was carried out at room temperature (26-28°C)

The results of PMEDP grafted NR were displayed in Figure 4.20. The LOI value of unmodified NR was observed at 17.0. PMEDP free homopolymer, with a phosphorus content of 8.6%, showed an LOI value of 27.5 which was in the range of self extinguishing material [35]. The grafting of MEDP onto NR had indeed increased the LOI value of NR. An increase to the maximum initial MEDP content of 20 wt% (translated to the phosphorus content of 1.7%) led to an increase of LOI value up to

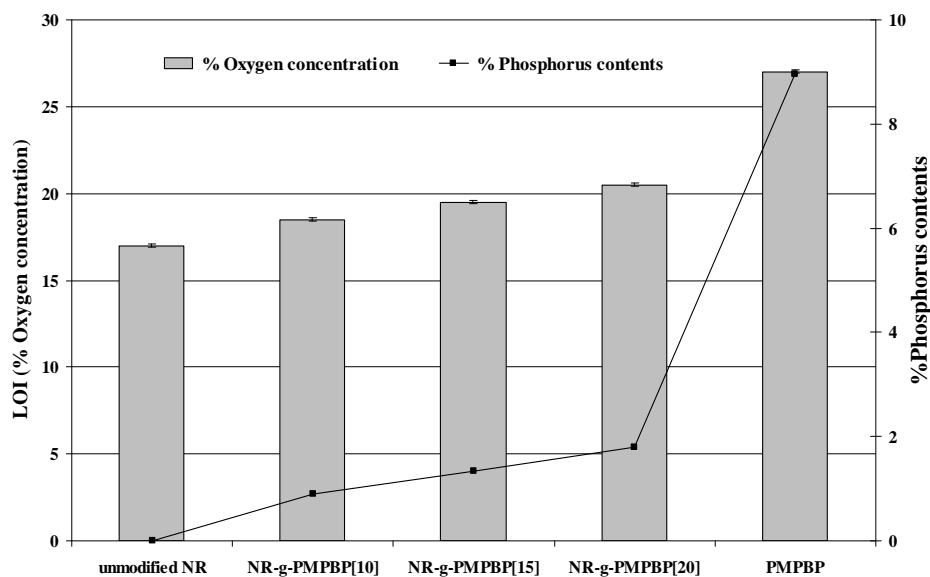
19.0. Moreover, the LOI values of PMEDP grafted NR before and after soxhlet extraction to remove the free MEDP and PMEDP phase were investigated for comparison. After extraction, the LOI values decreased from 19.0 to 18.0 for 15 wt% MEDP and to 18.5 for 20 wt% MEDP, whereas no change was observed for 10 wt% of MEDP (Table 4.10). This result indicated that the homopolymer phase of PMEDP played a role to provide the increasing tendency of flame resistance.



**Figure 4.20** Relationship between initial MEDP contents and LOI values of grafted NR films

PMPBP homopolymer with phosphorus content of 8.96% (Figure 4.21), exhibited an LOI value of 27.0, which is also in the range of self extinguishing material. For NR-g-PMPBP, at maximum initial MPBP content of 20 wt% which translates into phosphorus content of 1.8 wt%, LOI value has increased to 20.5. In addition, the LOI values of NR-g-PMPBP after soxhlet extraction were lower than that without soxhlet (Table 4.10). Increasing the MPBP contents and free PMPBP phase also resulted in a significantly higher value than that of NR (17.0). This led to an enhancement of the flame retardancy of NR.



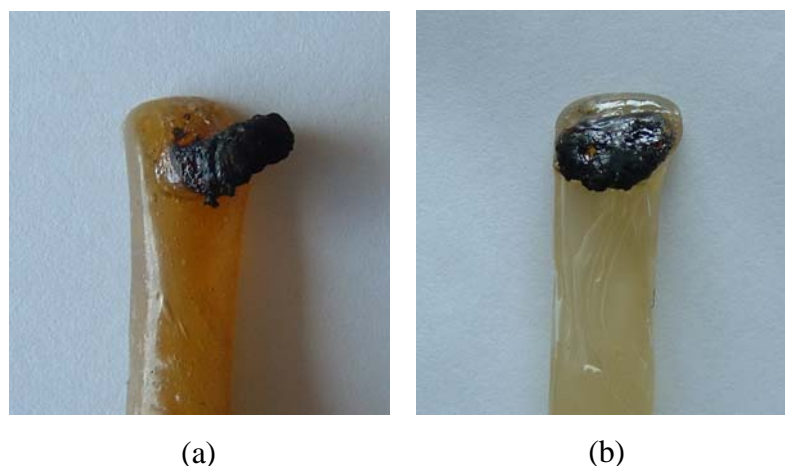


**Figure 4.21** Relationship between initial MPBP contents and LOI values of grafted NR films

These copolymers showed higher LOI values and presumably a higher degree of flame retardancy of NR compared with unmodified NR. This correlated to increase in phosphorus contents. Additionally, PMEDP homopolymer showed higher LOI values than PMPBP. This result was in accordance with the TGA test results that the carbonaceous char residues observed from TGA analysis of PMEDP was higher than PMPBP as discussed earlier. Based on the same grafting conditions, NR-g-PMPBP films showed higher LOI values than NR-g-PMEDP because the free PMPBP was produced in a larger amount than that of PMEDP during the grafting process (Table 4.12). Furthermore, the higher amount of oxygen contents in grafted PMEDP compared that in grafted PMPBP can accelerate the flammability of polymers. In addition, the grafted PMPBP showed higher amounts of the phosphorus contents compared to those of grafted PMEDP resulting in the higher level of flame retardancy.

#### 4.4.5 General observation of carbonaceous char residues

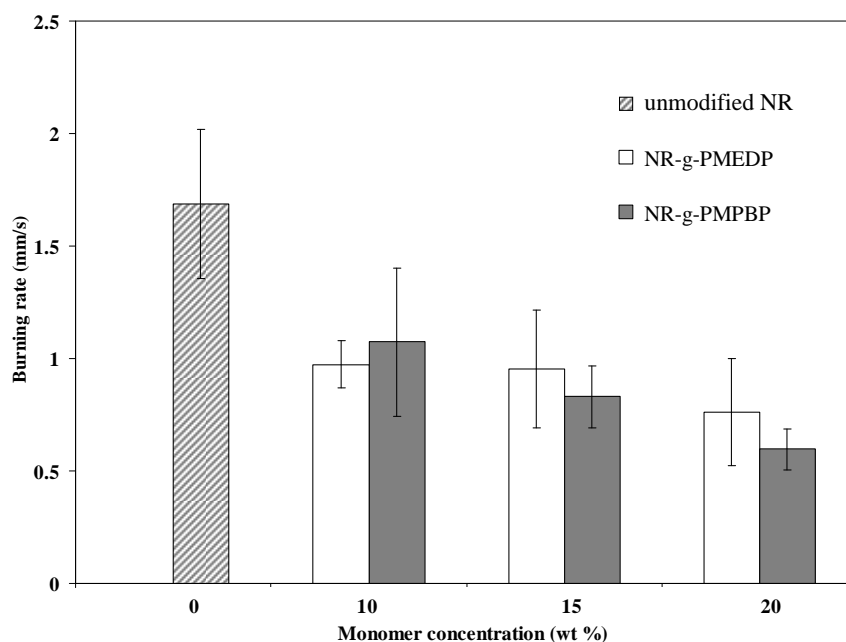
Figure 4.22 showed that, during burning, a carbonaceous char residue on the surface of materials became a thermal insulator and provoked flame extinguishment. These are attributed to the char of phosphorus compounds which behaved as thermal insulation to prevent the combustion gases, from feeding the flame, as well as to separate oxygen from the burning materials.






**Figure 4.22** Photographs of carbonaceous char residues of (a) PMEDP and (b) PMPBP samples after burning

#### 4.4.6 Burning rate

Burning rate was determined by recording the time for flame propagated to the gauge mark. The burning rate of unmodified NR and grafted copolymers films are plotted as shown in Figure 4.23. The unmodified NR showed the highest rate of burning, whereas the burning rate decreased with increasing monomer contents in the grafted NR films.



**Figure 4.23** Burning rates of  unmodified NR and grafted copolymers with increasing the initial monomer concentration of  MEDP and  MPBP. The values presented were averaged from 3 samples (n=3).

