

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**DOPO-BASED PHOSPHORUS AND NITROGEN RICH
FLAME RETARDANT ADDITIVES**



M.Sc. THESIS

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Department of Chemistry

Chemistry Programme

AUGUST 2024

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**DOPO BAZLI FOSFOR VE AZOT ZENGİNİ
ALEV GECİKTİRİCİ KATKI MADDELERİ**

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To my family,



FOREWORD

I feel very lucky and proud to have been a member of the ITU family for 7 years. I have truly grown here, had the opportunity to meet wonderful people, created many memories, and learned so much. When I graduated from my bachelor degree, I never imagined that my master's years would be this enjoyable. Pursuing a master's degree is one of the best decisions I have made in my life.

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ABBREVIATIONS

^{13}C NMR	: Carbon nuclear magnetic resonance
^1H NMR	: Proton nuclear magnetic resonance
^{31}P NMR	: Phosphorus nuclear magnetic resonance
Ar	: Aromatic
CDCl_3	: Deuterated chloroform
CONE	: Cone Calorimeter
CuAAC	: Copper-Catalyzed Azide-Alkyne Cycloaddition
DOPO	: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
EP	: Epoxy Resin
FR	: Flame Retardant
LOI	: Limiting Oxygen Index
m	: Multiplet
ML	: Machine Learning
MOF	: Metal-Organic Framework
OPFR	: Organic Phosphorus-Containing Flame Retardant
s	: Singlet
t	: Triplet
TGA	: Thermogravimetric analysis



SYMBOLS

%	: Percentage
°C	: Degree Celcius
cm⁻¹	: Wavenumber
δ	: ppm
T₅	: 5% degradation temperature
T₁₀	: 10% degradation temperature
T_{max}	: Maximum degradation temperature



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DOPO-BASED PHOSPHORUS AND NITROGEN RICH FLAME RETARDANT ADDITIVES

SUMMARY

One of the most destructive natural events on Earth is fire. In addition to injuring and killing thousands of people, this disaster also poses a threat to other living things. Furthermore, fires cause serious material damage and economic loss. In this content, the synthesis of new and effective flame retardant materials is an important research area.

Simply described, flame retardants (FRs) are chemicals that are incorporated or added to materials to provide varying degrees of flammability protection. There exist numerous flame retardant additives and they can be classified different ways. Halogenated, organophosphorus-based, silicon-containing, nitrogen-containing, nanocomposites, and metal-containing compounds are examples of common flame retardants. One of the most preferred FR was the halogen-based ones. However, harmful products formed as a result of decomposition of halogen-containing FRs at high temperatures. Forming contaminants are persistent in the environment and have the capacity to migrate over long distances. Moreover, they cause significant biological harm and tend to accumulate organisms. Some of the halogen-based FRs have been forbidden due to environmental and biological concerns which resulted in development of halogen-free FRs in recent years. Phosphorus (P)-containing and nitrogen (N)-containing FRs are the most promising of all the halogen-free FRs. Their high efficiency, molecular diversity, multiple flame retardant processes and low toxicity have made them compatible to plenty different polymers including epoxy resins (EPs).

Flame retardant additives interrupt the combustion process via various mechanisms. The basic mechanisms are such as gas phase mechanism, endothermic mechanism and char-layer mechanism. Different additives retard the fire via different mechanisms. To increase the efficiency of flame retardancy, groups have several flame retardant effects can be used together. The most famous and influential example is the combination of phosphorus and nitrogen. During combustion, P and N can formed synergy to enhanced the flame retardancy. Organophosphorus structures generate phosphorus radicals during combustion which quench the flammable radicals. Moreover, they produce a protective char layer to block reaching oxygen to material. Nitrogen-containing structures dilute the density of combustible gasses by producing inert gases. Furthermore, as a result of the gases generated by the synergistic effect of P and N-containing structures, intumescent forms a barrier against oxygen which is called intumescent effect.

Flame retardant additives are utilized in numerous industries such as electrical and electronics, construction, transportation, textile and furniture industries. FRs are generally used to improve the non-flammability of polymers used in these areas. Among these polymers, epoxy resins are the most preferred ones due to excellent

properties such as high tensile strength and modulus, strong adhesion to substrates, excellent chemical, corrosion, moisture and solvent resistances, good dimensional stability, effective electrical properties, low shrinkage on cure, toughness, high versatility. Epoxy resins are used so extensively that it is critical to enhance their non-flammability. For this purpose, it is known that FRs containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and triazole units are particularly effective.

In this thesis, two different novel FR containing phosphorus and triazole units were synthesized by using activated alkynes and metal-free azide-alkyne click chemistry. The FRs were designed to have different N/P ratios. Nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopies were used to characterize the synthesized FRs. The FRs were mixed into an epoxy resin in different ratios, and the mixture was thermally cured. The thermal, mechanical, and the flame retardancy properties of the thermosets were characterized. The thermal degradation temperatures of the epoxy thermosets was reduced to lower temperatures but the char yields increased. The combination of the triazole and DOPO units led to superior flame retardancy. The limiting oxygen index (LOI) value of the thermosets was found to be as high as 47.4%. All the FR-containing thermosets were rated as V-0 according to the UL-94 test. Furthermore, owing to the presence of N and P, intumescent behavior was observed.

Finally, according to the WCA test, it was observed that the contact angle of thermosets with the surface decreases with increasing additive content. This result was attributed to the presence of polar triazole and phosphorus groups leading to more hydrophilic surfaces. As a result, it can be said that EPs containing FRs become much more polar, which is beneficial for composite and adhesive preparation.

DOPO BAZLI FOSFOR VE AZOT ZENGİNİ ALEV GECİKTİRİCİ KATKI MADDELERİ

ÖZET

Yangınlar yeryüzündeki en yıkıcı olaylardan biridir. Bu felaket binlerce insanın ölümüne ve yaralanmasına neden olmakla birlikte, diğer canlı türlerini de tehdit etmektedir. Ayrıca, yangınlar önemli maddi hasara ve ekonomik kayba yol açmaktadır. Farklı endüstriler, yangınla başa çıkmak için çeşitli pek çok yöntem geliştirmişlerdir. Bu yöntemlerin başında alev geciktirici katkı malzemeleri gelmektedir.

Basitçe tanımlamak gerekirse; alev geciktiriciler, çeşitli derecelerde yanmazlık sağlamak üzere malzemelerin yapısına kimyasal reaksiyon ile dahil edilen veya direkt olarak malzeme ile blend edilerek malzemeye entegre edilen kimyasal bileşiklerdir. Alev geciktiriciler için oldukça kapsamlı bir sınıflandırma yapılabilir. Temel olarak organik ve inorganik olarak sınıflandırılırlar da yapılarındaki gruplara göre pek çok alt başlıkta incelenirler. En çok kullanılan alev geciktiriciler ise halojen bazlı, organofosfor bileşik içerenler, silikon içerenler, nanokompozitler ve metal içeren bileşiklerdir. Ancak, halojen içeren alev geciktiriciler yüksek sıcaklıklara maruz bırakıldıklarında bozunarak dioksin oluşturur. Dioksin ise doğada kolayca kaybolmayan organik bir kirleticidir. Organizmalarda birikme eğilimi, uzun mesafeye göç kabiliyeti ve biyolojik toksisite gibi istenmeyen özelliklere sahiptir. Bu yüzden, halojen içermeyen alev geciktirici katkı maddeleri toksik bileşen içermeyen yapıları nedeniyle çevre ve biyolojik sistemlerin sağlığı açısından büyük bir ilgi görmektedir.

Alev geciktirici katkı maddeleri yanma sürecini çeşitli mekanizmalarla kesintiye uğratar. Temel mekanizmalar gaz fazı mekanizması, endotermik mekanizma ve kömür tabakası mekanizmasıdır. Farklı türdeki katkı maddeleri yanmayı farklı mekanizmalarla geciktirir.

Halojen bazlı alev geciktiricilere en mükemmel alternatif fosfor bazlı bileşiklerdir. Fosfor bileşikleri, kimyasal bileşenlerine ve aleve maruz kalma sırasında entegre edildikleri polimer ile etkileşime girme biçimlerine göre buhar fazında veya yoğun fazda alev geciktirici olarak işlev görme özelliğine sahiptir. Gaz fazında, yanma sırasında oluşan, $H\bullet$ ve $OH\bullet$ yanıcı radikalleri yanma döngüsünü tetikleyen ekzotermik reaksiyonlara katkı sağlar. Organofosfor bazlı alev geciktiricilerin yanma sırasında oluşturdukları $PO\bullet$, $PO_2\bullet$, $HPO_2\bullet$ gibi fosfor radikalleri serbest yanıcı radikalleri söndürerek yanıcı olmayan türler oluşturur. Böylece fosforlu alev geciktirici katkılar tarafından yanma döngüsü gaz fazında kesintiye uğratılır. Diğer yandan fosfor bakımından zengin organofosfor bileşikleri yanarak bir kömür tabakası oluşturur. Kömür tabakalarının varlığı yoğun fazda fiziksel bir bariyer etkisi sağlayarak yanma sürecini bozar. Oksijenin ve diğer yanıcıların malzemeye ulaşmasını geciktirir ya da engeller.

Yapılan araştırmalara göre, organofosfor içeren alev geciktirici bileşikler içerisinde en çok tercih edilen 9,10-dihidro-9-oksa-10-fosfafenantren-10-oksit (DOPO) türevi alev

geciktiricilerdir. DOPO ve türevlerinin araştırmacılar için cazibesi, yüksek termal kararlılık, hidroliz ve oksidasyona karşı direnç gibi dikkate değer özelliklerinin yanı sıra etkili alev geciktirici özellikleri nedeniyle giderek artmıştır. DOPO bileşiğinin yapısından kaynaklı olarak oluşturduğu P-H ve P-OH tautomerik denge, DOPO bazlı alev geciktiriciler katılma, moleküler yeniden düzenlenme ve Atherton-Todd reaksiyonları ile sentezlenebilirler.

Halojen içeren alev geciktirici katkı maddeleri yerine tercih edilen bir diğer katkı ise azot içeren katkılardır. Azot içeren alev geciktiriciler, az orandaki toksisite, uygun maliyet ve polimer matrislerle mükemmel uyumluluk gibi önemli avantajlar sunar. Azot içeren alev geciktirici kimyasallar yanma prosesi sırasında ayrışır ve gaz fazında, oksijen ve yanıcı gazların konsantrasyonunu seyrelten N_2 ve NH_3 gibi yanıcı olmayan gazlar oluşturur. Benzersiz beş üyeli N-heterosiklik yapıları, yüksek azot içeriği ve güçlü termal kararlılıkları sayesinde triazol halkaları, üstün alev geciktiriciliğe sahip moleküllerin sentezlenmesinde ve alev geciktirici özellikle epoksi reçine bazlı kompozitlerin oluşturulmasında büyük umut vaat etmektedir.

Alev geciktiriciliğin etkinliğini artırmak için, farklı alev geciktirici etkiye sahip gruplar birlikte kullanılabilir. En ünlü ve etkili örnek fosfor ve nitrojen kombinasyonudur. Yanma sırasında P ve N, alev geciktiriciliği arttırmak için sinerji oluşturabilir. Organofosfor yapılarının yanma sırasında yanıcı radikalleri söndüren fosfor radikalleri üretmesi, malzemeye oksijen ulaşmasını engellemek için koruyucu bir kömür tabakası üretmesi ile; azot içeren yapıların inert gazlar üreterek yanıcı gazların yoğunluğunu seyreltmesi birleşerek bir sinerji oluşturur. P ve N içeren bu yapıların sinerjik etkisiyle oluşan gazlar sonucunda intümesan oluşumu yani bir şişme gözlemlenir. Böylece yapının yüzeyinde koruyucu bir karbon bariyeri oluşmuş olur. Bu intümesan etki olarak adlandırılır.

Alev geciktirici katkı maddeleri çok sayıda endüstride kullanılmaktadır. Alev geciktiricilere elektrik ve elektronik, inşaat, ulaşım, tekstil ve mobilya endüstrileri gibi alanlarda sıkça rastlanmaktadır. Bu alanlarda pek çok polimerik malzeme kullanılır. Bunların başında epoksi reçineler gelmektedir. Yüksek gerilme mukavemeti, alt tabakalara güçlü yapışma, mükemmel kimyasal, korozyon, nem ve solvent dirençleri, iyi boyutsal kararlılık, etkili elektriksel özellikler, kurlenme sırasında düşük büzülme, incelik, yüksek çok yönlülük epoksi reçinelerin dikkat çekici özelliklerinden sadece birkaçıdır. Olağanüstü özellikleri nedeniyle epoksi reçineler biyoteknoloji, makine mühendisliği, çevre mühendisliği, ulaşım, inşaat, elektronik ve elektrik endüstrileri, tıbbi cihazlar, mikroelektronik ambalaj malzemeleri, yüzey kaplama, yapıştırıcılar, boyama ve çömlek malzemeleri, kompozitler, laminatlar, yarı iletken ve yalıtım malzemeleri için kapsülleyiciler, dökülebilir malzemeler, kalıplama malzemeleri ve enjeksiyon kalıplama malzemeleri dahil olmak üzere çeşitli alanlarda yaygın uygulamalar için tercih edilmektedirler. Bununla birlikte, geleneksel EP'nin sınırlayıcı oksijen indeksi (LOI) yaklaşık %19,8'dir ve bu da önemli bir yangın riskine işaret etmektedir. Bu yüzden epoksi reçinelerin yanmazlık özelliğini geliştirmek oldukça önem taşımaktadır.

Yapılan araştırmalar, penta-süstitüe fosfor ve $P=O$ bağına sahip organofosfor alev geciktirici katkıların, azot bakımından zengin konjuge sistemlerle birleştirilmesiyle elde edilen alev geciktirici sinerjizmini kanıtlamıştır. Bu kapsamda, DOPO ve triazol birimleri alev geciktirme sinerjisi için en etkili kombinasyon olarak ortaya çıkmıştır.

Bu tez kapsamında, fosfor ve triazol birimleri içeren iki farklı yeni alev geciktirici, aktive edilmiş alkinler ve metalsiz azid-alkin click kimyası kullanılarak sentezlenmiştir. Katkılar farklı N/P oranlarına sahip olacak şekilde tasarlanmıştır.

Öncelikle, DOPO ve paraformaldehitin ksilen içerisinde yüksek sıcaklıkta geri soğutucu altında reaksiyonu sonucunda elde edilen DOPO-OH molekülü propiyolik asit ile esterleştirilmiştir. Öte yandan oda sıcaklığında gerçekleşen azidoetanol ve DOPO arasındaki Atherton-Todd reaksiyonu sonucu DOPO-N₃ adı verilen azid fonksiyonlu bir organik bileşik sentezlenmiştir. Elde edilen alkin fonksiyonlu DOPO-propiyolat ile azid fonksiyonlu DOPO-N₃ bileşikleri arasında herhangi bir metal katalizörü kullanmadan sadece termal olarak bir click reaksiyonu gerçekleştirilmiştir. Bu click reaksiyonu sonucunda P2T1 adı verilen ilk katkı maddesi başarı ile sentezlenmiştir. P3T2 adı verilen ikinci alev geciktirici katkı maddesini sentezlemek için öncelikle oda sıcaklığında DOPO ve tris(hidroksimetil)etan arasındaki Atherton-Todd reaksiyon mekanizması ile elde edilen DOPO-diol adı verilen difonksiyonel bileşik propiyolik asit ile esterleştirilerek difonksiyonlu bir alkin bileşiği elde edilmiştir. DOPO-dipropiyolat adı verilen bu molekül ile azid fonksiyonlu DOPO-N₃ bileşikleri arasında herhangi bir metal katalizörü kullanmadan sadece termal olarak bir click reaksiyonu gerçekleştirilmiştir. Bu click reaksiyonu sonucunda P3T2 adı verilen ikinci katkı maddesi de ilki ile benzer şekilde başarı ile sentezlenmiştir. Daha sonrasında sentezlenen iki katkı da farklı oranlarda DGEBA epoksi reçinesine DDM sertleştiricisi varlığında karıştırılmış ve karışım termal olarak kürlenmiştir. Termosetlerin termal, mekanik ve alev geciktiricilik özellikleri karakterize edilmiştir. Epoksi termosetlerin termal bozunma sıcaklıkları daha düşük sıcaklıklara düşürülmüş ancak kömür verimleri artmıştır. Triazol birimleri ve P kombinasyonu üstün alev geciktiriciliğe yol açmıştır. Termosetlerin maksimum sınırlayıcı oksijen indeksi (LOI) değeri %47,4 kadar yüksek bulunmuştur. Tüm alev geciktirici içeren termosetler UL-94 testine göre V-0 olarak derecelendirilmiştir. Ayrıca, N ve P'nin varlığı nedeniyle intümesan oluşumu gözlemlenmiştir. Son olarak, yapılan WCA testine göre termosetlerin yüzey ile yaptığı temas açısının, katkı oranı arttıkça düştüğü gözlemlenmiştir. Bu sonuç, daha hidrofilik yüzeylere yol açan polar triazol ve fosfor gruplarının varlığına bağlanmıştır. Sonuç olarak alev geciktirici katkı içeren termosetlerin çok daha polar hale geldiği ve bunun da kompozit ve yapıştırıcı tasarımı için faydalı olduğu söylenebilir.



1. INTRODUCTION

Epoxy resins (EPs) utilize in various industries such as adhesives, coatings, laminates, composites, and electronics due to their excellent thermal and mechanical properties which make them outstanding to numerous other thermoset materials [1-5]. Besides, the favoured properties of EPs like excellent solvent and chemical resistance, low shrinkage, low water absorption, high adhesion to various surfaces, and good dielectric characteristics stand out [4-6]. However, EPs are not sufficiently flame resistant despite their remarkable thermal properties. As a result, flame retardants (FRs) additives are required to give EPs fire resistance property.

One of the exciting research area is the synthesis and development of new FRs specifically designed for EPs. To that purpose, a number of FRs have been designed, and synthesized and incorporated into EPs formulations [7-12]. Previously, it has been accepted that halogen-based flame retardants, particularly brominated FRs, are very successful at enhancing the flame retardancy of EPs. However, there are several worries regarding the using of halogenated FRs because of the possible release of toxic smoke and the bioaccumulation of halogen [12]. That is why the goal is to design and synthesize molecules that can replace halogen-containing flame retardant chemicals. Among these compounds are organophosphorus-containing compounds [10-12].

Recent searches have focused on integrating machine learning (ML) techniques into the designing of flame retardants. In order to identify the optimal qualities of the FR for EPs, Chen et al. conducted a screening of more than 300 articles and using ML methods. The study concluded that compounds with the most sufficient flame retardant properties for epoxy resins contain a tri-substituted phosphorus structure such as $R_3P=O$, a conjugated system and nitrogen. This ML strategy proved that among the organophosphorus possibilities fitting the given parameters, derivatives of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) containing nitrogen emerged as the best option [13].

Piperazine, triazine-trione, triazine, imidazole, tetrazole, and triazole derivatives molecules are used to synthesized DOPO-derived compounds which are containing nitrogen elements. Especially containing triazole units, exhibit high nitrogen content, good thermal stability, high N₂ gas release upon combustion, and low smoke production within N-containing compounds. Due to these properties, triazole units provide an effective contribution to flame retardancy. Therefore, the synergistic effect that enhancing flame resistance can be utilized [14,15]. Among the studies conducted on this area, molecules that 4-amino-4H-1,2,4-triazole [14,16], 3-amino-1H-1,2,4-triazole [17, 18], 3,5-diamino-1,2,4-triazole (TDA) [19-21] are utilized to synthesized the units of phosphorus- and triazole-containing FRs. On the contrary, a triazole unit can also be formed by the cyclo-addition reaction between azide and alkyne, which is known as Huisgen addition and is considered as click chemistry. This method offers several benefits such as greater versatility, and presents novel synthetic possibilities. Because of the challenges of removing the copper metal catalyst (CuAAC) used in the traditional azide-alkyne click reaction, as an alternative approach involves conducting the same reaction at higher temperatures (80-120 °C) and longer reaction times (12-24 h) without the using of a catalyst [22]. Reactions between activated propiolates and azides, which occur with high efficiency, are insensitive to oxygen and moisture, and can be carried out in an open atmosphere [23]. According to a study by Wang and colleagues on this topic, they used thermal azide-alkyne click reaction to synthesize a phosphate compound with carboxylic acid end groups containing triazole units. They started by reacting phenylphosphonic dichloride with propargyl alcohol. They next used 4-azidomethyl benzoic acid to react with this bispropargyl phosphate. Then, the phosphate compound was utilized by the authors to create a Co-based metal-organic framework (MOF), which was then used as a flame retardant in EPs [24]. Our group has recently focused on broadening the range of activated alkynes' metal-free click reactions. By utilizing activated alkynes' metal-free click reactions, we have produced a number of polymers [25–36]. We also synthesized flame-retardant monomers for photocurable coatings using metal-free azide-alkyne click reactions [37-39].

In this thesis, two novel flame retardant additives were described which contain phosphonate, phosphinate and triazole units by using metal-free click reaction (Figure 1.1). Based on the estimates from the previously mentioned ML study, the unique FRs were created [13]. Initially, mono- and di-functional, propiolated DOPO-derivatives

molecules and azide-functional DOPO were synthesized. Then, DOPO-derived compounds with activated alkyne group were reacted with azide-functionalized DOPO-derived compound. Thus, two novel flame retardant additives were obtained by utilizing metal-free click reaction. These additives were added into a commercial epoxy resin with various ratios. Next, their influence on the flame resistance, mechanical, thermal and thermomechanical characteristics of the epoxy resins were studied. Both the ratio of N/P and the triazole/P effects on the flammability of the EPs were evaluated more easily thanks to the alteration of the ratios of flame retardant additive compounds.

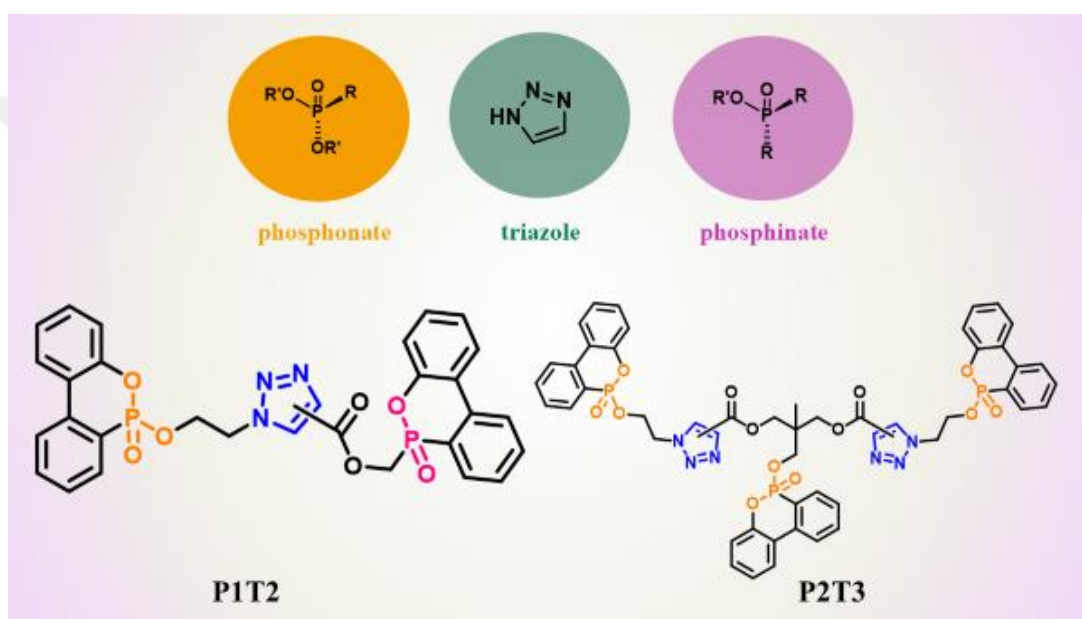


Figure 1.1 : Two novel flame retardant additives.



2. THEORITICAL PART

2.1 Definition of Flame Retardants

Fires emerge as one of the most devastating phenomenon in the Earth. This disaster not only causes death and injuries of thousand of people, but also threatens other living species. Besides, fires result in significant material damage and economic loss. According to National Fire Protection Association (NFPA), in 2022, fire departments in the United States responded to a fire incident approximately every 24 seconds, on average. Considering that fires occur so frequently and cause fatalities and property losses, highlight the using of flame retardant additives in several areas [37, 40 , 41].

Although being a challenging phenomenon to control, diverse methods have been developed by different industries to deal with fire. The important outcomes of all of this commitment and labor are sprinkler systems, non-water fire extentionction systems, smoke and fire detection devices, and thermal protection systems. Flame retardants are a part of the chemical, or more accurately polymer industry. Flame retardants (FR), to put it simply, are chemical substances that are added to or somehow integrated into materials to offer different levels of protection against flammability [41].

2.2 Classification of Flame Retardants

In general, FR compounds can be classified as organic or inorganic compounds. They can also be subdivided into many subdivisions depending on the groups they contain. According to KemI (1996), classification of FR chemical types shown in Figure 2.1 [42]. In addition, durability of FRs is another factor used to categorize them. In textile industry, flame retardants can be categorized as durable, non-durable, or semi-durable depending on their resistance to laundering. There is a differentiation between reactive and additive flame retardants. Reactive components are chemically incorporated into polymer molecules to obtain reactive FRs. On the other hand, additive FRs can be added to the polymer either before, during or, most commonly, after polymerization [42].

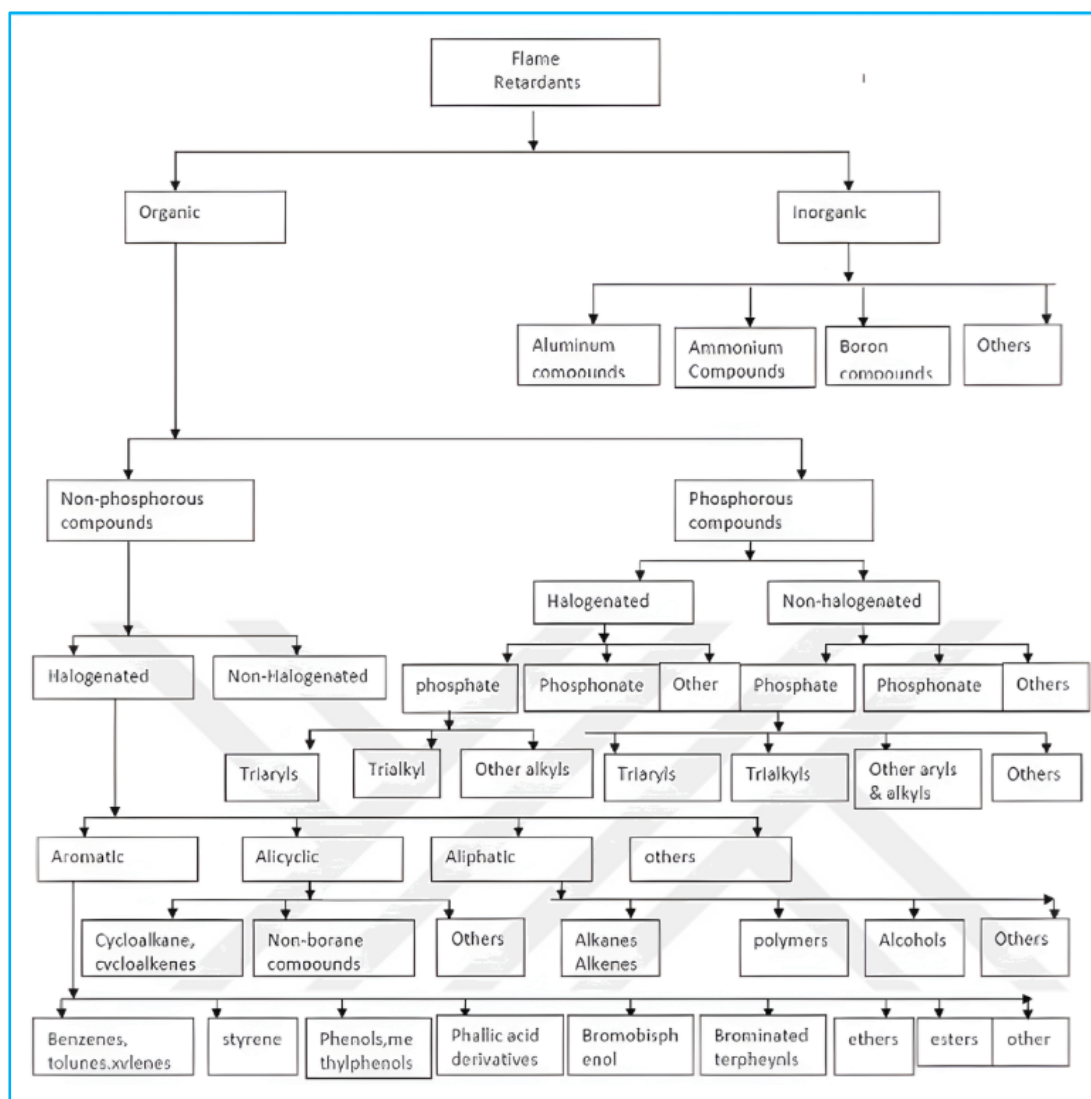


Figure 2.1 : Classification of FRs.

Common flame retardants are halogenated, organophosphorus, silicon-containing compounds, nanocomposites and metal containing compounds. Nevertheless, halogen-containing FRs have decomposed when exposed to high temperatures, resulting in the formation of dioxin. Dioxins are persistent organic pollutants, exhibit characteristics such as enduring presence in the environment, tendency to accumulate organisms, capability for long-range migration, and substantial biological toxicity. As a result, halogen-free flame retardants have attracted considerable attention in terms of environmental protection due to their composition devoid of toxic components [9].

2.2.1 Phosphorus-containing flame retardants

As implied by their name, phosphorus-based flame retardants incorporate phosphorus into their structure. The majority of phosphorus-based flame retardants are combined with phosphorus-oxygen bonds, with organic groups typically attached to these oxygen atoms. Common examples of P-based FRs are bisphenol A diphosphate, triphenylphosphate, resorcinol diphosphate, phosphinate salts, ammonium polyphosphate and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [43].

Phosphorus compounds possess the distinctive ability to function as flame retardants either in the vapor phase or in the condensed phase, determined by their chemical composition and how they interact with the polymer during fire exposure. [43]. Combustion of a polymeric material and the role of phosphorus-based flame retardants in flame retardancy mechanism are shown in Figure 2.2 [44]. Phosphorus radicals quench free radicals, thus interrupting combustion in the gas phase, while on the other hand, the presence of phosphorus-rich char layers provides a physical barrier effect in the condensed phase, disrupting the combustion process [11, 43].

In the condensed phase, numerous phosphorus-based flame retardants (P-FRs) facilitate the creation of char by promoting cyclization, cross-linking, and aromatization/graphitization through the dehydration of the polymeric structure. This carbonaceous char formation diminishes the emission of volatile substances, namely, fuel. Certain P-FRs also function via intumescence: a multi-cellular residue forms a protective layer that reduces the rate of heat transfer to the material underneath. Gas-phase effects, which often act in parallel with condensed-phase mechanisms, significantly enhance FR effects, reducing combustible gas density and combustion efficiency. During the combustion of hydrocarbon fuels, $H\bullet$ and $OH\bullet$ radicals are formed, which propagate the fuel combustion cycle most notably through the strongly exothermic reaction $OH\bullet + CO\bullet \rightarrow H\bullet + CO_2$. Plenty P-FRs decompose to generate active free radicals such as $PO\bullet$, $PO_2\bullet$, $HPO_2\bullet$, which react with $H\bullet$ and $OH\bullet$ radicals to reduce the concentration of combustible radicals and form stable compounds [11, 44].