#### 4.4.7 Tensile properties

The effect of grafting content on the mechanical properties of both grafted NR was investigated. In this study, tensile test was performed and reported in terms of 300% modulus, tensile strength, and elongations at break (Table 4.11 and Figure 4.24 (a)-(c)). In general, the addition of copolymers or pendant groups onto rubber chain part is expected to increase the mechanical properties because it can interfere the mobility of rubber chains [19].

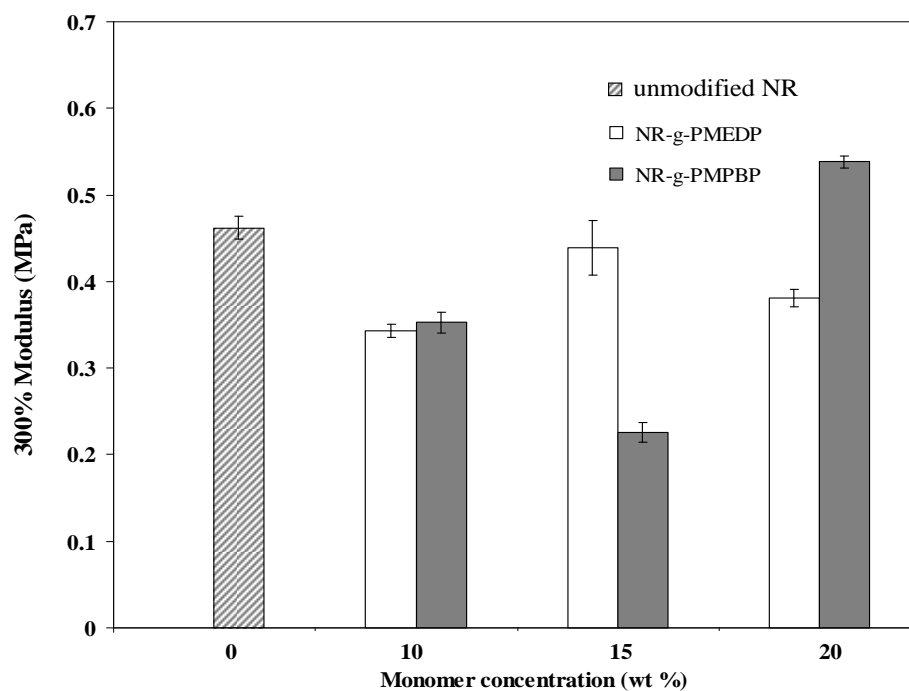
**Table 4.11** Mechanical properties of unmodified NR, grafted copolymers of MEDP, and MPBP with increasing the initial monomer contents

Sample	Modulus at 300% elongation (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
unmodified NR	0.46 ± 0.01	1.86 ± 0.32	886 ± 60.4
NR-g-PMEDP [10]	0.34 ± 0.01	1.37 ± 0.27	905 ± 80.6
NR-g-PMEDP [15]	0.44 ± 0.03	1.24 ± 0.11	768 ± 64.9
NR-g-PMEDP [20]	0.38 ± 0.01	1.03 ± 0.14	796 ± 44.2
NR-g-PMPBP [10]	0.35 ± 0.01	1.12 ± 0.18	812 ± 69.2
NR-g-PMPBP [15]	0.23 ± 0.01	0.54 ± 0.03	979 ± 0.00
NR-g-PMPBP [20]*	0.54 ± 0.01	1.51 ± 0.13	700 ± 10.3

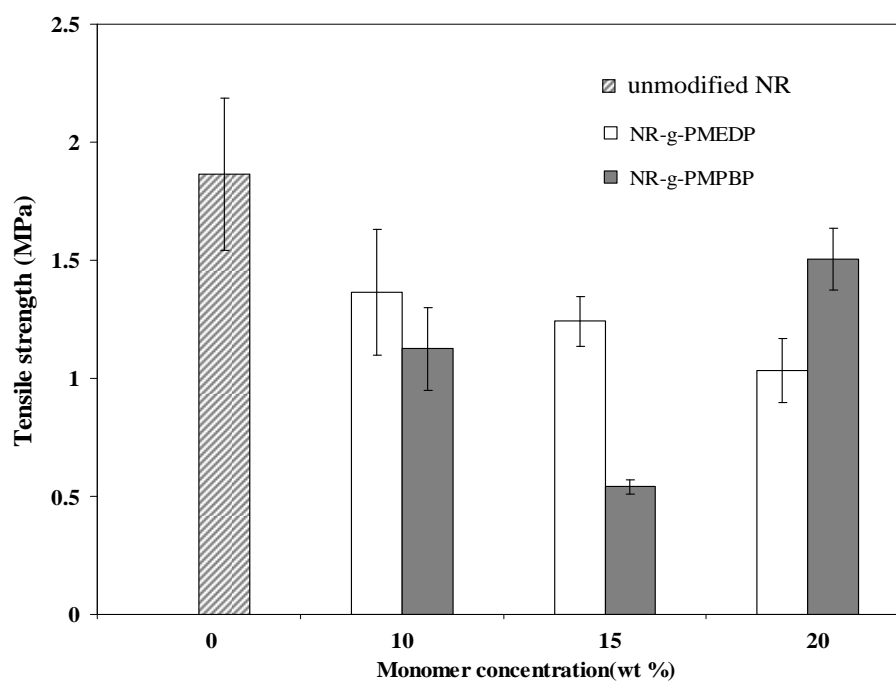
The values presented here are based on 4 specimens

\*reaction was carried out at room temperature (26-28 °C)

Figure 4.24 showed the comparative study of ungrafted NR, PMEDP grafted NR, and PMPBP grafted NR prepared from the initial monomer contents of 10, 15, and 20 wt%. Young's modulus results indicated the relative stiffness of the material. In addition, tensile strength was an important characteristic of polymeric materials because it indicated the limit of final stress in most application. As expected, the unmodified NR possessed the highest tensile strength because the NR crystallinity occurred upon stretching. As the initial monomer contents were increased, the modulus at 300% elongation slightly increased, whereas tensile strength at break decreased as compared to that of unmodified NR. The elongation at break of both grafted NR was not significantly different when compared with the unmodified NR. From the results, the monomer concentrations was insufficient to affect the mechanical properties of NR.

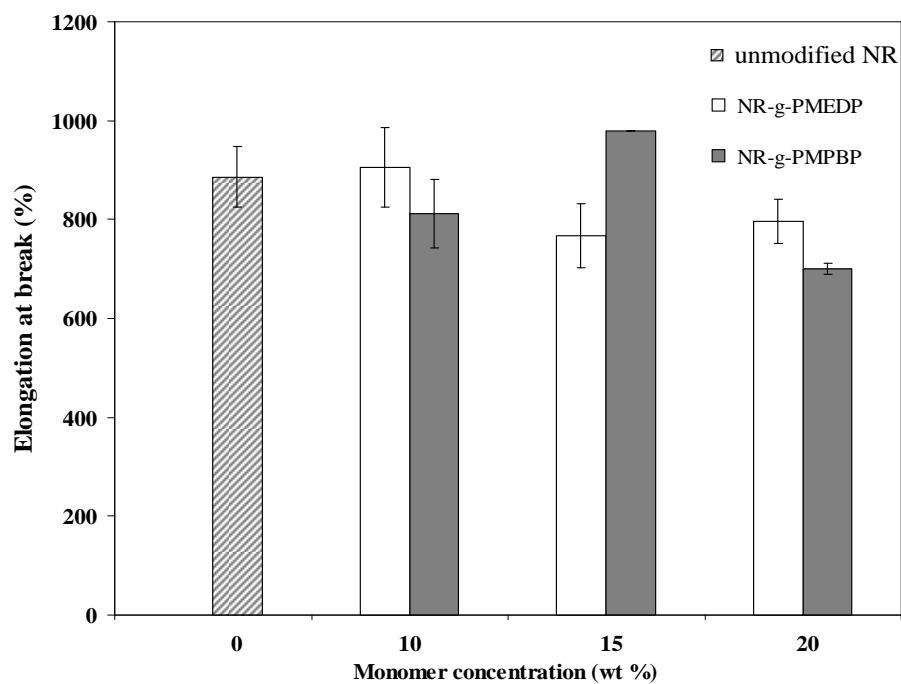


(a) 300% modulus



(b) Tensile strength at break

**Figure 4.24** Mechanical properties of grafted NR thin films: (a) 300% modulus, (b) tensile strength at break, and (c) elongation at break, with increasing the initial monomer concentration of ▨ unmodified NR, □ MEDP, and ■ MPBP. The presented values were averaged from 4 specimens (n=4) cut from the same rubber films. (continued on the next page)



(c) Elongation at break

**Figure 4.254** Mechanical properties of GNR thin films: (a) 300% modulus, (b) tensile strength at break, and (c) elongation at break, with increasing the initial monomer concentration of ▨ unmodified NR, □ MEDP, and ■ MPBP. The presented values were averaged from 4 specimens (n=4) cut from the same rubber films.