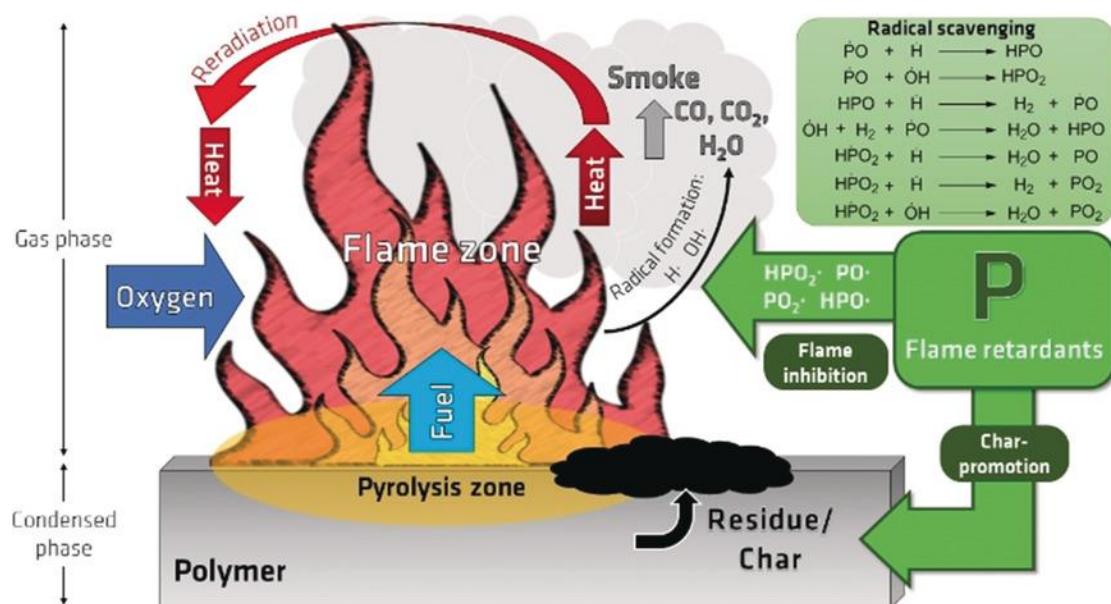


Figure 2.2 : The role of P-based flame retardants in flame retardancy mechanism.

2.2.1.1 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)

DOPO-based flame retardants serve as significant precursors in organophosphorus flame retardants. The appeal of DOPO and its derivatives to researchers has grown steadily due to their notable characteristics such as high thermal stability, resistance to hydrolysis and oxidation, as well as their effective flame retardant properties [9].

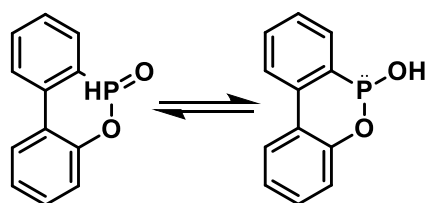


Figure 2.3 : The tautomeric equilibrium of DOPO.

Due to the presence of the tautomeric equilibrium of phosphorus in solution, which means the P-H or P-OH functionality in DOPO (Figure 2.3), DOPO-based flame retardants can be primarily synthesized through addition reactions, molecular rearrangement and the Atherton-Todd reaction. The chemical reaction here is determined by the electronic characterization of substituents around phosphorus, leading to changes in the pyrolysis route of DOPO. This allows for the emergence of different flame retardant effects. The hydrogen atom in the P-H bond is eventually substituted by other atoms or groups, resulting in the creation of P-C, P-O, and P-N bonds, among other structures, to produce the DOPO-FRs. The suggested pathway of degradation and the flame retardant properties of DOPO are shown in Figure 2.4 [45].

The predominant flame retardant effect of DOPO is the radical quenching effect in the gas phase. However, it has an insufficient effect in the condensed phase. Especially in epoxy resins, it is necessary to increase the phosphorus content for DOPO-based additives to show high flame retardant properties [45]. In addition, a research by Lyon and coworkers at the Federal Aviation Administration, proved that materials with aliphatic groups have a higher heat release capacity when compared to aromatic group bearing ones [43]. Based on the findings of the study, the existence of aromatic groups in the structure of DOPO makes it a favorable choice in designing flame retardant additives.

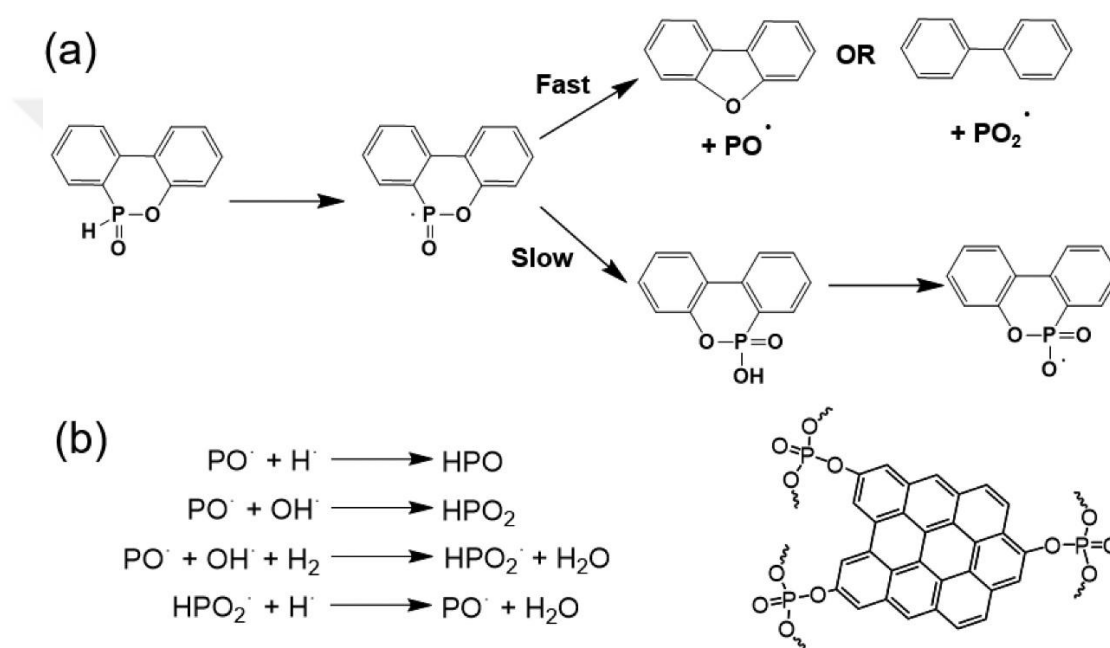


Figure 2.4 : The suggested pathway of degradation and flame retardant properties of DOPO.

2.2.2 Nitrogen-containing flame retardants

As the name describes, nitrogen-based flame retardants incorporate nitrogen element into their structure. Nitrogen-based compounds have applications in flame retardant systems [42]. Flame retardants containing nitrogen offer notable benefits including reduced toxicity, cost-effectiveness, and excellent compatibility with polymer matrices. Nitrogen-containing flame retardant chemicals decomposed during combustion process and non-flammable gases such as N_2 and NH_3 occurs, which dilute the concentration of oxygen and combustible gases. [11]. Owing to their unique five-membered N-heterocyclic structure, high nitrogen content, and strong thermal

stability, triazole rings show great promise in synthesizing molecules with superior flame retardancy and creating flame-retardant EP-based composites [15].

2.2.3 Synergistic flame retardants and phosphorus-nitrogen (P-N) synergism

When some flame retardants are used individually, they might not offer an adequate level of flame-retardant effectiveness. However, when employed together, their flame retardant efficiency can be enhanced because of synergistic effects [11]. At present, there is growing attention on phosphorus/nitrogen synergistic flame retardants because of their remarkable flame retardant properties and thermal stability [9]. In addition, one of the most promising recognized synergistic systems for halogen-free flame retardants is the combination of phosphorus-nitrogen (P-N) compounds [44]. Regrettably, nitrogen-containing flame retardants are less effective when utilized independently due to the restricted quantity of nitrogen present [9]. Usually, the purpose of combining phosphorus with nitrogen is to improve the oxidative durability or char formation caused by the phosphorus flame retardant [43].

DOPO, among the numerous phosphorus-based flame retardants, is extensively utilized in epoxy (EP) formulations owing to its exceptional flame retardant properties and robust molecular design capabilities. According to several studies, the inclusion of nitrogen- or phosphorus-containing groups like phosphate, cyclotriphosphazene, triazine, tetrazole, maleimide, triazine-trione, and triazole can notably enhance the flame retardant and charring capabilities of DOPO derivatives. Triazole, characterized by its nitrogen-rich heterocyclic structure, is widely utilized in the formulation of flame retardant systems due to its high nitrogen content and stable molecular structure [17]. The findings of the study via ML modelling demonstrated the flame retardant synergism achieved by combining a P=O bond containing penta-substituted phosphorus with nitrogen-rich conjugated systems, and it identifies DOPO and triazole units as the most effective combination for this synergism [13].

2.2.4 Intumescent flame retardants

The name "intumescent" refers to the way these chemicals behave in a fire situation to reduce flame spread. In particular, they react to heat by rising to the surface and producing a protective layer of carbon foam (intumesce). They use their own structure or the polymer into which they are integrated as a carbon source and show their effects in the condensed phase. The intumescent effect basically consists of three components.

The first is a carbon source. The second component is an acid catalyst that causes it to form a thermally stable form of carbon. The final component is a gas generator that allows the carbon source to become carbon foam. These three components work together to make the intumescence material work for the intumescent effect. However, three components may not always be required to produce the intumescent effect. A single structure may exhibit the properties of all three components or a single chemical may exhibit both properties. Consequently, the composition and structure of intumescent flame retardancy can vary widely [43].

2.3 Principles and Mechanisms of Flame Retardants

The process of pyrolysis is defined as the thermal decomposition of a polymer into small fragments because of the high heat. The small fragments which are formed result of the pyrolysis process become more volatile with heat and mix with oxygen, triggering the combustion process [43]. The four basic steps of the combustion process are heating, thermal breakdown, ignition, and combustion, as seen in Figure 2.5 [11]. As a result of this combustion, more heat is released and spreads rapidly to the non-burning parts of the polymer. The pyrolysis process continues until the material is no longer in contact with oxygen [43]. In this context, principle of flame retardant additives is to inhibit the combustion cycle at specific points such as heating, decomposition, ignition, or spreading of flame in the burning process by using chemical and physical methods in the solid, liquid, or gas phase [42].

It is difficult to identify a single dominant mechanism because burning is a recognized to be a complex chemical and physical process in which several mechanical ideas act simultaneously. The flame zone, the char layer, the molten polymer, and the underlying polymer are some of the zones formed as a result of burning [46].

The flame retardant mechanism of flame retardant additives can basically be examined under 3 headings: Gas phase mechanism, endothermic mechanism and char-forming mechanism [43].

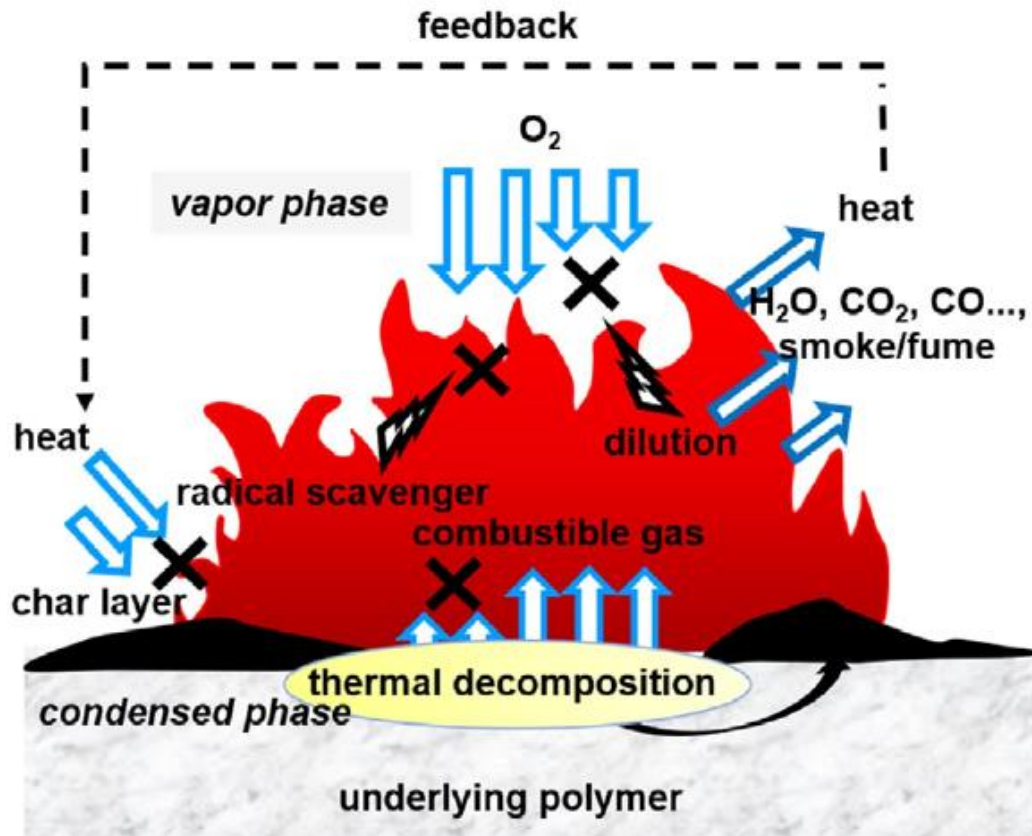


Figure 2.5 : The steps of combustion process.

2.3.1 Gas phase mechanism

Combustion and heat release occur within the flame zone when volatile species resulting from polymer decomposition mix with atmospheric oxygen. The gas phase is indicated the flame region, while the condensed phase is indicated the remaining regions. If a flame retardant disrupts the combustion process in the gas phase via a radical mechanism, it is called a gas phase mechanism [46]. The exothermic process is stopped due to the FRs, the system cools down and the triggering of combustible gases is reduced and eventually stopped completely. For instance, halogenated flame retardants formed free radicals, prevent hydroxide and hydrogen free radicals from reacting with oxygen and carbon monoxide. When the radicals are captured by the flame retardant additives, the chemical process of the flame is disrupted and combustion is inhibited [42, 46]. The reactions that occur in vapor phase basically as shown in Figure 2.6.

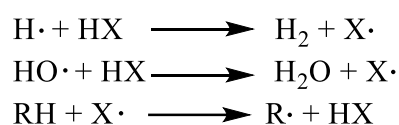


Figure 2.6 : Vapor phase reactions.

2.3.2 Endothermic mechanism

Through the decomposition of flame retardant additives in an endothermic reaction mechanism releases non-flammable gases such as H_2O , CO_2 that dilutes the density of flammable gases at the gas and condensed phase. In addition, it provides cooling of the environment. Low temperature dilute gases slows down the pyrolysis rate [42, 46]. Inorganic FRs such as $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ decompose endothermically and evaporate water, absorbing heat in the condensed phase and cooling the gas phase [44].

2.3.3 Char-layer mechanism

The flame retardant additive that is utilized burns out before the material and composes char layer which means non-pyrolyzed carbon layer. Char layer that is formed prevents the emission of fuel gasses and provide a thermal protection to the material [46].

2.4 Applications of Flame Retardant Additives

Flame retardant additives are utilized in numerous industries. Flame retardants are commonly encountered in areas such as electrical and electronics, construction, transportation, textile and furniture industries [41]. In general, in the electrical and electronic industry, a plastic product or component that is in close proximity to or in touch with a component that conducts electric current needs to have its flame resistance enhanced. Among the applications of flame retardants can be found in electric and electronics market, components and parts of ovens, microwaves, dishwashers, refrigerators, washing machines, and dryers, as well as in computer parts used in offices and homes such as screens, monitors, keyboards, fax machines, telephones, cable and wire coatings. In transportation industry, FRs are used in parts of automobiles and passenger seat, similarly, passenger compartments and aeroduct of public transport. In addition, they are preferred in floor coverings and furnishings in marine vessels and in air transportation, utilized in passenger seats and restroom stuffs. Other sector is building and construction. FR application include walls, windows, structural materials, roof and floor coverings [41]. Moreover, the significance of fire retardant monomers, polymers, or agents employed in various household items such as home textiles, furnitures, beddings, carpets, curtains, coatings, may be comprehended when taking into account the elevated rate of fatalities caused by house fires [37].

2.5 Flame Retardant Efficiency

2.5.1 Limiting oxygen index (LOI)

The limit oxygen index (LOI) is a technique used to determine a flammability of a polymer. It represents the lowest level of oxygen concentration needed for the sample to sustain combustion in a gas mixture of oxygen and nitrogen, indicated as the percentage of oxygen volume. A material having a high LOI value indicates that its flame retardancy properties are correspondingly advanced. This test technique is characterized by its simplicity, high precision, and consistent reproducibility. It has proven to be an efficient way of assessing the flame retardant properties of polymers [11].

2.5.2 Vertical and horizontal combustion

Vertical and horizontal combustion measurement is another technique used to determine a flammability of a polymer. The fundamental of measurement is holding one end of the material either vertically or horizontally, applying the gas flame to the free end of the material. At the end, combustion performance is eventually characterized by measuring the related parameters. The linear combustion rate is used to assess the horizontal combustion behavior, and the combustion range, molten droplets, residual flame and afterglow time are used to assess the vertical combustion behavior. There are four levels of combustion grading in the UL-94 vertical burning test: V-0, V-1, V-2, and 5-V. This test is commonly utilized to analyze the flammability of polymers and the behavior of molten droplets during combustion [11].

2.5.3 Cone calorimeter

Based on the concept of oxygen consumption, the cone calorimeter (CONE) is a technique to measure the ignition efficiency of polymers. Parameters such as ignition time (TTI), heat release rate (HRR), total heat release (THR), smoke production rate (SPR), total smoke production (TSP) obtained from this technique can be used to analyze the flame retardant and smoke production properties of polymers. This method has the advantage of properly obtaining the HRR, SPR, and efficient heat from combustion during the burning process, as well as simulating the genuine combustion of polymers [11].

2.6 Epoxy Resins

Epoxy resins are identified by the existence of epoxide groups before they undergo curing, and they can additionally feature aliphatic, aromatic, or heterocyclic arrangements within their molecular structure [8]. Since epoxy resin (EP) was first developed in the 1930s, notable advancements have been made, enhancing its ability to meet diverse needs in practical usage [9]. High tensile strength and modulus, strong adhesion to substrates, excellent chemical, corrosion, moisture and solvent resistances, good dimensional stability, effective electrical properties, low shrinkage on cure, toughness, high versatility are just a few of the remarkable characteristics of epoxy resins. Due to their exceptional properties, epoxy resins find widespread applications across various areas including biotechnology, mechanical engineering, environment engineering, transportation, construction, electronic and electrical industries, medical devices, microelectronics packaging materials, surface coating, adhesives, painting and potting materials, composites, laminates, encapsulants for semiconductor and insulating materials, castables, molding materials and injection molding materials [4,5,6,9,10,24]. Nevertheless, limiting oxygen index (LOI) of conventional EP is approximately 19.8% which indicating a significant fire risk. Substantial heat and harmful smoke is emitted during the ignition process which considerable threat to both lives and property. Additionally, the production of molten droplets during combustion can lead to rapid fire propagation, further limiting the practical use of epoxy resins [11]. As a result, it is crucial to alter epoxy resin (EP) to improve its flame retardant characteristics while preserving its other desirable properties [9]. Recently, numerous researchers have conducted extensive investigations into the flame-retardant properties, smoke suppression capabilities, and anti-dripping behavior of epoxy resins to fulfill the flame retardant specifications of epoxy resins for real-world applications [11]. Until today, multiplexed studies have been conducted on flame retardants for EPs. Incorporating flame retardants into EPs offers several benefits, including straightforward processing, cost-effectiveness, availability of raw materials, and a noticeable flame retardant impact among these approaches. Halogen-containing, organophosphorus based additives, intumescent effect agents, nanocomposites, metal and silicon-containing compounds are considered favourable flame retardants additives. However, the known harmful effects of halogen-based materials on living organisms and the environment restrict the use of halogen-based flame retardants.

Therefore, developing alternative additives to halogen-based flame retardants has become a favored topic among researchers [9]. Phosphorus-containing FRs are the most promising choices of all the halogen-free FRs. Their low toxicity, great efficiency, variety of flame-retardant mechanisms, and molecular diversity have made them suitable for numerous polymer matrices, including EPs [12].

Zhao and colleagues, synthesized a new polymeric intumescent flame retardant called poly(4,40-diamino diphenyl sulfone 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol (PEPA)-substituted phosphoramidate) (PSA). Synthesis route of PEPA and PSA is showed in Figure 2.7. [1]. The synthesized flame retardant additive and epoxy resin (DGEBA) are mixed until a homogeneous mixture is formed, after the curing agent, m-phenylene diamine (m-PDA), is added to the mixture. The mixture is cured initially at 80° C for two hours and then at 120° C for another two hours to form epoxy thermosets [1]. The relevant analyses proved that the synthesized PSA additive has high thermal stability, with a residual char content of 66.3 wt.% observed at 700 °C. The maximum LOI value of EP/PSA composites reached 32.0%, passing the UL-94 V-0 rating. Significant synergistic effects between PSA and ammonium polyphosphate (APP) were observed through CONE tests and TGA. As a result of this study, it can be said that an effective intumescent flame retardant polymeric additive has been synthesized for epoxy resins [1].

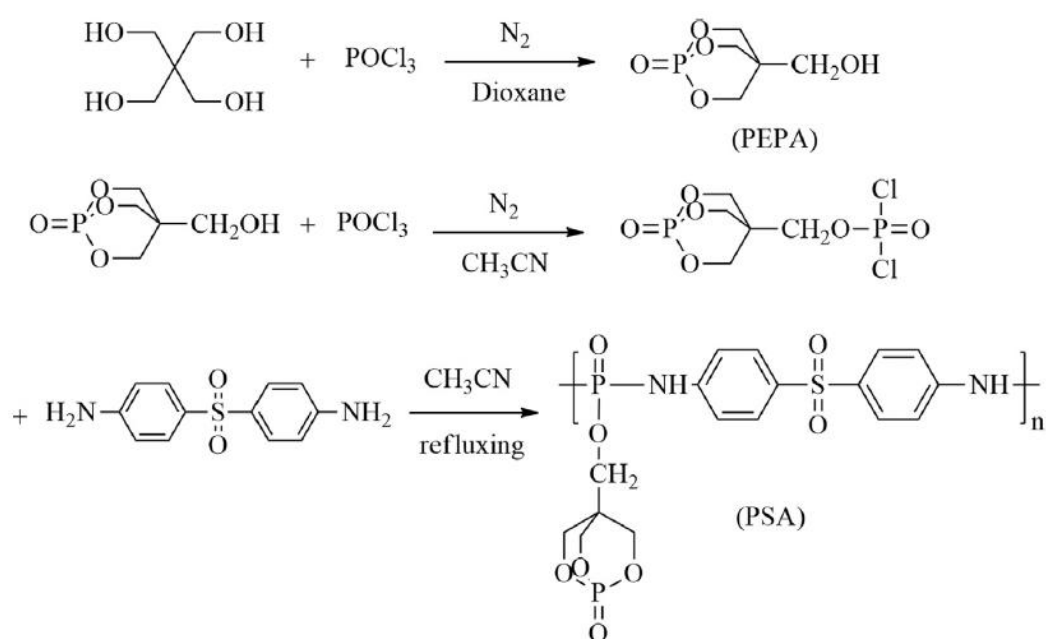


Figure 2.7 : Synthesis route of PEPA and PSA.

Qian and coworkers, synthesized containing both phosphaphenanthrene and triazine-trione groups flame retardant which is tri-(3-DOPO-2-hydroxypropan-1-yl)-1,3,5-triazine-2,4,6-trione (TGIC-DOPO) [2]. Diglycidyl ether of bisphenol-A (DGEBA) was used as the epoxy resin, and 4,4'-diamino-diphenyl methane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), and m-phenylenediamine (m-PDA) were used as curing agents. It has been observed that the TGIC-DOPO additive works best with the EP/DDM combination. The LOI value of thermosets that have been cured using DDM is 35.6% and UL-94 test result is V-0 rating. High LOI values result from the residues' formation of a cage-like char crown that inhibits the release of phenol and PO free radicals and blocks oxygen penetration. This effect is enhanced via TGIC-DOPO in EP/DDM, which traps more carbon components and releases concentrated PO and phenol radicals, effectively putting out the flame. The combination of free radical quenching and cage-hindering properties gives epoxy thermosets exceptional flame retardancy [2].

In another study, Wang and Cai, improved a novel flame retardant additive which is containing DOPO and triazole units. DOPO-based triazole molecule (DTA) was synthesized as shown in Figure 2.8 [14].

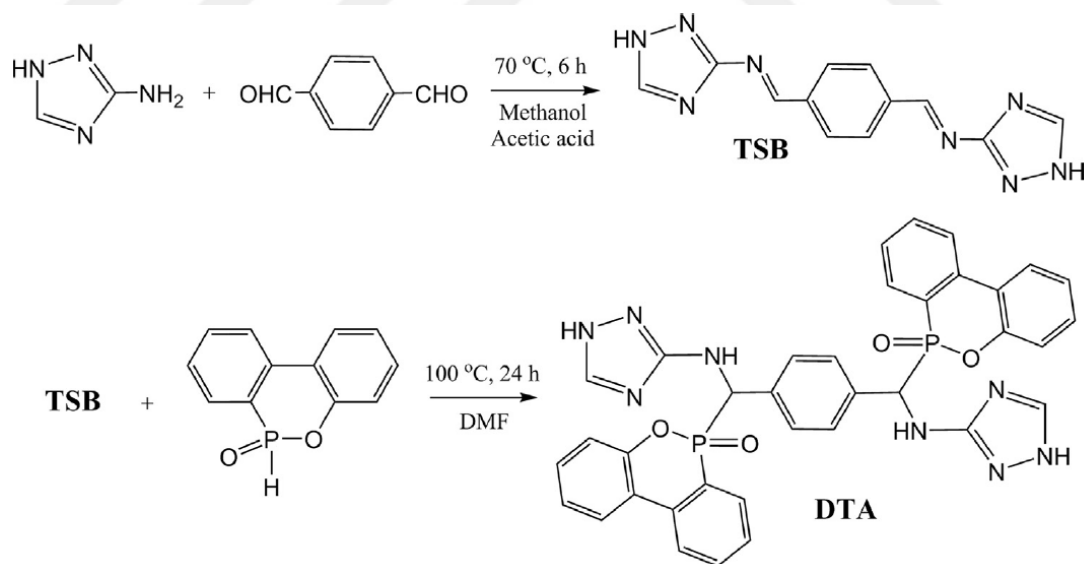


Figure 2.8 : Synthesis route of DTA.

DTA was added to epoxy resin as a co-curing agent to increase its flame retardancy. The synthesized DTA and epoxy resin (DGEBA) are mixed until a homogeneous mixture is formed at 140° C for two hours. Then, the curing agent DDM was added to blend when the temperature decreased to 90° C and stirring for 10 min. The mixture is

cured initially at 120° C for two hours and then at 160° C for another two hours in PTFE molds to form epoxy thermosets. In the UL-94 test, the thermoset modified with 4% DTA received a V-0 rating and a LOI value of 34.8%. During combustion, modified thermosets showed intumescent effect. The phosphorus-rich char layers with polyaromatic structures in the condensed phase, the quenching impact of radicals based on phosphorus, and the diluting effect of nonflammable gases in the gas phase were identified as the flame-retardant mechanism. As a result, DTA have a great flame retardancy due to its chemical structure containing triazole and DOPO groups [14].

In another investigation, two new phosphorus-nitrogen type flame retardants N-DOPO and PPDAT based on triazole were synthesized by Zhang and his group [15]. Phosphonic dichloride and 3,5-diamino-1,2,4-triazole (TDA) were used to synthesize polymeric flame retardant PPDAT, while using DOPO and TDA flame retardant N-DOPO was synthesized via Atherton-Todd reaction. Schemes of synthesis shown in Figure 2.9 and Figure 2.10 [15].

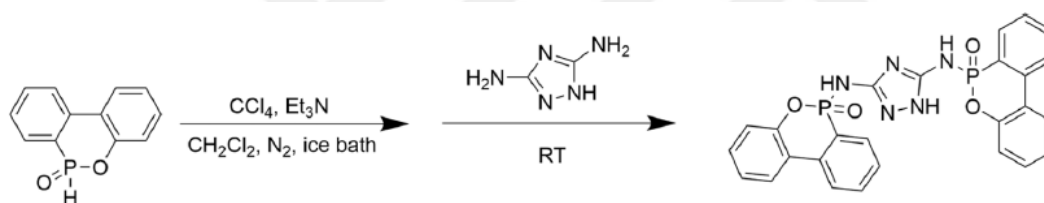


Figure 2.9 : Synthetic pathway of N-DOPO.

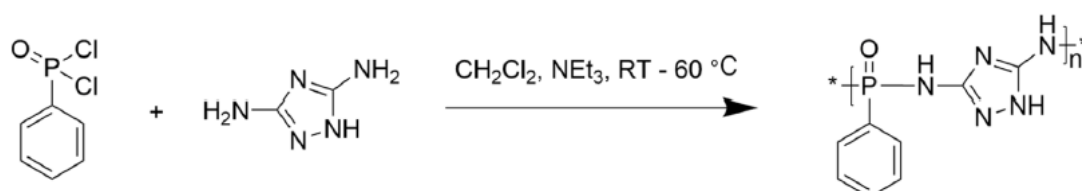


Figure 2.10 : Synthetic pathway of PPDAT.

Similar to previous studies, the synthesized additives were incorporated into epoxy resin (DGEBA) in varying amounts. DDM was used as the curing agent. The findings of flame retardant tests showed that V-0 rating in the UL-94 test and value of LOI 33.5% were obtained after adding 7.5 wt% N-DOPO. However, PPDAT is not effective as N-DOPO with value of LOI 30% and V-1 rating. It was found that EP/PPDAT composite could accelerate the production of dense continuous carbon layers, with an effective flame retardant effect in the condensed phase [15].

Sagdic and colleagues, novel P- and N-containing flame retardant monomers for photocurable coatings are synthesized via metal-free azide-alkyne click reactions [37]. The schematic representation of the formation of flame retardant thiol-ene photocured thermosets is shown in Figure 2.11 [37]. They synthesized azide-functionalized DOPO (DOPO-N₃) using the Atherton-Todd reaction, and then reacted with acetylene dicarboxylic acid diallyl ester (ACDAE) to obtain DOPO-triazole diallyl ester (DTDAE). Different amounts of diallyl phthalate (DAP) and DTDAE are stirred at 60° C for 10-15 minutes. 2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxide (TPO) is added to the prepared mixture. After cooling, pentaerythritoltetrakis(3-mercaptopropionate) (4SH) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) are added to the mixture. The mixtures are cured under UV irradiation in Teflon molds for 10 minutes. The gel content of the thermoset materials prepared using DTDAE was above 90%. Additionally, the thermal stability, char yield, and glass transition temperatures of these materials increased. As the content of DTDAE increased, LOI values of the cross-linked materials also increased, reaching maximum 27.8% and result of UL-94 test is V-0 rating [37].