## CHAPTER V

### CONCLUSION AND SUGGESTIONS

#### 5.1 Conclusions

This investigation reported the synthetic procedure of two new reactive phosphorus based flame-retardant compounds, namely, 2-methacryloyloxyethyl diphenyl phosphate (MEDP) and 2-methacryloyloxyethyl phenyl benzenephosphonate (MPBP). Subsequently each compound was grafted onto NR latex *via* seeded emulsion polymerization by using cumene hydroperoxide (CHPO) and tetraethylenepentamine (TEPA) as redox initiator system.

Graft copolymers of natural rubber with poly(2-methacryloyloxyethyl diphenyl phosphate) (NR-*g*-PMEDP) and poly(2-methacryloyloxyethyl phenyl benzenephosphonate) (NR-*g*-PMPBP), were successfully prepared as confirmed by FT-IR and <sup>1</sup>H NMR techniques. The weight of both grafted copolymers increased with increasing monomer concentrations. However, the amount of grafted copolymers was less than the amount of initial monomer used because incomplete conversion and free homopolymer was observed.

The influential factors affecting grafting properties of copolymers were studied. It was found that an increase in the reaction temperature afforded high grafting efficiency and a decreased amount of homopolymer. However, high reaction temperatures in the range of 60 to 70°C led to the precipitation of latexes at high monomer concentration. Furthermore, the percentage of grafting efficiency and percentage of grafted NR were not significantly different with an increasing concentration of monomer in the grafting reaction, while the conversion decreased to 50%. An increase in the amount of initiator concentration resulted an increase in percentage of grafted NR since higher grafting positions were available, whereas the crosslinking of NR was observed resulting in the decrease in the grafting efficiency. TEM micrographs confirmed the success in the grafting onto natural rubber particles since shell layers of graft copolymers were observed around the NR core particles in a

core-shell formation.

Thermal properties of both grafted NR films were analyzed using TGA and DSC. The TGA results showed that the decrease in the main decomposition temperature and the increase in percent remaining of carbonaceous char residue at 700°C related directly to the amount of phosphorus content on NR. The results of DSC curves, the glass transition temperature ( $T_g$ ) of uncrosslinked NR was found at -64.2°C, whereas the  $T_g$  of PMEDP and PMPBP were found at 17.0 and 2.5°C, respectively. The  $T_g$  of both NR-*g*-PMEDP and NR-*g*-PMPBP were observed as a single transition temperature at -64°C corresponding to the  $T_g$  of rubber chains.

The LOI values of grafted NR products increased with increasing monomer concentrations. In addition, the rate of burning decreased in both grafted copolymers. Furthermore, grafted copolymers of PMEDP and PMPBP exhibited much improved flame retardancy with char formation on the burnt surface of NR. It was also found that the grafted polymers influenced the tensile properties of NR. The 300% modulus and tensile strength were not significantly different with increasing the monomer contents as compared with that of unmodified NR.

## 5.2 Suggestion for future works

A more overview of studies that need to be undertaken and directions that could be further explored are in the following aspects:

- Investigation of other possible techniques which also modify NR through chemical bonding such as photopolymerization in latex medium or solution medium.
- Comparison of efficiency of chemically modified flame retarding NR *via* graft copolymerization and that of modification of flame-retarding properties of NR through conventional method with organophosphorus compounds as additives.
- Investigation of the physical properties of grafted NR vulcanized compounds.
- Increasing the amount of phosphorus moiety in organophosphorus compounds to increase in the flame-retardant properties of NR.

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## **APPENDICES**

## APPENDIX A

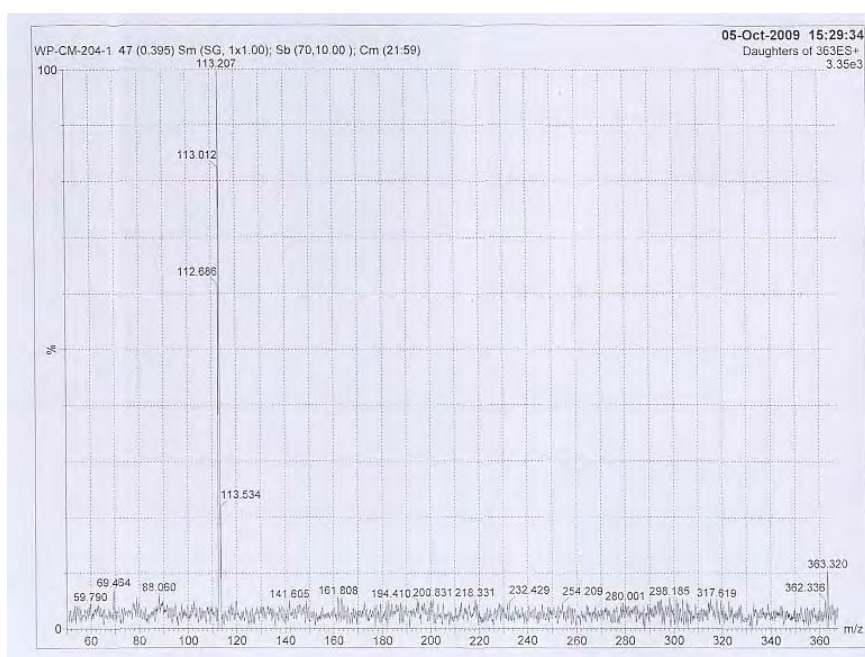


Figure A.1 MS (ESI) spectrum of MEDP.

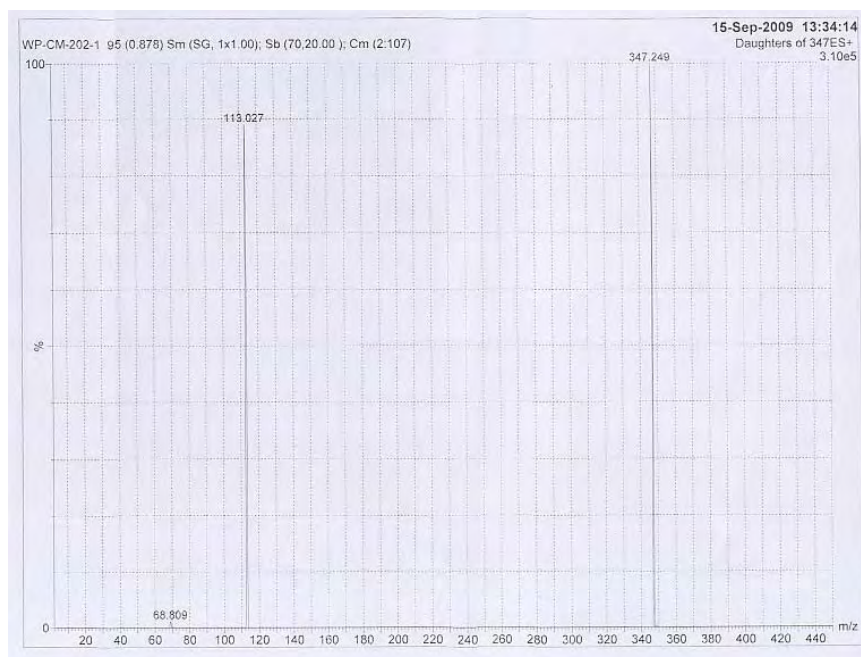


Figure A.2 MS (ESI) spectrum of MPBP.

## APPENDIX B

- B.1** The 17<sup>th</sup> Science Forum, Faculty of Science, Chulalongkorn University, Bangkok, Thailand.
- B.2** The 2<sup>nd</sup> Polymer Graduated Conference 2009, Chulalongkorn University, Bangkok, Thailand. Best Oral Presentation Award in Symposium: Polymer Chemistry
- B.3** The 11<sup>th</sup> International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC) 2009, Kyoto University, Kyoto, Japan.
- B.4** The Functionalized and Sensing Materials (FUSEM) Conference 2009, Faculty of Engineering, Silpakorn University, Thailand.
- B.5** Joint Conferences the 12<sup>th</sup> International Seminar on Elastomers 2010 (ISE 2010), 2<sup>nd</sup> Thailand-Japan Rubber Symposium, Holiday Inn Resort Regent Beach, Cha-am, Thailand. Best Poster Award



# การประชุมวิชาการ

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## Preparation of flame-retardant natural rubber by grafting with phosphorus-containing monomers

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Natural rubber (NR) is commonly used in many industries due to its excellent mechanical properties. However, it has a high flammability causing limits to its usage for highly demanding applications. One of the efficient ways to reduce flammability of NR is to graft flame retardant compound(s) into the NR backbone. The aim of this research was to synthesize the two phosphorus-containing monomers, methacryloyloxyethyl diphenyl phosphate (MEDP) and methacryloyloxyethyl phenyl benzene phosphonate (MPBP). Subsequently, these two phosphorus-containing monomers were grafted onto NR latex particles via emulsion polymerization by using cumene hydroperoxide/ tetraethylcncpentamine (CHP/TEPA) as a redox initiator system. Proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) nuclear magnetic resonance (NMR) spectroscopy as well as Fourier Transform Infrared (FT-IR) spectroscopy were used to confirm the monomer structures. The optimal grafting conditions for each monomer was investigated. The morphology, thermal stability, and flammability of the grafted NRs were studied by transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and limiting oxygen index (LOI) test.

**Keywords:** Natural rubber, flame retardant, graft copolymerization

## Modeling analysis of growth rate enhancement in selective area growth of c-GaN under MOVPE via a vapor-phase diffusion model

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In this work, we study the growth feature of cubic-phase GaN (c-GaN) stripes deposited between dielectric masks aligned to [110] on GaAs (001) substrates. The cross-sectional areas of these selectively grown c-GaN layers were investigated by scanning electron microscopy. The epitaxial layers were found to be thicker adjacent to the mask. The perturbations in the thickness and/or growth feature of c-GaN grown around a given mask [110]-stripe pattern significantly depended on the mask fill factor (ratio of the open width to the pattern period). No effect of the growth temperature on the growth features of the c-GaN stripes was observed. The growth rate enhancement at the edges was analyzed and lateral movement of the precursor from the masked regions to the windows areas was found to take place in the gas above the wafer surface. The vapor-phase diffusion model, based on Laplace's equation, was selected to simulate the thickness and/or growth feature caused by selective area growth. The effect of the mask fill factor on growth rate enhancement profiles were generated and compared with the experimental data obtained from surface profilometry. This growth rate enhancement was also interpreted in terms of the vapor-phase diffusion length of the precursor on both masks and window areas.

**Keywords:** Vapor-phase model, selective area growth, GaN, growth rate

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**Chulalongkorn University**

**May 21-22, 2009**

**Faculty of Science**

**Chulalongkorn University**



## Modification of Natural Rubber by Grafting with Methacryloyloxyethyl Phenyl Benzenephosphonate

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### Abstract

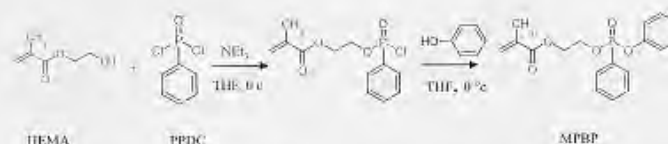
Methacryloyloxyethyl phenyl benzenephosphonate (MPBP) was successfully synthesized. Subsequently, MPBP was grafted onto NR latex particles to improve thermal stability and flame retardant. Emulsion polymerization in which cumene hydroperoxide/tetraethylenepentamine (CHP/TEPA) was used as a redox initiator system was carried out. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy and Fourier Transform Infrared (FT-IR) spectroscopy were used to confirm the monomer structure. The reaction temperature of graft copolymerization at 60 °C and 70 °C gave the grafting efficiency of up to 80%. TGA results revealed that the thermal stability of grafted NR increased with increasing the concentration of the monomer.

**Keywords:** Natural rubber, Graft copolymerization

### 1. Introduction

Natural rubber (NR) known as 98-100% *cis*-1,4-polyisoprene is commonly used in many industries because of its high elasticity and good mechanical properties. However, high flammability and low thermal stability limit the usage in highly demanding applications such as aerotires, power cables, etc. [1]. In recent years, phosphorus-based flame retardants are among the best group of compounds used to reduce flammability of polymers. Upon ignition and burning the surface of polymers will be protected by char layers caused by the degradation of phosphorus compounds which can reduce flame spread. In addition, these compounds generate less toxic gases while burning. The incorporation

of phosphorus compounds into the polymer backbone through chemical bonding cause low migration of reactive species and less influence on physical properties of polymers [2]. In 2006, Wang *et al.* synthesized 2-methacryloyloxyethyl phenyl phosphate (MEPP) for copolymerization of MEPP/MMA. It was found that the burning of copolymers can be inhibited by the polymer with as less as 1.17% of phosphorus content [3]. Graft copolymerization is one of the efficient ways to improve flame retardancy of NR by reacting through latex medium [4]. Graft copolymerization of hydrophilic (DMAEMA, DMAEA) [5] and hydrophobic (MMA) [6] monomers onto NR latexes was monitored by using various types of redox initiator systems. It was found that cumene



**Scheme 1.** Outline of the synthesis of MPBP.

hydroperoxide (CHP) /tetraethylenepentamine (TEPA) gave the highest grafting efficiency and lowest homopolymers.

This research aims to prepare flame retardant NR by grafting with methacryloyloxyethyl phenyl benzenephosphonate (MPBP) via emulsion polymerization by using CHP/TEPA as a redox initiator system. Optimal grafting conditions were investigated such as reaction temperature, monomer and initiator concentrations. The thermal stability of the grafted NRs was studied by thermogravimetric analysis (TGA).

## 2. Experimental

### 2.1 Synthesis of MPBP

Phenylphosphonic dichloride (PPDC), triethylamine (TEA), and dry tetrahydrofuran (THF) were placed in a 1000 mL round bottom flask with mechanical stirring under an inert atmosphere and cooled down in an ice bath. 2-Hydroxyethyl methacrylate (HEMA) in dry THF was added dropwise. After addition of HEMA solution, the mixture was stirred for 2 h. Phenol was added afterwards and the reaction kept at 0°C for 4 h. The reaction was stirred at room temperature overnight. After the reaction was complete, the triethylamine hydrochloride salt was filtered off. The filtrate was placed in a rotary evaporator to remove THF and unreacted starting materials. Finally, the crude mixture was

purified by flash silica gel chromatography (eluent: hexanes/ethyl acetate, 3:2 v/v). The product was obtained as a light yellowish liquid in 40% yield.

### 2.2 Preparation of grafted NR latexes (NRL)

NRL (60% dry rubber content, DRC) was diluted by 0.7% ammonia to 30% DRC. Grafting reaction was carried out in a 500 mL round bottom flask under a N<sub>2</sub> atmosphere. KOH, sodium dodecyl sulfate (SDS), oleic acid, and MPBP, were added, respectively and the solution was stirred for 15 min. The latex was stirred at room temperature for 30 min to absorb the monomer on latex particle. Next, the latex was heated to 40–70°C. CHP (initiator) was added, and the mixture was stirred for 15 min. TEPA (amine activator) was then added and the mixture was allowed to stir for an additional 1 h.

### 2.3 Characterizations

#### 2.3.1 Determination of grafting properties

The weight of free homopolymers, ungrafted NR, and grafted NR were determined after a solvent Soxhlet extraction method. The ungrafted NR was extracted by light petroleum ether for 24 h. The free homopolymers was extracted by acetone for 24 h. Grafting efficiency is defined as the weight of graft copolymers divided by total weight of polymer formed. The percentage of homopolymers, ungrafted NR, and grafted NR were calculated by eq. (1)

$$\% \text{ Grafted NR} = \left( \frac{b}{a+b+c} \right) \times 100 \quad (1)$$

where *a*, *b*, *c* are the weights of the ungrafted NR, grafted NR, and free homopolymers, respectively. The conversion was determined by the percentage increase in the rubber weight using eq. (2).

$$\text{Conversion (\%)} = \frac{\text{Total weight of polymer formed} \times 100}{\text{Weight of monomer charged}} \quad (2)$$

### 2.3.2 Fourier transform Infrared spectroscopy (FT-IR)

Functional group of grafted NR was characterized by FT-IR spectrometer (Perkin Elmer: spectrum RX-1) with 64 scans at the resolution of 4  $\text{cm}^{-1}$ . The sample was dissolved in dichloromethane and cast on a NaCl cell.