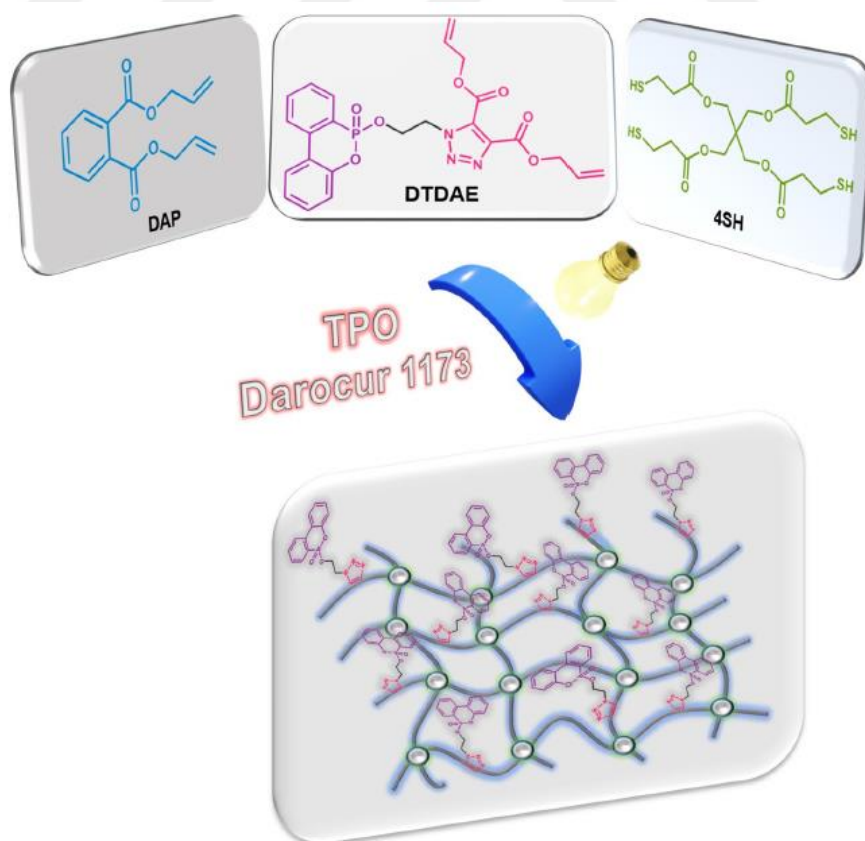


Figure 2.11 : The schematic representation of the formation of flame retardant thiol-ene photocured thermosets.

2.7 Specific Reactions Used in This Thesis

2.7.1 Atherton-Todd reaction mechanism

As previously mentioned, DOPO-based flame retardants can be primarily synthesized through addition reactions, molecular rearrangement and the Atherton-Todd reaction [45]. In 1945, Atherton and Todd reported the first report of this reaction. In the Atherton–Todd reaction, carbon tetrachloride is used in the presence of an organic base to convert a P–H bond into a P–Cl bond. The oxidation of the phosphorus atom, which renders it open to attack by nucleophiles such as nitrogen and oxygen, is the most important aspect of this reaction. It's a reaction that proceeds with high efficiency, resulting in a high yield of products. The precise Atherton–Todd reaction mechanism remains unclear although many research being done to understand it [47]. The proposed mechanism is as follows (Figure 2.12) [47].

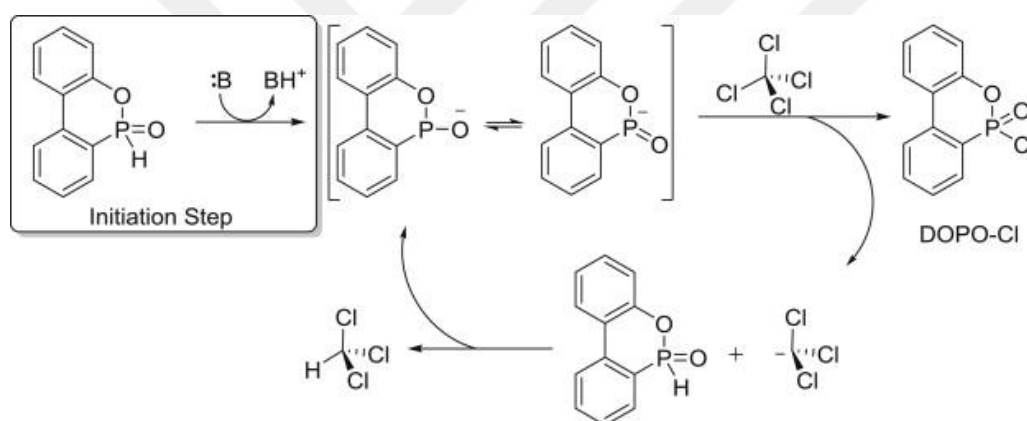


Figure 2.12 : Proposed reaction mechanism of Adherton-Todd mechanism.

2.7.2 Metal-free azide-alkyne click reaction

The term "click" chemistry was first used by Sharpless to describe highly efficient synthetic reactions that happened under mild synthetic conditions and were tolerant of different functional groups, even though Huisgen had found it in the 1950s. The click reaction happens at relatively low temperatures and with high transformation in almost any solvent, including aqueous solvent systems. This reaction's consistency and predictability make it incredibly useful for the high-yield synthesis of 1,2,3-triazoles. [48]. In addition, the azide-alkyne click reaction is a regioselective reaction. One of the most popular techniques to produce 1,2,3-triazoles is the copper-catalyzed azide-alkyne click reaction (CuAAC), which generates 1,4 substituted 1,2,3 triazole with relatively high selectivity under simple reaction conditions that are typically

performed at room temperature. In CuAAC, Cu(I) salts are typically utilized. Due to the toxicity of copper(I) species, silver(I) can be used as a catalyst as an alternative to the copper-catalyzed azide-alkyne click reaction. This reaction is also 1,4 isomer regioselective and occurs at room temperature. In contrast, the 1,5 substituted 1,2,3-triazoles have been synthesized with ruthenium-catalyzed azide-alkyne click chemistry [22].

However, catalysis is not necessary for the azide-alkyne click reaction to occur. Compared to reactions utilizing catalysis, metal-free click reactions occur over a longer period of time (12-24 h) and at a higher temperatures (80-120° C). Additionally, mixture of regioisomers which are 1,4 and 1,5 substituted 1,2,3 triazol rings are obtained. Being non-toxic due to absence of metal catalysis is an advantage of this process [22].

The scheme of alkyne-azide cycloaddition is shown in Figure 2.13 [49].

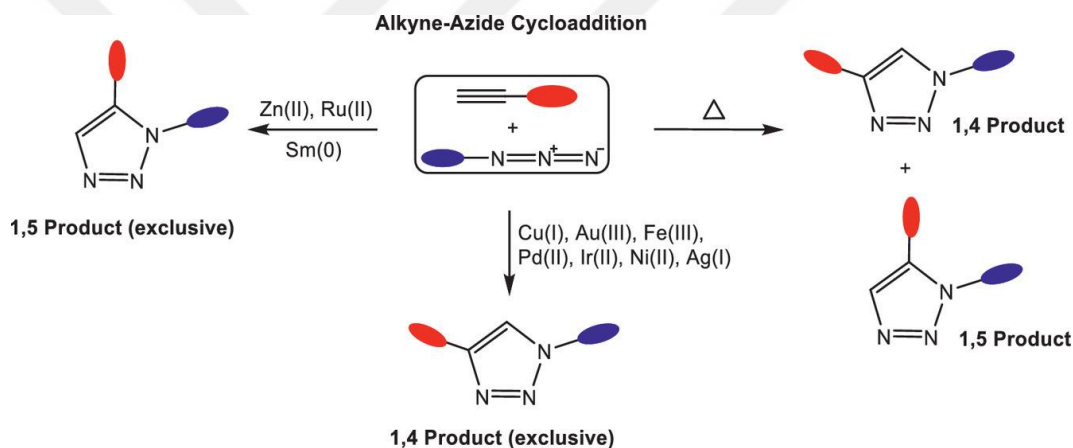


Figure 2.13 : Scheme of azide-alkyne cycloaddition.



3. EXPERIMENTAL PART

3.1 Materials

2-bromoethanol, sodium azide (NaN_3), acetone, xylene, paraformaldehyde, the epoxy resin, diglycidyl ether of bisphenol-A/F (DGEBA/F, commercial name: Der 351), 4,4-diamino diphenyl methane (DDM), tris(hydroxymethyl)ethane, dichloromethane (DCM), hexane, trimethylamine (Et_3N), carbon tetra chloride (CCl_4), chloroform (CHCl_3), sodium sulfate (Na_2SO_4), para-toluene sulfonic acid (PTSA), benzene, N,N-dimethylformamide (DMF), methanol, propiolic acid, 2-Methyltetrahydrofuran (2-MeTHF), and diethyl ether were purchased from Sigma Aldrich. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from TCI.

3.2 Instrumentation Methods

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using an Agilent VNMRs 500 instrument in CDCl_3 . FT-IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR instrument over the range of $4000\text{--}400\text{ cm}^{-1}$. Thermogravimetric analyses (TGA) of the photocured films were performed by using a PerkinElmer thermogravimetric analyzer (Pyris 1 TGA model). Samples were run from 30 to $750\text{ }^\circ\text{C}$ with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ under a nitrogen and air atmospheres. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere on the TA instruments Q1000 series DSC apparatus. Samples were heated from $0\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere, followed by cooling to $0\text{ }^\circ\text{C}$ with rate of $10\text{ }^\circ\text{C}/\text{min}$. Finally, samples were re-heated to $250\text{ }^\circ\text{C}$ with the same rate. At $0\text{ }^\circ\text{C}$ and $250\text{ }^\circ\text{C}$ the temperature was kept constant for 2 minutes.

3.3 Synthesis of Organic Compounds and Flame Retardant Additives

3.3.1 Synthesis of 2-azidoethan-1-ol (azidoethanol)

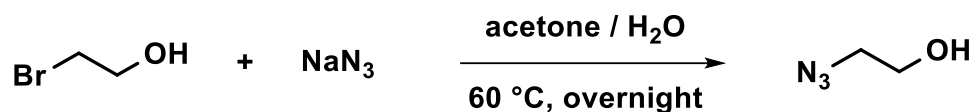


Figure 3.1 : Synthesis scheme of azidoethanol.

The synthesis scheme of azidoethanol is shown in Figure 3.1. To a 250 mL round bottom flask equipped with a magnetic stir bar was added 2-bromoethan-1-ol (14 mL, 197.18 mmol) and dissolved in 120 mL of acetone. NaN_3 (19.23 g, 295.76 mmol) was dissolved in a beaker with 70 mL of water and the solution was added to the flask. After that, flask allowed to stir in reflux system overnight at 60° C. Acetone was evaporated and the mixture extracted with 70 mL of DCM three times. The organic layers were dried over Na_2SO_4 , filtered, and evaporated to dryness to give 2-azidoethan-1-ol as a pale yellow liquid. Yield: 14.05, %81.83.

3.3.2 Synthesis of 6-(2-azidoethoxy)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO- N_3)

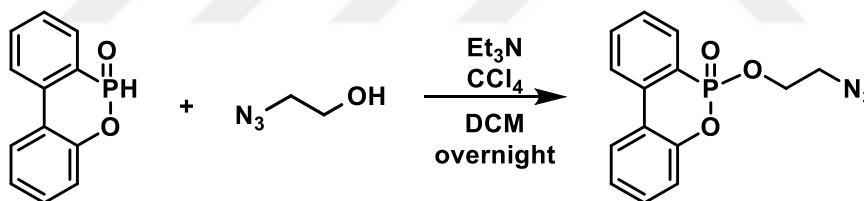


Figure 3.2 : Synthesis scheme of DOPO- N_3 .

DOPO- N_3 was synthesized according to previous study [37]. The synthesis scheme of DOPO- N_3 is shown in Figure 3.2. To a 250 mL round bottom flask equipped with a magnetic stir bar was added DOPO (12.45 g, 57.59 mmol) and partially dissolved in 60 mL of DCM and triethylamine (8.83 mL, 63.35 mmol) was added to flask. Then 2-azidoethanol (3.79 mL, 49.88 mmol) was added to the flask when DOPO was completely dissolved. The mixture was cooled to 0°C in an ice bath. After that, CCl_4 (6.13 mL, 63.35 mmol) was added to the reaction medium dropwise, then the flask was removed from the ice bath and allowed to stir overnight at room temperature. The mixture was diluted with 40 mL of DCM and extracted with 100 mL of distilled water three times. The organic layers were dried over Na_2SO_4 , filtered, and evaporated to dryness to give DOPO- N_3 as a pale yellow liquid. Yield: 11.40 g, 65.71%.

^1H NMR (CDCl_3 , δ) 7.95 - 7.27 (m, 8H, Ar-H), 4.31 (m, 2H, $\text{P}=\text{OOCH}_2\text{CH}_2\text{N}_3$), 3.43 (t, 2H, $\text{P}=\text{OOCH}_2\text{CH}_2\text{N}_3$).

^{13}C NMR (CDCl_3 , δ) 149.69, 137.08, 133.78, 130.60, 128.30, 124.90, 124.07, 122.40, 120.89, 120.13, 77.32, 64.83, 50.95.

^{31}P NMR (CDCl_3 , δ) 10.89.

FTIR (cm^{-1}): 3065, 2987, 2927, 2117, 1712, 1595, 1476, 1431, 1300, 1265, 1241, 1198, 1030, 915, 751.

3.3.3 6-(hydroxymethyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-OH)

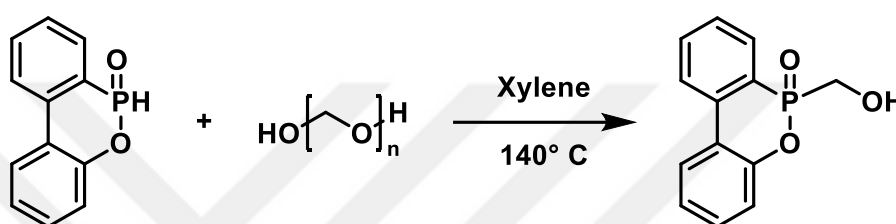


Figure 3.3 : Synthesis scheme of DOPO-OH.

The synthesis scheme of DOPO-OH is shown in Figure 3.3. DOPO-OH [50] was synthesized according to synthesis procedure in the study by Dai et al. To a 50 mL round bottom flask equipped with a magnetic stir bar was added DOPO (8.64 g, 39.97 mmol) and 20 mL xylene. The mixture was stirred and heated to 90° C until DOPO was dissolved completely. Then paraformaldehyde (1.2 g, 39.97 mmol) was added into the flask. The temperature was increased to 140°C and kept at the reflux system for two hours. Finally, the precipitate was filtered, washed with xylene, cooled to room temperature and dried in a vacuum oven for a while. The product which white powder was DOPO-OH. Yield: 9.76 g, 99.19%.

3.3.4 Synthesis of 6-(3-hydroxy-2-(hydroxymethyl)-methylpropoxy)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-diol)

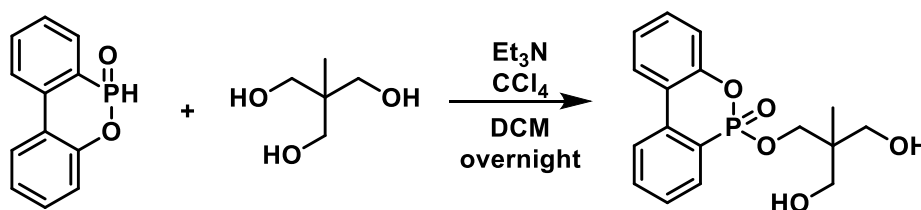


Figure 3.4 : Synthesis scheme of DOPO-diol.

The synthesis scheme of DOPO-diol is shown in Figure 3.4. To a 250 mL round bottom flask equipped with a magnetic stir bar was added tris(hydroxymethyl)ethane (6.67 g, 55.51 mmol) and partially dissolved in 60 mL of DCM and triethylamine (19.34 mL, 138.78 mmol). DOPO (6.00 g, 27.76 mmol) was also added and upon complete dissolution of DOPO, the mixture was cooled to 0°C in an ice bath. After that, CCl₄ (5.37 mL, 55.51 mmol) was added to the reaction medium dropwise, then the flask was removed from the ice bath and allowed to stir overnight at room temperature. Solid fragments were filtered and the mixture was diluted with 40 mL of DCM and extracted with 100 mL of distilled water three times. The organic layers were dried over Na₂SO₄, filtered, and evaporated to dryness to give DOPO-diol as a viscous brown liquid. Yield: 5.86 g, 63.13%.

¹H NMR (CDCl₃, δ) 7.96 - 7.26 (m, 8H, Ar-H), 4.43 (t, 1H, P=OOCH₂), 4.08 (t, 1H, P=OOCH₂), 3.62 - 3.57 (m, 4H, CCH₂OH), 3.27 (br, 2H, -OH), 0.72 (s, 3H, CCH₃).

¹³C NMR (CDCl₃, δ) 149.62, 137.07, 133.84, 130.66, 130.12, 128.47, 128.34, 125.29, 124.97, 124.15, 122.48, 122.23, 120.78, 120.18, 68.63, 67.56, 67.17, 41.35, 15.65.