### 2.3.3 Thermal stability

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo, TGA/SDTA 851<sup>o</sup>. Approximately 10 mg of the sample was placed into an aluminum oxide crucible at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under a  $\text{N}_2$  atmosphere and the sample was scanned from 25–700  $^{\circ}\text{C}$ .

## 3. Results and discussion

### 3.1 Synthesis and characterization of MPBP

The phosphorus-containing monomer, MPBP, was synthesized via a 2-step reaction in dry THF and TEA (acid acceptor). In the first step, PPDC was reacted with HEMA. The next step, phenol was added to the mixture to get MPBP as shown in Scheme 1. MPBP was characterized by  $^1\text{H}$  NMR. The signals of methylene protons were observed at 5.5 and 6.1 ppm. The signal of methyl, ethylene, and phenyl protons were found at 1.9, 4.3–4.4, and 7–8 ppm, (Figure 1) respectively. In addition, the structure of MPBP was also confirmed by FT-IR analysis.

The spectrum showed the C=O stretching of ester groups at 1730  $\text{cm}^{-1}$ , the P=O stretching at 1267  $\text{cm}^{-1}$ , and the P-O-C (aromatic) at 1172 and 980  $\text{cm}^{-1}$  indicating that the monomer can be successfully synthesized.

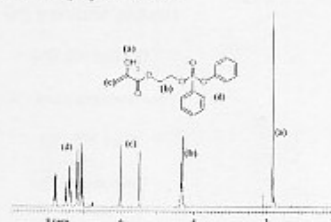


Figure 1.  $^1\text{H}$  NMR spectrum of MPBP.

### 3.2 Characterization of grafted NR

#### 3.2.1 FT-IR analysis

The spectra of NR, polyMPBP, and NR-g-polyMPBP samples are shown in Figure 2. The transmission peaks of the aliphatic C-H stretching at 2970  $\text{cm}^{-1}$  and C=C bending at 837  $\text{cm}^{-1}$  indicated the characteristic peaks of NR (a). The peaks of NR-g-polyMPBP show not only the characteristic peaks of NR but also a new transmission peaks of carbonyl group (C=O) and P=O stretching of MPBP at 1730  $\text{cm}^{-1}$  and 1265  $\text{cm}^{-1}$ . The presence of these peaks confirmed the grafting of polyMPBP onto the NR backbone.

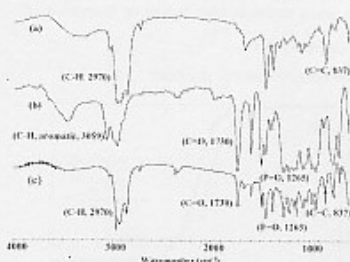


Figure 2. The FT-IR spectra of (a) NR, (b) polyMPBP, (c) NR-g-polyMPBP.

### 3.3 Grafting condition (Effect of reaction temperature)

**Table 1.** The effect of reaction temperature (NR: MPBP, 90:10 %wt, CHPO 0.5 phr)

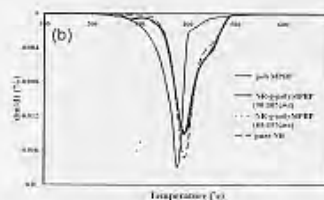
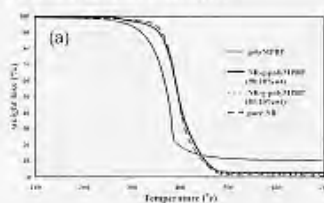
Reaction properties	Temperature (°C)			
	40	50	60	70
Grafting efficiency (%)	75.1	72.4	82.8	85.8
Grafted NR (%)	81.4	77.9	80.2	72.1
Free homopolymer (%)	3.4	3.8	2.3	1.8
Free NR (%)	15.2	18.3	17.6	27.6
Conversion (%)	82.9	83.0	79.8	76.8

**Table 2.** Thermal behavior and char residue of copolymers

Type of copolymer	T <sub>1</sub> (°C)		T <sub>2</sub> (°C)		Char residue (%)
	Range	Peak	Range	Peak	
polyMPBP	-	-	220-400	381	10.1
NR-g-polyMPBP (90:10%wt)	260-300	281	320-480	395	3.5
NR-g-polyMPBP (85:15%wt)	260-300	286	320-480	400	3.0
pure NR	-	-	320-480	395	1.5

In general, the decomposition rate of an initiator depends on reaction temperature. We investigated the effect of reaction temperature at 40-70°C (Table 1). The grafting efficiency was obtained in up to 80% at 60-70 °C because of high concentration of cumyl oxyl radicals at high temperature and great graft site on NR particles which tends to cause low degree of formation of free homopolymers.

### 3.4 Thermogravimetric analysis



**Figure 3.** (a) TG and (b) DTG curves of copolymers.

As evident from Table 2 and Figure 3, TGA thermograms of polyMPBP showed single step degradation at temperature range 220-400 °C and the percentage of char residues was about 10%. The thermograms of both grafted NRs showed two-step degradation at temperature range of 260-300 °C and 320-480 °C. Char residue of NR at both concentrations were determined to be about

3.0-3.5% (Figure 3a). From the DTG curves (figure 3b), the decomposition temperature of polyMPBP, NR-*g*-polyMPBP (90:10%wt), and NR-*g*-polyMPBP (85:15%wt) were 381, 395, and 400 °C, respectively. The results indicated that grafted NR exhibited greater thermal stability than that of pure NR (395 °C).

#### 4. Conclusions

<sup>1</sup>H NMR and FT-IR analyses confirmed that the methacryloyloxyethyl phenyl benzenephosphonate (MPBP) was successfully synthesized and grafted onto NR. The presence of polyMPBP was confirmed by FT-IR. It was found high grafting efficiency was obtained at high reaction temperature. TGA analysis revealed that an increasing in the monomer concentration resulted in an increase of thermal stability of NR from 395 to 400 °C.

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## สมาคมโพลีเมอร์ (ประเทศไทย)

ขอขอบเกียรติบัตรฉบับนี้ไว้เพื่อแสดงมา

### นายกิตติคุณ กกกสิณ

ได้รับรางวัลการนำเสนอผลงานดีเด่น ประเภทบรรยาย  
ในการประชุมวิชาการบัณฑิตศึกษาสาขาโพลีเมอร์แห่งประเทศไทย ครั้งที่ ๒  
ระหว่างวันที่ ๒๑ - ๒๒ พฤษภาคม พุทธศักราช ๒๕๕๒

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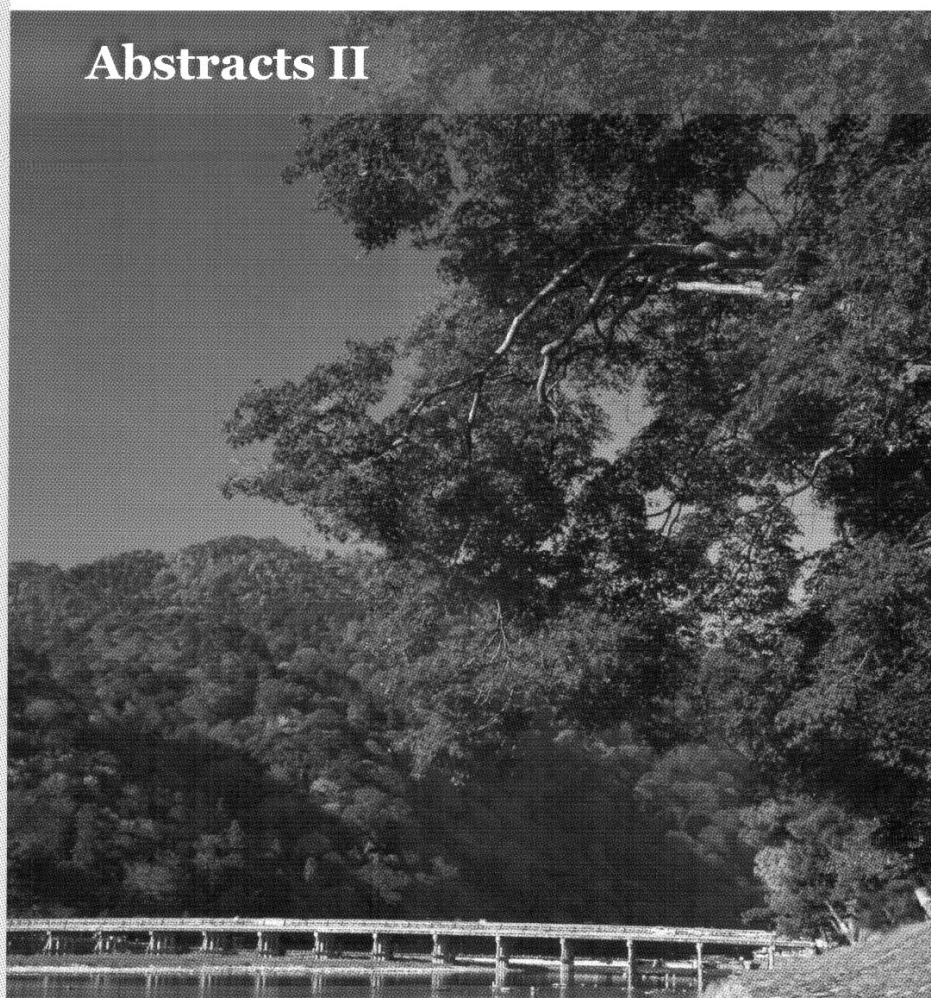




# ***IKCOC-11***

**The Eleventh International Kyoto Conference  
on New Aspects of Organic Chemistry**

## **Abstracts II**



**NOVEMBER 9-13, 2009  
Rihga Royal Hotel Kyoto, Japan**

**Sponsored by The Kinki Chemical Society, Japan**

## PC-085

**An Efficient Method for the Incorporation of a Positron-Emitting  $^{11}\text{C}$  Radionuclide into Various Heteroaromatic Frameworks by Pd(0)-Mediated Rapid Coupling of Methyl Iodide with Hetero-Arylstannanes**

Masaaki Suzuki,\*<sup>1</sup> Kengo Sumi,<sup>2</sup> Hiroko Koyama,<sup>2</sup> Siqin,<sup>2</sup> Takamitsu Hosoya,<sup>2</sup> Misato Takashima-Hirano,<sup>1</sup> and Hisashi Doi<sup>1</sup>

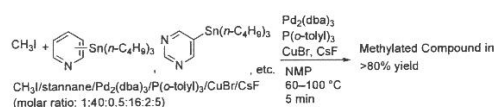
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In order to synthesize PET<sup>1</sup> tracers, we have developed the rapid cross-coupling of methyl iodide with excess amounts of aryltributylstannanes.<sup>2</sup> However, as indicated by us and others, the reaction conditions for such a rapid C-methylation using the stannane seem to be not optimized yet, particularly for heteroaromatic frameworks such as thiophene and furan as well as pyridine type structures with basic nitrogen(s) in the core structure. Here, we elaborated an efficient protocol for the Pd(0)-mediated rapid trapping of methyl iodide by heteroaromatic compounds described above. The utility of the method was demonstrated by the synthesis of 2- and 3- $^{11}\text{C}$ ]picolines.

Reference and notes: [1] PET = positron emission tomography. [2] Suzuki, M.; Doi, H.; Hosoya, T.; Långstöm, B.; Watanabe, Y. *Trends Anal. Chem.* **2004**, *23*, 595–607.

[3]  $^{11}\text{C}$ :  $T_{1/2}$  = 20.3 min.



## PC-086

**Graft Copolymers of Polyphosphate and Polyphosphonate onto Natural Rubber Latexes**

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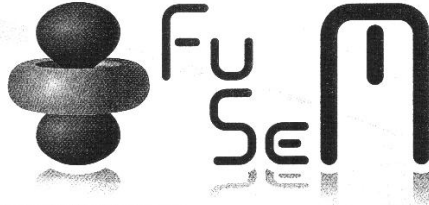
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Graft copolymerization is one of the efficient ways to modify natural rubber (NR) through chemical bonding. This research aims to synthesize phosphorus-containing monomers, methacryloyloxyethyl diphenyl phosphate and methacryloyloxyethyl phenyl benzenephosphonate which can increase flame retardancy of the material to which they are incorporated.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and FT-IR techniques were used to verify the monomer structures. Subsequently, each type of phosphorus-containing monomer was grafted onto NR latexes via emulsion polymerization by using CHP/TEPA as a redox initiator system. The reaction temperature from 50 to 70 °C afforded the grafting efficiency of up to 80%. TGA indicated a two step degradation of grafted NR. The percentage of char residue increased from 1.5% (pure NR) to 3.7% (grafted NR). Flame retardant properties of grafted NR were determined by LOI to be 20.5% and NR of 17.0%. The morphology was observed by TEM and will be described.

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**BOOK OF ABSTRACTS**

## Grafting of Phosphonate Monomer onto Natural Rubber Latexes via Emulsion Polymerization

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**Keywords:** natural rubber, organophosphorus, flame retardant

**Abstract.** The synthesis of phosphorus-containing monomer, methacryloyloxyethyl phenyl benzenephosphonate (MPBP), was carried out. The monomer was successfully prepared as evidenced by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and MS analyses. Subsequently, MPBP was grafted onto natural rubber particles *via* emulsion polymerization. It was found that as the reaction temperature increased from 40 to 70 °C, percent grafting efficiency increased from 72% to 85%. Transmission electron microscopy (TEM) of the grafted NR showed a semi core-shell morphology. Thermogravimetric analysis (TGA) of grafted NR indicated a two step degradation. Moreover, the grafted polyMPBP promoted the char residue of up to 3.5%. Flame tests revealed that the grafted NR exhibited an increased LOI value (20.5 %) over that of pure NR (17.0 %).

### Introduction

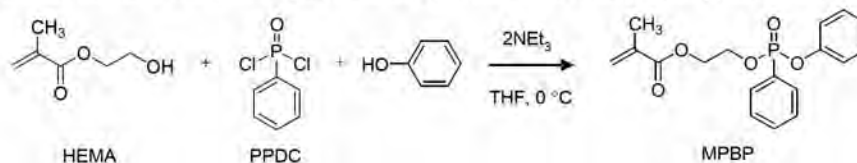
Natural rubber (NR) from *Hevea brasiliensis*, which is 98-100% *cis*-1,4-polyisoprene is commonly used in many industries. However, NR is highly flammable and consequently limits the usage in highly demanding applications such as aerotires, power cables, *etc.* [1]. For a few decades, phosphorus-based flame retardants have been shown to efficiently reduce flammability of polymers. Upon ignition and burning the surface of polymers will be protected by char layers caused by the degradation of phosphorus compounds which helps reduce flame spread. In addition, these compounds generate less toxic gases compared to halogenated counterparts [2]. Moreover, since only a small amount is required to give effective flame retardancy, for example, the burning of the MEPP/MMA copolymer can be inhibited by as low as 2.17%wt phosphorus content, less influence on physical properties of polymers was observed [3]. Since graft copolymerization is one of the techniques for modification of NR *via* latexes medium, this research, therefore, aims to prepare flame retardant NR by grafting with methacryloyloxyethyl phenyl benzenephosphonate (MPBP) *via* emulsion polymerization by using cumene hydroperoxide (CHP)/tetraethylenepentamine (TEPA) as a redox initiator system since it was found to give highest grafting efficiency and lowest homopolymers [4,5]. Optimal grafting conditions were investigated. The morphology, thermal properties, and flammability of the grafted NRs were studied by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and limiting oxygen index (LOI) test.

### Experimental

**Synthesis of MPBP.** MPBP was synthesized by a reaction of phenylphosphonic dichloride (PPDC), 2-hydroxyethyl methacrylate (HEMA), and phenol (Scheme 1). A 3 necked round bottom flask was charged with a solution of PPDC and triethylamine (TEA) in tetrahydrofuran (THF) and cooled in an ice bath. A solution of HEMA in THF was added dropwise. The mixture was stirred for 2 h. Phenol was added and the reaction was stirred at 0 °C for 4 h then at room temperature (rt) overnight. NH<sub>4</sub>Cl salt was then separated out. THF and unreacted starting materials were removed under reduced pressure. The crude mixture was purified by column chromatography



(hexanes/EtOAc, 7:3) to give a light yellowish liquid (60%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  7.0-8.0



**Scheme 1.** Synthesis of MPBP

(10H, Ar), 6.1 (1H, *trans*,  $\text{CH}_2=\text{C}$ ), 5.5 (1H, *cis*,  $\text{CH}_2=\text{C}$ ), 4.3-4.4 (4H,  $\text{CH}_2-\text{CH}_2-\text{O}-\text{P}$ ), 1.9 (3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  170 (C=O), 152, 138, 126, 120 (Ar-C), 125 ( $\text{CH}_2=\text{C}$ ), 64, 63 ( $\text{CH}_2-\text{CH}_2-\text{O}-\text{P}$ ), 18 ( $\text{CH}_3-\text{C}=\text{CH}_2$ ); FT-IR (NaCl,  $\text{cm}^{-1}$ ): 3063 (C-H str., Ar), 2957 and 2932 (C-H str., aliphatic), 1730 (C=O), 1635 (C=C), 1600 and 1493 (C=C, Ar), 1440 (P-Ph), 1265 (P=O), 1161 and 975 (P-O-C, Ar), 1070 and 928 (P-O-C, aliphatic); MS (FAB)  $m/z$  347.25 ( $\text{C}_{18}\text{H}_{19}\text{O}_5\text{P}+\text{H}$ ) $^+$ .