³¹P NMR (CDCl₃, δ) 13.27, 11.66.

FTIR (cm⁻¹): 3391, 2961, 2879, 1597, 1476, 1448, 1431, 1237, 1084, 1000, 924, 747.

ESI-MS, m/z C₁₇H₁₉O₅P calculated: 334.0970; Found: 335.1046 [M+H]⁺.

3.3.5 Synthesis of (6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)methyl propiolate (DOPO-propiolate)

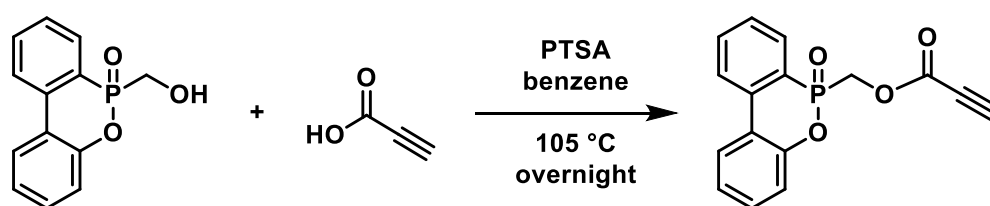


Figure 3.5 : Synthesis scheme of DOPO-propiolate.

The synthesis scheme of DOPO-propiolate is shown in Figure 3.5. To a 100 mL round bottom flask equipped with a magnetic stir bar was added DOPO-CH₂OH (2.40 g, 9.75 mmol) and 20 mL benzene. Propiolic acid (3.63 mL, 58.49 mmol) and then PTSA (0.927 g, 4.87 mmol) were also added to the flask. After that, the flask was attached to a Dean-Stark apparatus and allowed to stir in reflux system overnight at 105° C. Benzene was evaporated and the mixture was diluted with 100 mL of DCM and

extracted with 100 mL of distilled water three times. The organic layers were dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness to give DOPO-propiolate as a pale brown solid. Crude product was washed with small amounts of cold methanol to give white solid. Yield: 2.74 g, 94.23%.

^1H NMR (CDCl_3 , δ) 8.04 - 7.26 (m, 8H, Ar-H), 4.84 - 4.74 (m, 2H, $\text{P}=\text{OCH}_2$), 2.82 (s, 1H, $\text{C}\equiv\text{CH}$).

^{13}C NMR (CDCl_3 , δ) 151.23, 151.03, 149.27, 136.57, 134.28, 130.86, 130.26, 128.83, 128.07, 124.89, 123.69, 121.75, 121.36, 120.75, 120.24, 73.04, 61.16, 60.22.

^{31}P NMR (CDCl_3 , δ) 31.84, 26.33.

FTIR (cm^{-1}): 3155, 2927, 2104, 1712, 1595, 1476, 1425, 1313, 1254, 1193, 937, 739.

ESI-MS, m/z $\text{C}_{16}\text{H}_{11}\text{O}_4\text{P}$ calculated: 298.0395; Found: 299.0468 $[\text{M}+\text{H}]^+$.

3.3.6 Synthesis of 2-methyl-2-(((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)oxy)methyl)propane-1,3-diyl dipropiolate (DOPO-dipropiolate)

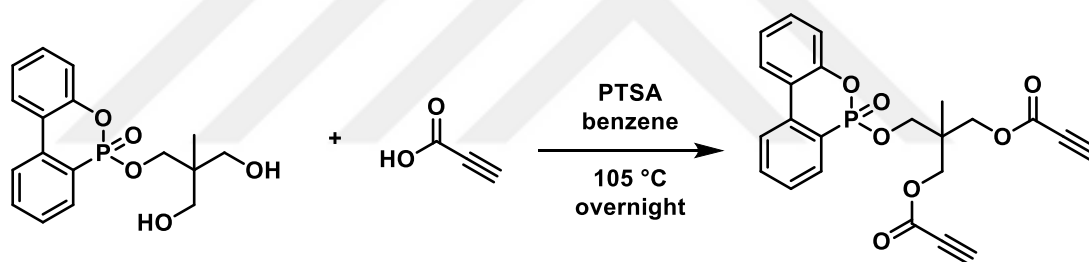


Figure 3.6 : Synthesis scheme of DOPO-dipropiolate.

The synthesis scheme of DOPO-dipropiolate is shown in Figure 3.6. To a 100 mL round bottom flask equipped with a magnetic stir bar was added DOPO-diol (3.60 g, 10.77 mmol) and 30 mL benzene. Propiolic acid (2.67 mL, 43.07 mmol) and PTSA (0.41 g, 2.15 mmol) was also added to the flask. After that, flask allowed to stir in reflux system with Dean-Stark apparatus overnight at 105°C . Benzene was evaporated and the mixture was diluted with 100 mL of DCM and extracted with 100 mL of distilled water three times. The organic layers were dried over Na_2SO_4 , filtered, and evaporated to dryness to give DOPO-dipropiolate as a viscous brown liquid. Yield: 4.42 g, 93.63%.

^1H NMR (CDCl_3 , δ) 7.95 - 7.27 (m, 8H, Ar-H), 4.10 (s, 2H, $\text{P}=\text{OOCH}_2$), 3.94 (m, 4H, $\text{C}=\text{OOCH}_2$), 2.92 (s, 2H, $\text{C}\equiv\text{CH}$), 0.93 (s, 3H, CCH_3).

^{13}C NMR (CDCl_3 , δ): 152.07, 149.69, 137.13, 133.80, 130.72, 130.25, 128.47, 124.97, 124.15, 122.50, 122.24, 120.79, 120.12, 77.02, 75.59, 74.08, 66.92, 66.54, 38.98, 16.34.

^{31}P NMR (CDCl_3 , δ) 10.64, 5.84.

FTIR (cm^{-1}): 3278, 2976, 2896, 2115, 1712, 1597, 1474, 1269, 1202, 1084, 1021, 1002, 922, 747.

ESI-MS, m/z $\text{C}_{32}\text{H}_{37}\text{N}_6\text{O}_7\text{P}$ calculated: 438.0868; Found: 439.0940 $[\text{M}+\text{H}]^+$.

3.3.7 Synthesis of (6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)methyl 1-(2-((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)oxy)ethyl)-1H-1,2,3-triazole-4-carboxylate (P2T1)



Figure 3.7 : Synthesis scheme of P2T1.

The FR; P2T1 was synthesized from the reaction of DOPO-N₃ [37] and DOPO-propiolate. The synthesis scheme of P2T1 is shown in Figure 3.7. Briefly, to a 50 mL Schlenk tube was added DOPO-N₃ (4.85 g, 16.09 mmol) and DOPO-propiolate (4.00 g, 13.41 mmol) equipped with a magnetic stir bar and dissolved in 20 mL of 2-MeTHF. After 2 freeze-pump-thaw cycles, the tube was placed in an oil bath at 80 °C for 24 h. Prior to precipitation, the solution was homogenized with chloroform and precipitated into 200 mL of diethyl ether. The excess solvent was removed by decantation and the white precipitate was recovered. The obtained crude product was further purified by a second dissolution–precipitation (CHCl_3 -diethyl ether) procedure. Finally, excess solvent was filtered and the precipitate was dried in vacuum for 48h to give as a white powder. Yield: 6.35 g, 79%.

^1H NMR (CDCl_3 , δ) 7.92 - 7.04 (m, 17H, Ar-H), 4.97 - 4.46 (m, 2H, $\text{P}=\text{OOCH}_2$), (m, 2H, triazole- CH_2), (m, 2H, $\text{P}=\text{OCH}_2$).

^{13}C NMR (CDCl_3 , δ): 158.59, 149.87, 149.25, 137.97, 136.97, 136.46, 134.12, 130.88, 128.32, 125.17, 124.42, 123.71, 121.77, 121.68, 119.84, 77.04, 63.65, 61.05, 59.96, 50.46.

^{31}P NMR (CDCl_3 , δ) 27.38, 11.13.

FTIR (cm^{-1}): 3481, 3132, 3062, 1742, 1593, 1474, 1448, 1429, 1237, 1198, 1034, 918, 751.

ESI-MS, m/z $\text{C}_{32}\text{H}_{37}\text{N}_6\text{O}_7\text{P}$ calculated: 599.1011; Found: 600.1090 $[\text{M}+\text{H}]^+$.

3.3.8 Synthesis of 2-methyl-2-(((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)oxy)methyl)propane-1,3-diyl bis(1-(2-(((6-oxidodibenzo[c,e][1,2]oxaphosphinin -6-yl)oxy)ethyl)-1H-1,2,3-triazole-4-carboxylate) (P3T2)

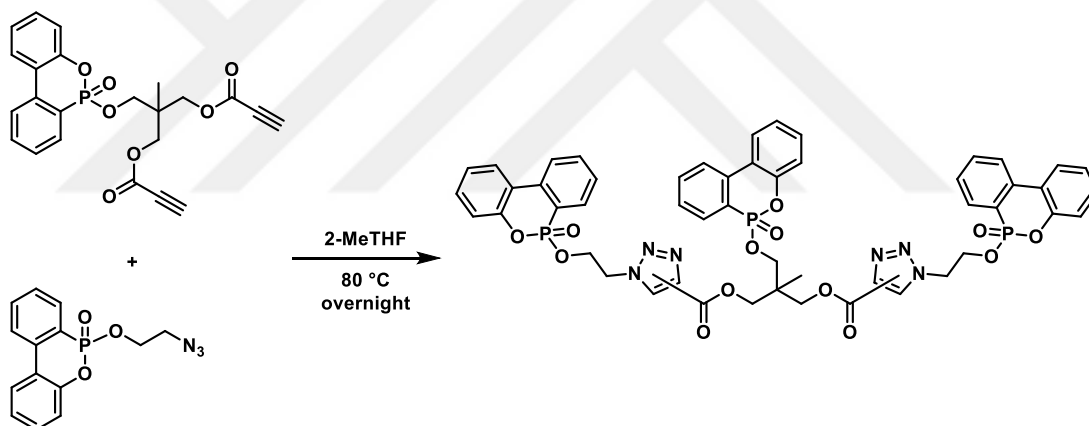


Figure 3.8 : Synthesis scheme of P3T2.

The synthesis scheme of P3T2 is shown in Figure 3.8. To a 25 mL Schlenk tube was added DOPO- N_3 (4.95 g, 16.42 mmol) and DOPO-dipropiolate (3.00 g, 6.84 mmol) equipped with a magnetic stir bar and dissolved in 11 mL of 2-MeTHF. After 2 freeze-pump-thaw cycles, the tube was placed in an oil bath at 80 °C for 24 h. Prior to precipitation, the solution was homogenized with chloroform and precipitated into 200 mL of diethyl ether. The excess solvent was removed by decantation and the white precipitate was recovered. The obtained crude product was further purified by a second dissolution-precipitation (CHCl_3 -diethyl ether) procedure. Finally, excess solvent filtered and the precipitate was dried in vacuum for 48h to give a white powder. Yield: 5.23 g, 73.42%.

^1H NMR (CDCl_3 , δ): 7.99 - 7.13 (m, 26H, Ar-H), 4.87 - 3.86 (m, 2H, $\text{P=OOCH}_2\text{CCH}_3$), (m, 4H, C=OOCH_2), (m, 4H, triazole- CH_2), (m, 4H, triazole- CH_2CH_2), 0.99 (s, 3H, CCH_3).

^{13}C NMR (CDCl_3 , δ): 159.87, 157.69, 149.40, 139.21, 137.65, 136.99, 134.03, 130.79, 128.84, 128.43, 125.05, 124.23, 122.25, 119.95, 77.04, 67.54, 66.56, 63.79, 50.49, 39.39, 16.84.

^{31}P NMR (CDCl_3 , δ): 11.17, 10.57.

FTIR (cm^{-1}): 3065, 2955, 1735, 1595, 1476, 1448, 1431, 1239, 1030, 926, 754.

ESI-MS, m/z $\text{C}_{32}\text{H}_{37}\text{N}_6\text{O}_7\text{P}$ calculated: 1041.2179; Found: 1041.2178 $[\text{M}+\text{H}]^+$.

3.4 Preparation of flame retardant DGEBA/F resins

FR-containing DGEBA/F were synthesized according to the ratios given in Table 3.1. Briefly, 10 grams of DGEBA/F was taken into a jar and heated to 100°C . Next, required amounts of the FR compound (P2T1 and P3T2) was added and stirred until homogenization. After a homogeneous, clear solution was obtained, the temperature was decreased to 80°C and DDM was added. Upon the dissolution of DDM, the liquid precursors were poured into pre-heated silicone molds at 80°C . After keeping the mixtures at this temperature for 1 h, they were heated and kept at 100°C for 1h, 120°C for 1h, and 160°C for 1h, respectively. The control sample, DGEBA/F+DDM, was prepared similarly but without the addition of any FR.

Table 3.1 : The recipe of the FR-containing epoxy formulations.

	DGEBA/F (g)	DDM (g)	P3T2 (g)	P2T1 (g)
DGEBA/F+DDM	10.0	2.83	-	-
P3T2-2	10.0	2.83	0.262	-
P3T2-4	10.0	2.83	0.535	-
P3T2-8	10.0	2.83	1.116	-
P3T2-16	10.0	2.83	2.44	-
P2T1-2	10.0	2.83	-	0.262
P2T1-4	10.0	2.83	-	0.535
P2T1-8	10.0	2.83	-	1.116
P2T1-16	10.0	2.83	-	2.44

4. RESULTS AND DISCUSSION

4.1 Structural Characterization of Organic Compounds and FRs

The synthesis scheme of organic molecules synthesized to obtain first FR called P2T1 was shown in the Figure 4.1. All these compounds were characterized via ^1H NMR, ^{13}C NMR, ^{31}P NMR, FTIR and Mass Spectroscopy respectively.

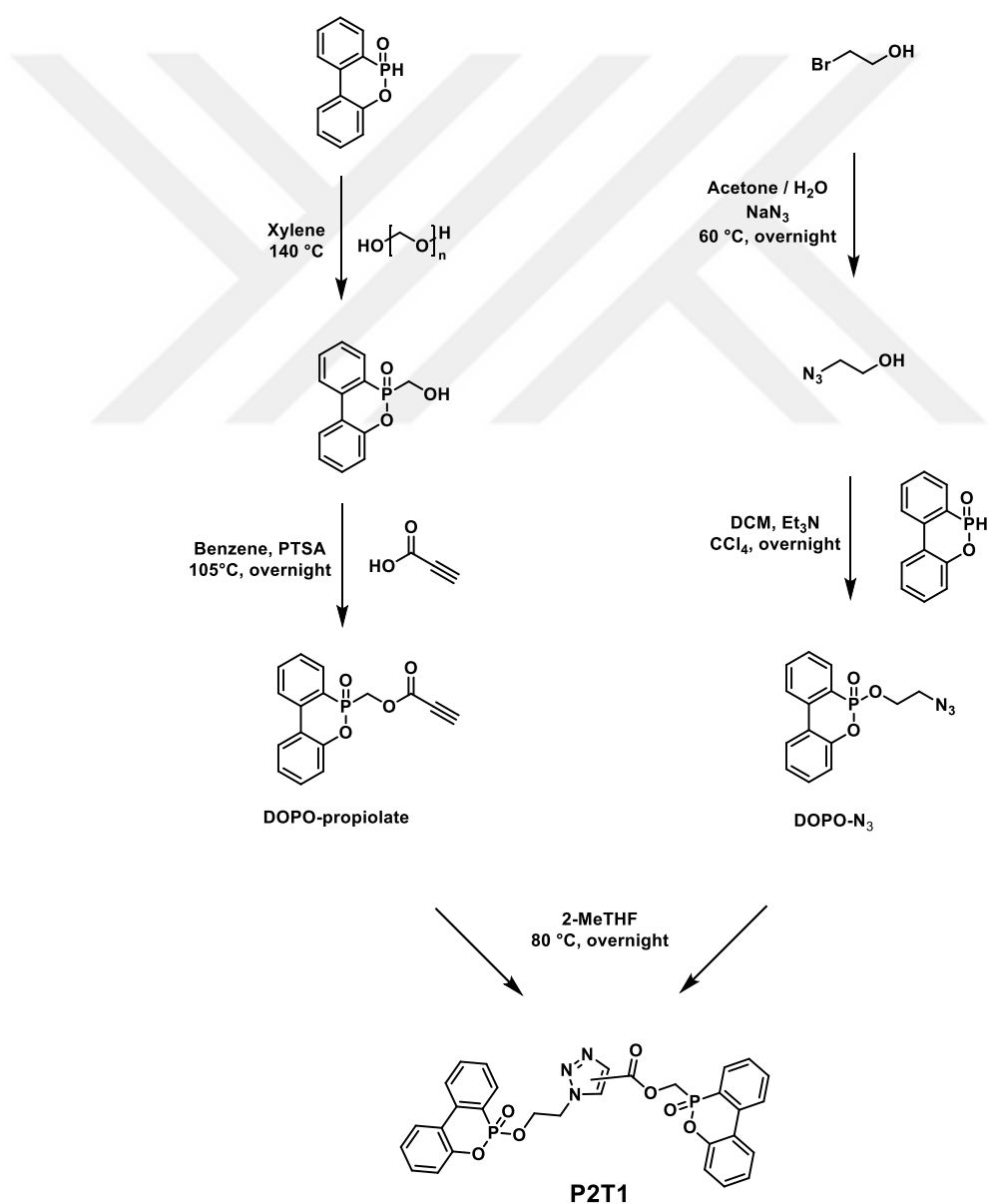


Figure 4.1 : Synthesis route of P2T1.