**Preparation of grafted NR latexes (GNRL).** NRL (60% dry rubber content, DRC) was diluted with 0.7% ammonia to 30% DRC. The latex was deoxygenated by bubbling nitrogen gas for 15 min. KOH, sodium dodecyl sulfate (SDS), oleic acid, and MPBP were added and the solution was stirred for 15 min. The latex was stirred at rt for 30 min to absorb the monomer on latex particle then heated to 40-70 °C. CHP (initiator) was added and the mixture was stirred for 15 min, TEPA (amine activator) was then added and the mixture was stirred for 1 h under nitrogen atmosphere.

**Determination of grafting properties.** The weight of free homopolymer, ungrafted NR, and GNR were determined after Soxhlet extraction. Ungrafted NR and free homopolymer were sequentially extracted off of GNR by petroleum ether and acetone for 24 h each. Grafting efficiency is shown in Eq. 1 and the percentage of homopolymers, free NR, and GNR were calculated by Eq. 2

$$\% \text{ Grafting efficiency} = \frac{\text{The weight of graft copolymers}}{\text{Total weight of polymer formed}} \times 100 \quad (1)$$

$$\% \text{ free homopolymer} = \left( \frac{b}{a+b+c} \right) \times 100 \quad (2)$$

where a, b, c are the weights of the free NR, free homopolymer, and GNR, respectively. The conversion was determined by the percentage increase in the rubber weight using Eq. (3)

$$\% \text{ Conversion} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad (3)$$

**Determination of thermal and flame retarding properties.** TGA was performed using a Mettler Toledo, TGA/SDTA 851 $^\circ$  at 20  $^\circ\text{C}/\text{min}$  heating rate under a  $\text{N}_2$  atmosphere and scanning from 25-700  $^\circ\text{C}$ . GNR samples were obtained after Soxhlet extraction. LOI test was determined by using an ASTM D2863 standard method with 52 $\times$ 140 $\times$ 1 mm film sheets.

## Results and discussion

**MPBP Characterization.** MPBP was successfully prepared as confirmed by  $^1\text{H}$  NMR. Important characteristic features of vinyl protons were observed at 5.5 (*cis*) and 6.1 (*trans*) ppm.  $^{13}\text{C}$  NMR also showed the C=O carbon at 170 ppm. In addition, FT-IR analysis further confirmed the presence of the C=O and P=O stretching absorptions of the monomer at 1730  $\text{cm}^{-1}$  and 1265  $\text{cm}^{-1}$ , respectively. The other detailed NMR and FT-IR data of MPBP are listed in the experimental.

**FT-IR analysis.** Spectra of NR, polyMPBP, and GNR (after Soxhlet extraction to remove all other ungrafted materials) are shown in Fig. 1(a)-(c). Peaks of aliphatic C-H stretching at  $2970\text{ cm}^{-1}$  and C=C bending at  $837\text{ cm}^{-1}$  are characteristic of NR. Not only does the GNR spectrum (Fig. 1(c)) show NR characteristics but it also exhibits new absorptions of C=O at  $1730$ , aromatic C=C at  $1600\text{ cm}^{-1}$ , and P=O of MPBP at  $1265\text{ cm}^{-1}$ . These absorptions, consistent with those representing functional groups found in MPBP and polyMPBP, therefore, confirm successful incorporation of phosphorus moiety onto the NR.

Table 1. Effect of temperature on the reaction (MPBP 10 wt%, CHP 0.5 phr)

Reaction properties	Reaction Temperature (°C)			
	40	50	60	70
Grafting efficiency (%)	75.1	72.4	82.8	85.2
Grafted NR (%)	81.4	77.9	80.2	78.9
Free NR (%)	15.2	18.3	17.6	19.2
Free polyMPBP (%)	3.4	3.8	2.3	1.9
Conversion (%)	82.9	83.0	79.8	76.8

Table 2. Effect of monomer concentration on the reaction (50 °C, CHP 0.5 phr)

Reaction properties	Monomer concentration (wt%)		
	10	15	20*
Grafting efficiency (%)	72.4	71.0	75.8
Grafted NR (%)	77.9	81.1	79.0
Free NR (%)	18.3	14.3	16.5
Free polyMPBP (%)	3.8	4.6	4.5
Conversion (%)	83.0	60.0	50.0

\*reactions were carried out at room temperature (28 °C)

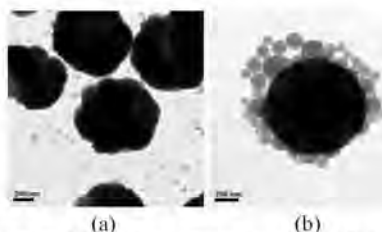


Figure 2. TEM micrographs of (a) NRL and (b) GNRL (MPBP 10 wt%) from emulsion reactor

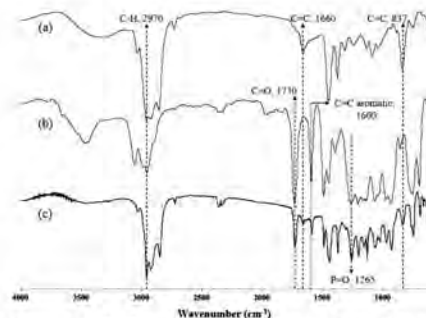


Figure 1. FT-IR spectra of (a) NR, (b) polyMPBP, (c) GNR (after Soxhlet extraction)

#### Grafting conditions and GNR morphology.

Graft copolymerizations were carried out at 40-70 °C (Table 1). A temperature increase afforded high grafting efficiency of up to 85% and a decreased amount of homopolymer. In general, initiator decomposition rate depends on reaction temperature. At high temperature, a high concentration of cumyloxy radicals was produced which generated more graft sites. This tends to cause low degree of homopolymer formation. Monomer concentration of 20%wt was achieved only at rt (Table 2) since attempts to increase concentration from 10 to 20 wt% at 50°C resulted in a precipitation of NR. At increased monomer concentration, grafting efficiency and homopolymer increased, while the conversion decreased to 50%. This can be ascribed to other possible side reactions such as combination, disproportionation, and chain transfers which can cause high termination rate. Since grafting of NR latexes was performed in the presence of CHP/TEPA, positions of grafting can be better controlled [4,5]. TEM micrographs of NRL particles and GNRL particles (10 wt% MPBP) stained with  $\text{OsO}_4$  were compared. Darker area represents a core region of NR as double bonds of NR were stained (Fig. 2(a)-(b)), whereas the lighter area in Fig. 2(b) represents shell layers of grafted polyMPBP. Another possible alternative is an accumulation of homopolymer phase. The grafted polyMPBP engulfed onto NR particles as a semi core-shell morphology. It was also found that the graft copolymer phase joined between the seed particles which exhibited the agglomeration of grafted NR latexes.

Table 3. Thermal behaviors and flame properties

Samples	T <sub>1</sub> (°C) Range	Mass loss in 1 <sup>st</sup> step (%)	T <sub>2</sub> (°C) Range	Mass loss in 2 <sup>nd</sup> step (%)	Char residue (%)	LOI (n=5)
polyMPBP	200-400	-	-	-	10.1	27.0
GNR [10]	220-320	3.9	320-480	93.1	3.0	18.5
GNR [15]	220-320	4.0	320-480	92.5	3.5	19.5
GNR [20]*	220-320	5.1	320-480	92.3	2.3	20.5
pure NR	-	-	320-480	-	1.5	17.0

\*Reaction temperature at room temperature (28 °C).

**Thermogravimetric Analyses** were carried out and results are in Table 3 and Fig. 3. PolyMPBP showed a single step degradation above 200 °C and at over 300 °C rapidly decomposed with char residue of 10%. TG curves of GNR are a two-step degradation with the first step at 220-320 °C as the degradation of functionalized copolymers [6]. The second step at 320-480 °C exhibited degradation of the NR domain. An increase in percent char residue from 1.5 (pure NR) to 3.5 (GNR) was observed. GNR showed the degradation of the phosphonate linkage to be at lower temperature than those of NR domain. This can easily generate low volatile phosphorus species as well as carbonaceous char which protects the NR surface and retards further burning [7].

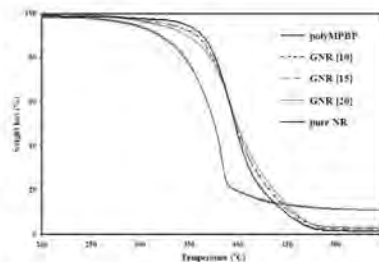


Figure 3. TG curves of materials

**Flame retarding properties.** Table 3 shows the LOI values of homopolymer (polyMPBP), pure NR and GNR films. GNR films were used as synthesized without Soxhlet extraction. PolyMPBP showed LOI of 27% which is in the range of self extinguishing material [8]. At monomer concentration of 20 wt% which translates into phosphorus content of 1.8 wt%, LOI value is increased to 20.5 which exhibited a significantly higher value than that of pure NR (17.0).

### Conclusions

P-containing monomer, MPBP, was successfully prepared and grafted onto NR particles with a semi core-shell morphology. GNR with 20%wt MPBP concentration exhibited higher amounts of char residue and higher LOI value than those of NR reflecting a much improved flame retardancy.

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Joint Conferences

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## Grafting of Phosphonate Monomer onto Natural Rubber Latexes *via* Emulsion Polymerization

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### Abstract

2-Methacryloyloxyethyl phenyl benzenephosphonate (MPBP) was successfully synthesized and grafted onto natural rubber latex using cumene hydroperoxide (CHPO)/tetraethylenepentamine (TEPA) as a redox initiator. The presence of grafted copolymers was confirmed by FT-IR. Transmission electron microscopy (TEM) micrograph showed the core shell particles of grafted NR. TGA thermograms showed two step degradations which indicated the decomposition of grafted polyphosphonate and NR domain at high temperature. Furthermore, percent char residue increased with increasing MPBP contents which enhanced the flame retardancy of NR as evidenced by increased LOI values.

### Introduction

Natural rubber (NR), *cis*-1,4-polyisoprene is commonly used in many industries because of good mechanical properties. However, NR is high flammability due to the presence of mostly hydrocarbon into the backbone chains. Consequently, the usage in highly demanding applications such as aerotires, power cables, *etc* is limited. For a few decades, phosphorus-based flame retardants have been shown to efficiently reduce flammability of polymers. Upon ignition and burning the surface of polymers will be protected by char layers caused by the degradation of

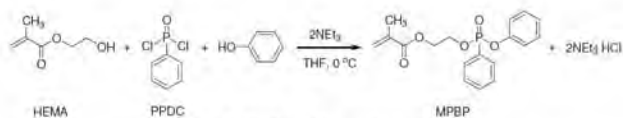
phosphorus compounds which can reduce flame spread. In addition, these compounds generate less toxic gases while burning compared to halogenated counterparts.<sup>1</sup> Since graft copolymerization is one of techniques for modification of NR *via* latexes medium, this research, therefore, aims to prepare flame retardant NR by grafting with MPBP *via* seeded emulsion polymerization.

### Experimental

MPBP was synthesized *via* 2-step condensation reaction between 2-hydroxyethyl methacrylate (HEMA), phenylphosphonic dichloride (PPDC), and phenol as shown in Scheme 1. Preparation of grafted NR was performed in latex medium that described in Satraphan *et al.*<sup>3</sup>

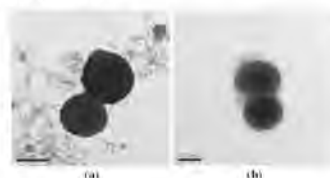
### Results and discussion

The success of synthesized MPBP was confirmed by <sup>1</sup>H and <sup>31</sup>P NMR. The signals of vinyl protons were observed at 5.5 (*cis*) and 6.0 (*trans*) ppm. The signal of methyl, ethylene, and aromatic protons were found at 1.9, 4.3-4.4, and 7.0-7.8 ppm, respectively. <sup>31</sup>P NMR exhibited only one signal at 17.0 ppm, corresponding to the phosphorus moiety into the molecule. FT-IR spectra of grafted NR showed the absorption peaks of carbonyl and phosphate groups at 1730 and 1265 cm<sup>-1</sup> indicating



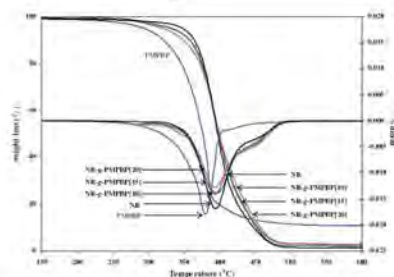
**Scheme 1.** Outline of the synthesis of MPBP

that confirmed the grafting of PMPBP onto the NR backbone. TEM micrographs are shown in Fig. 1. Darker area represents the NR particles (Fig. 1a), whereas the lighter shell layers (Fig. 1b) are the grafted PMPBP. MPBP grafted NR showed the core-shell morphology of grafted NR particles.



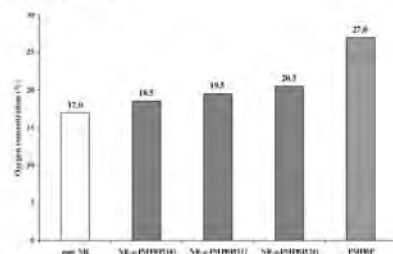
**Figure 1.** TEM micrographs of (a) NR particles and (b) NR-g-PMPBP particles stained with 1%  $\text{RuO}_4$  vapor.

As evident from thermogravimetric analysis (Fig. 2), PMPBP homopolymers showed rapid decomposition at over 300 °C with char residue of 10%. For NR-g-PMPBP, two-step degradation was observed. In the first step an onset temperature was found at 260 °C indicating the degradation of functionalized PMPBP.<sup>3</sup> The second degradation step started at 370 °C, caused by degradation of the NR domain.<sup>4</sup> Percentage char residues increased from 1.1 to 3.5% with increasing MPBP contents.



**Figure 2.** TG and DTG curves of grafted copolymer.

The data from LOI test are shown in Fig. 3. PMPBP showed LOI of 27% which is in the range of self extinguishing material. As the MPBP content increases to 20 wt%, the LOI values of grafted NR increased from 17.0% to 20.5% which exhibited a significantly higher value than that of pure NR and it also improved flame retardancy of NR.



**Figure 3.** LOI values of materials.

## Conclusion

$^1\text{H}$  NMR,  $^{31}\text{P}$  NMR and IR analyses confirmed that the MPBP was successfully synthesized and grafted onto NR. The grafted NR particles in latex were observed as core-shell morphology. The grafted copolymers of PMPBP and NR exhibited higher amounts of char residue and higher LOI values than those of neat NR.

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## VITAE

Mr. Kitikhun Kokklin was born on January 24<sup>th</sup>, 1986 in Nakhon Sawan, Thailand. He graduated with a Bachelor's degree of Science, majoring in Chemistry, Faculty of Science, Mahidol University in 2007. In the same year, he started as a Master Degree student with a major in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and finished his study in 2010.

### **Presentation in Conference:**

- |               |   |
|---------------|---|
| March 2009    | The 17 <sup>th</sup> Science Forum, Faculty of Science, Chulalongkorn University, Bangkok, Thailand.  |
| May 2009      | The 2 <sup>nd</sup> Polymer Graduated Conference 2009, Chulalongkorn University, Bangkok, Thailand. <u>Best Oral Presentation Award in Symposium: Polymer Chemistry</u>   |
| November 2009 | The 11 <sup>th</sup> International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC) 2009, Rihga Royal Hotel, Kyoto, Japan.  |
| December 2009 | The Functionalized and Sensing Materials (FUSEM) Conference 2009, Chulabhorn Convention Center, Bangkok, Thailand.  |
| March 2010    | Joint Conferences, The 12 <sup>th</sup> International Seminar on Elastomers 2010 (ISE 2010), 2 <sup>nd</sup> Thailand-Japan Rubber Symposium, Holiday Inn Resort Regent Beach, Cha-am, Thailand. <u>Best Poster Award</u> |