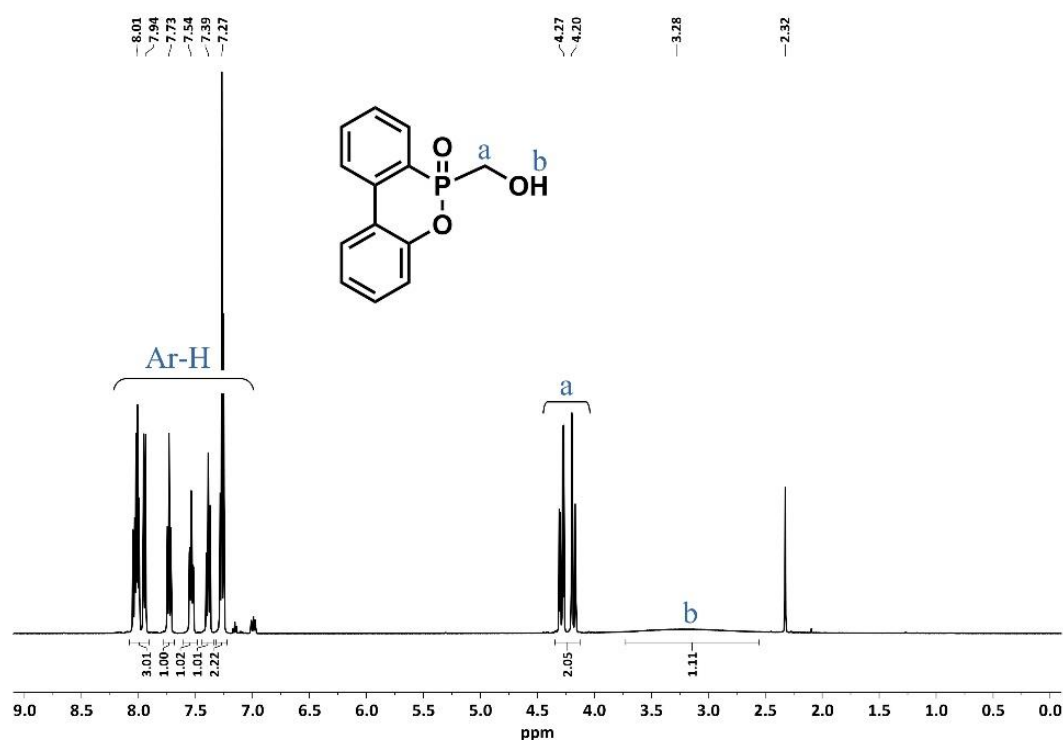


Figure 4.2 : ¹H NMR spectrum of DOPO-OH.

¹H NMR of DOPO-OH is given in Figure 4.2. The aromatic hydrogens resonated between 8.01-7.27 ppm. The chemical shifts 4.27-4.20 ppm are attributed to the protons of -CH₂. The peak at 3.28 ppm presented to the -OH proton [50].

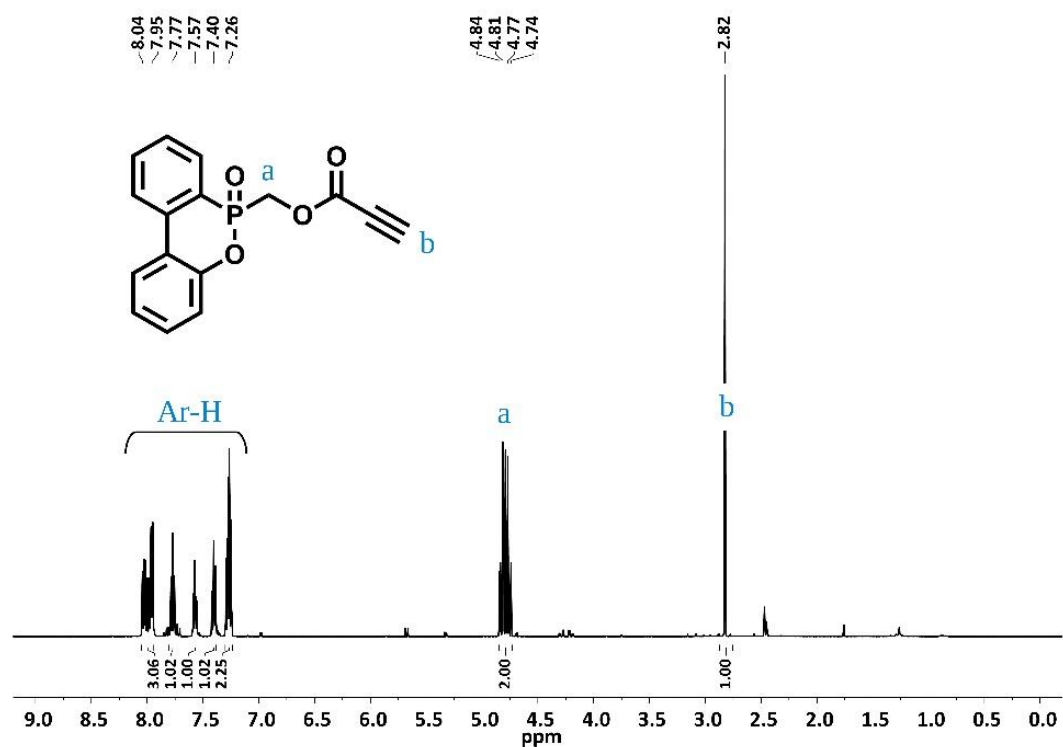


Figure 4.3 : ¹H NMR spectrum of DOPO-propiolate.

^1H NMR of DOPO-propiolate is given in Figure 4.3. The aromatic hydrogens resonated between 8.04-7.26 ppm. The hydrogens of P- CH_2 group resonated between 4.84-4.74 ppm. The single peak of alkyne proton was observed at 2.82 ppm. The structure of DOPO-propiolate was also confirmed via ^{13}C NMR (Figure A.1), and ^{31}P NMR (Figure A.2). The FTIR spectrum of DOPO-propiolate given in Figure 4.4. Characteristic peak of ester carbonyl group observed at 1712 cm^{-1} . The alkyne bands were also detected at 2104 cm^{-1} . The strong signal at 937 cm^{-1} was attributed to the P-O-Ph group and 1254 cm^{-1} P=O group of DOPO. The signal at 1476 cm^{-1} attributed P-Ph group [37, 51].

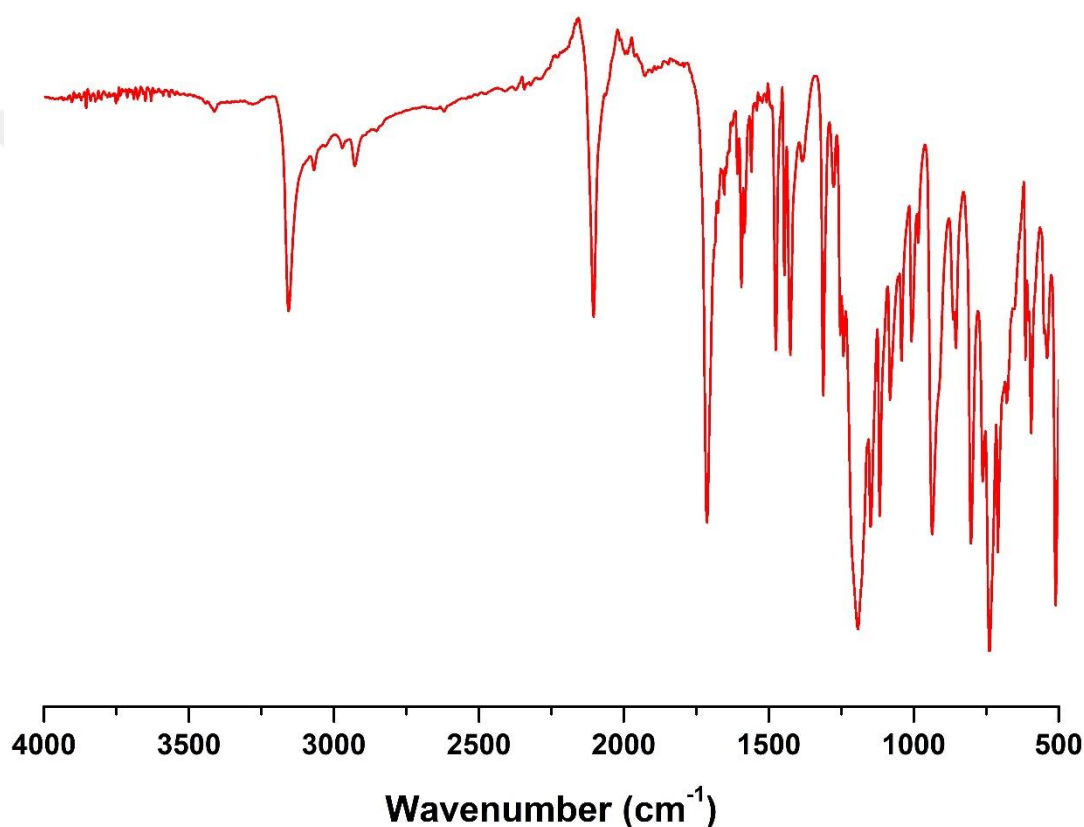


Figure 4.4 : FTIR spectrum of DOPO-propiolate.

According to MS analysis, the m/z of DOPO-propiolate was found as 299.0468 $[\text{M}+\text{H}]^+$ which corresponded to the molecular weight of DOPO-propiolate.

^1H NMR of DOPO- N_3 is given in Figure 4.5. The aromatic hydrogens resonated between 7.95-7.27 ppm. The hydrogens of carbon bonded to the oxygen atom resonated at 4.31 ppm. The triplet peaks of CH_2 were observed at 3.43 ppm. The structure of DOPO- N_3 was also confirmed via ^{13}C NMR (Figure A.3), and ^{31}P NMR (Figure A.4).

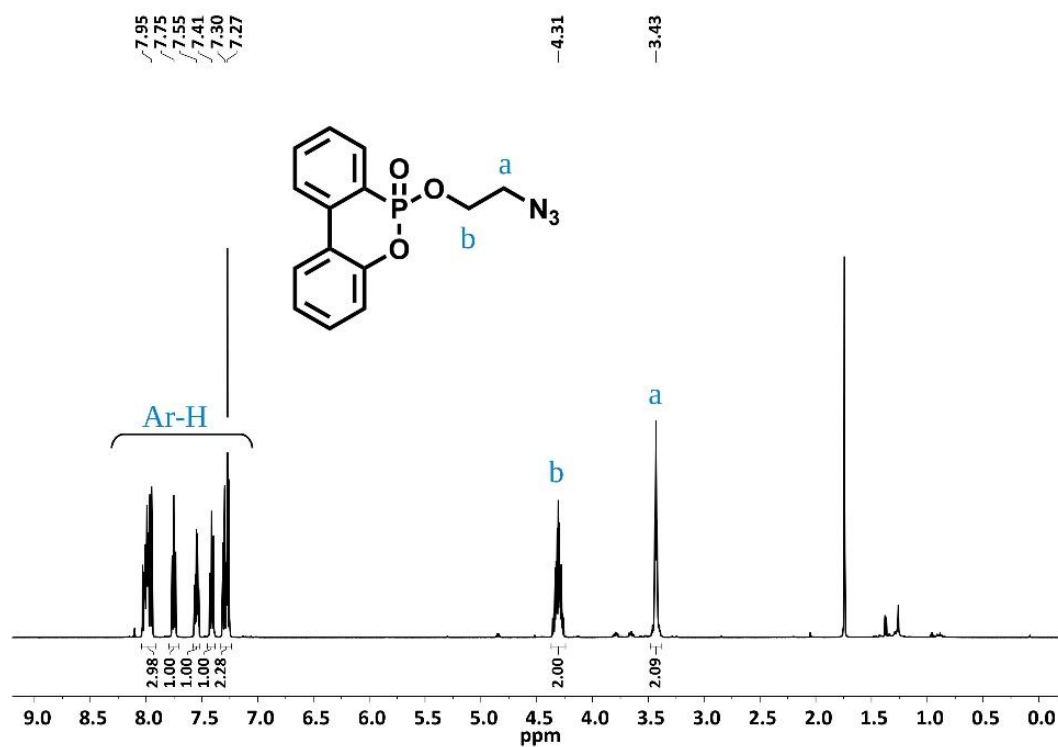


Figure 4.5 : ^1H spectrum of DOPO- N_3 .

The FTIR spectrum of DOPO- N_3 is given in Figure 4.6.

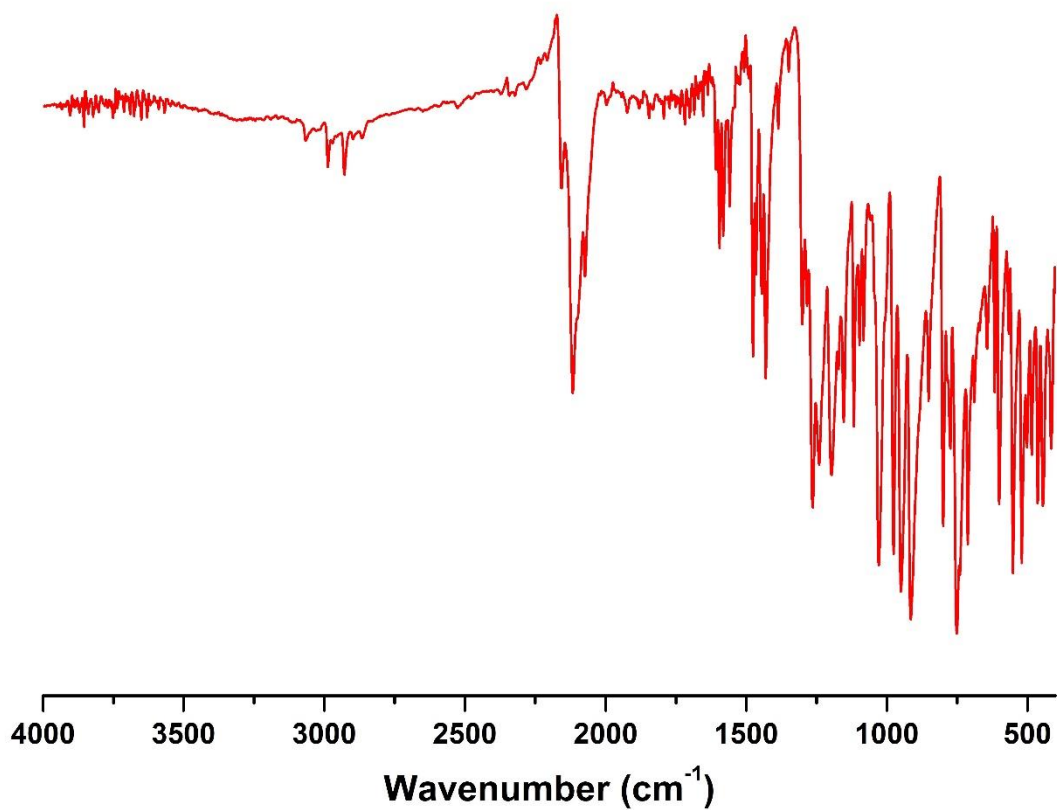


Figure 4.6 : FTIR spectrum of DOPO- N_3 .

The strong signal at 915 cm^{-1} was attributed to the P–O–Ph group and 1241 cm^{-1} P=O group of DOPO. The signal at 1030 cm^{-1} belongs to the P–O–C stretching [37]. The signal at 1265 cm^{-1} belongs to the N–C stretching. Characteristic –N=N=N stretching peak observed at 2117 cm^{-1} . The signal at 1476 cm^{-1} attributed P–Ph group [51].

P2T1 was synthesized from the reaction of DOPO-propiolate and DOPO- N_3 . P2T1 was obtained at a yield of 79%. ^1H NMR of P2T1 is presented in Figure 4.7.

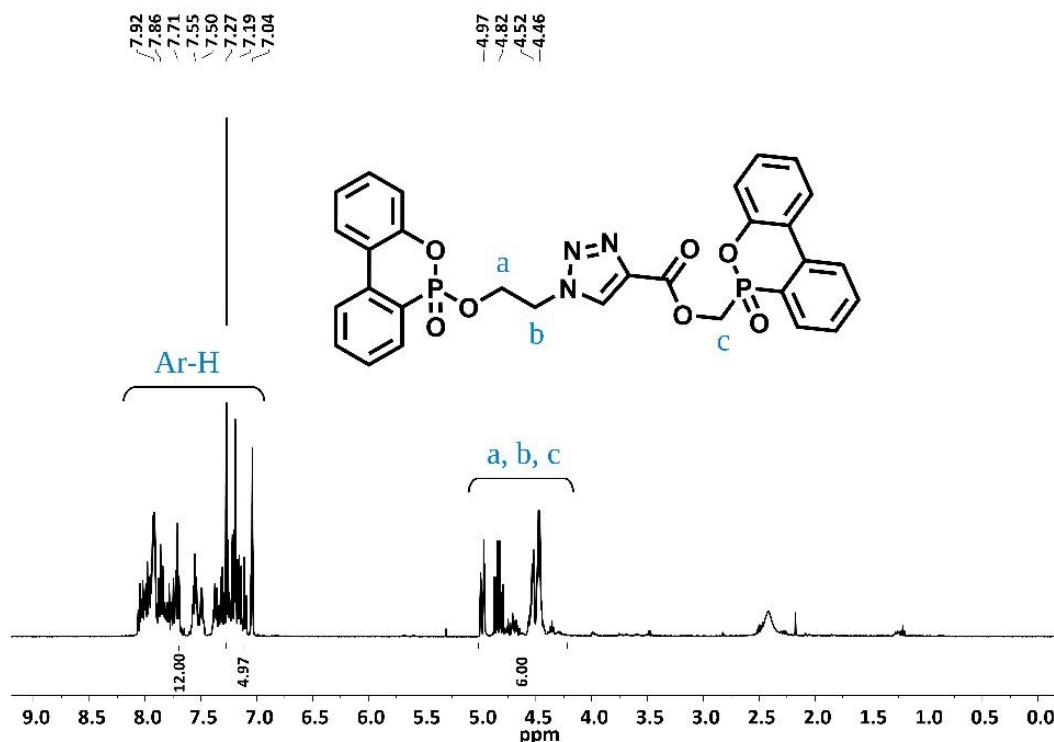


Figure 4.7 : ^1H NMR spectrum of P2T1.

As can be seen the aromatic hydrogens of P2T1 were observed between 7.92–7.04 ppm while the aliphatic hydrogens were resonated between 4.97–4.46 ppm. While its ^{13}C NMR (Figure A.5) further confirmed the structure of P2T1, its ^{31}P NMR (Figure A.6) also indicated its high purity.

The FTIR spectrum of P2T1 is given in Figure 4.8. The strong signal at 918 cm^{-1} was attributed to the P–O–Ph group and 1237 cm^{-1} P=O group of DOPO. The signals at 1448 and 1474 cm^{-1} P–CH₂ and P–Ph group, respectively. [37, 51]. The strong signal at 1742 cm^{-1} belongs to ester carbonyl group. Additionally demonstrating the success of the click reaction and the purity of the molecule is the absence of an azide stretching vibration band at around 2117 cm^{-1} [37]. Peaks at 3132 and 3062 cm^{-1} due to C–H and N–CH₂ stretching vibrations. The –N=N stretching peak was observed at 1593 cm^{-1} .

The peak 1429 cm^{-1} were attributed the -C=C group [52, 53]. The signal at 1034 cm^{-1} belongs to the P-O-C stretching.

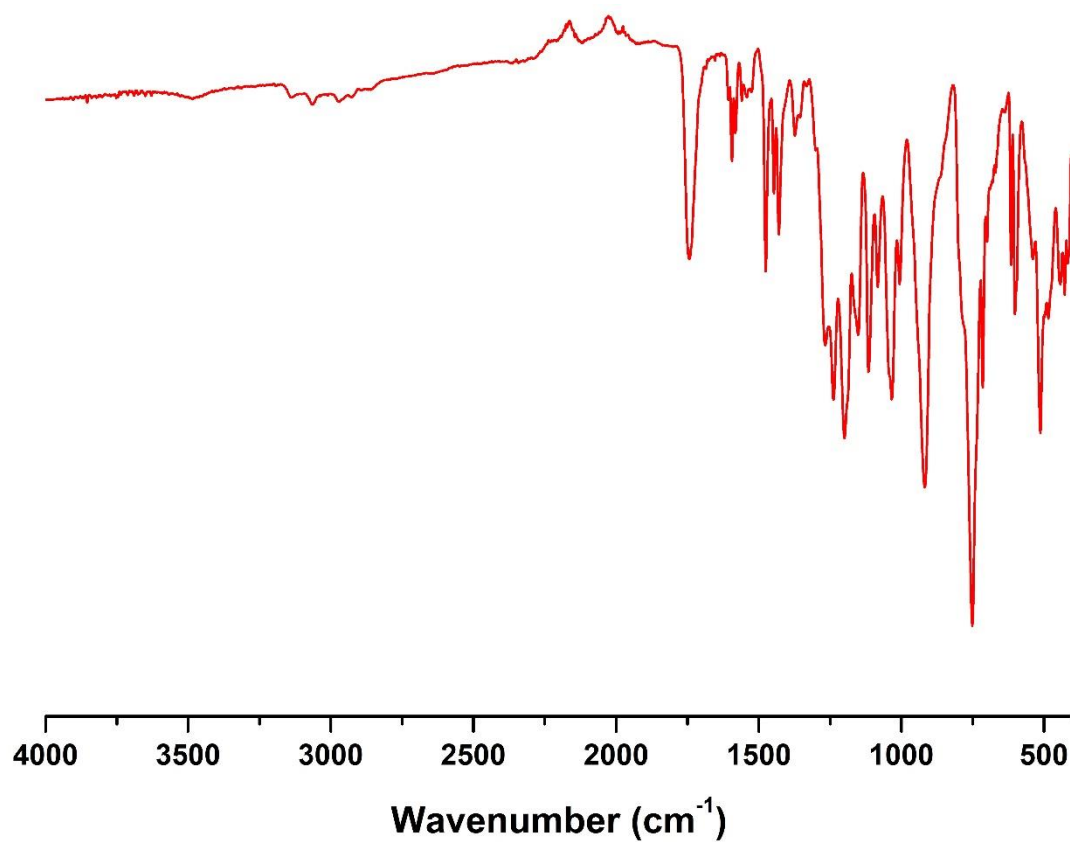


Figure 4.8 : FTIR spectrum of P2T1.

P3T2 was synthesized in a similar manner via a metal-free thermal click reaction. The synthesis scheme of organic molecules synthesized to obtain second FR called P3T2 was shown in the Figure 4.9. All these compounds were characterized via ^1H NMR, ^{13}C NMR, ^{31}P NMR, FTIR and Mass Spectroscopy, respectively.

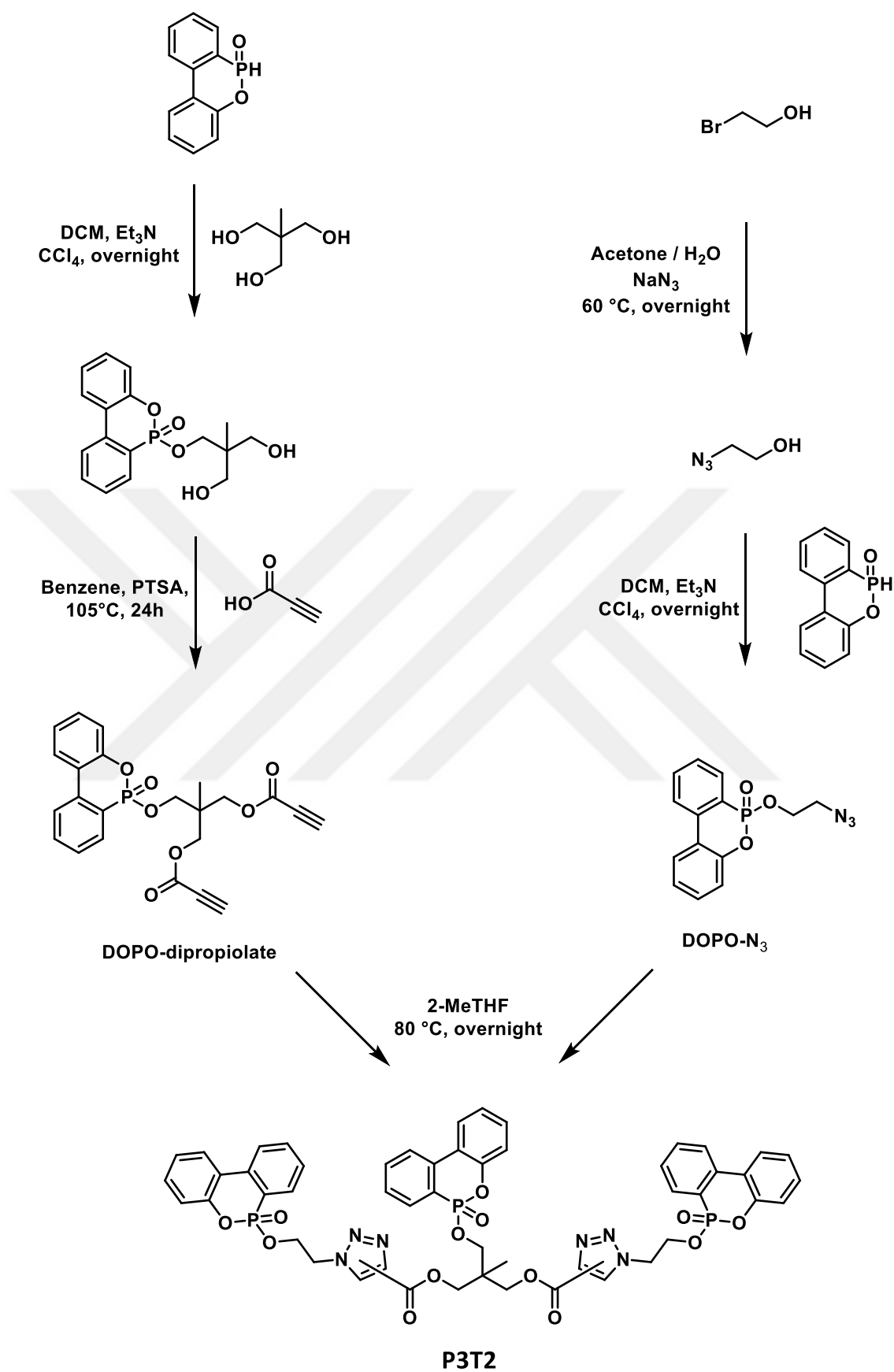


Figure 4.9 : Synthesis route of P3T2.

^1H NMR of DOPO-diol is given in Figure 4.10.

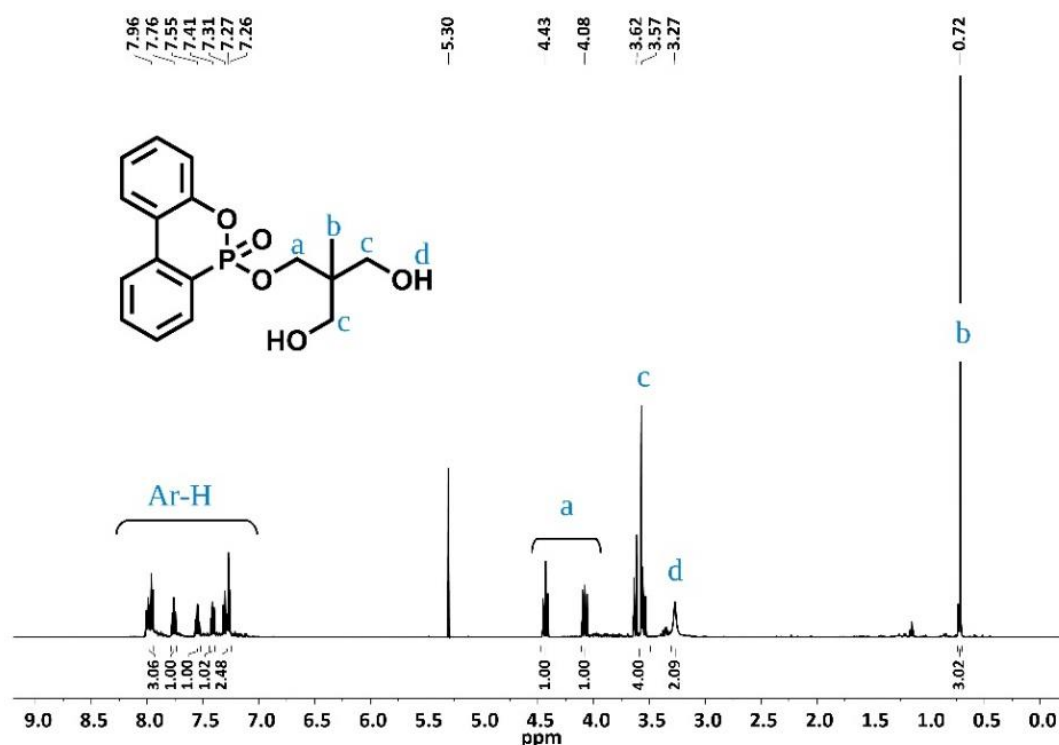


Figure 4.10 : ^1H NMR spectrum of DOPO-diol.

The aromatic hydrogens of DOPO resonated between 7.96-7.26 ppm. The triplet peaks at 4.34 and 4.08 ppm belongs to the hydrogens of $\text{P}=\text{OCH}_2$ group. The multiplet peaks in the range of 3.62-3.27 ppm are due to the signals of hydrogens in the CCH_2OH group. The broad peak at 3.27 ppm and the integral area of the peak confirm the presence of OH groups in the structure. Methyl protons formed a singlet peak at 0.72 ppm. The structure of the molecule was also proved via ^{13}C NMR (Figure A.7), and ^{31}P NMR (Figure A.8).

The FTIR spectrum of DOPO-diol is shown in Figure 4.11. Characteristic stretching peak of -OH observed at 3391 cm^{-1} . The strong signal at 924 cm^{-1} was attributed to the P-O-Ph group and 1237 cm^{-1} P=O group of DOPO. The signal at 1476 cm^{-1} attributed P-Ph group [51]. The signals at 2961 and 2879 cm^{-1} belong to C-H stretching vibrations. The signal at 1084 cm^{-1} belongs to the P-O-C stretching. The strong C-O stretching signal was observed at 1000 cm^{-1} .

The m/z of DOPO-diol was found as 335.1046 [M+H]^+ which corresponded to the molecular weight of DOPO-diol.

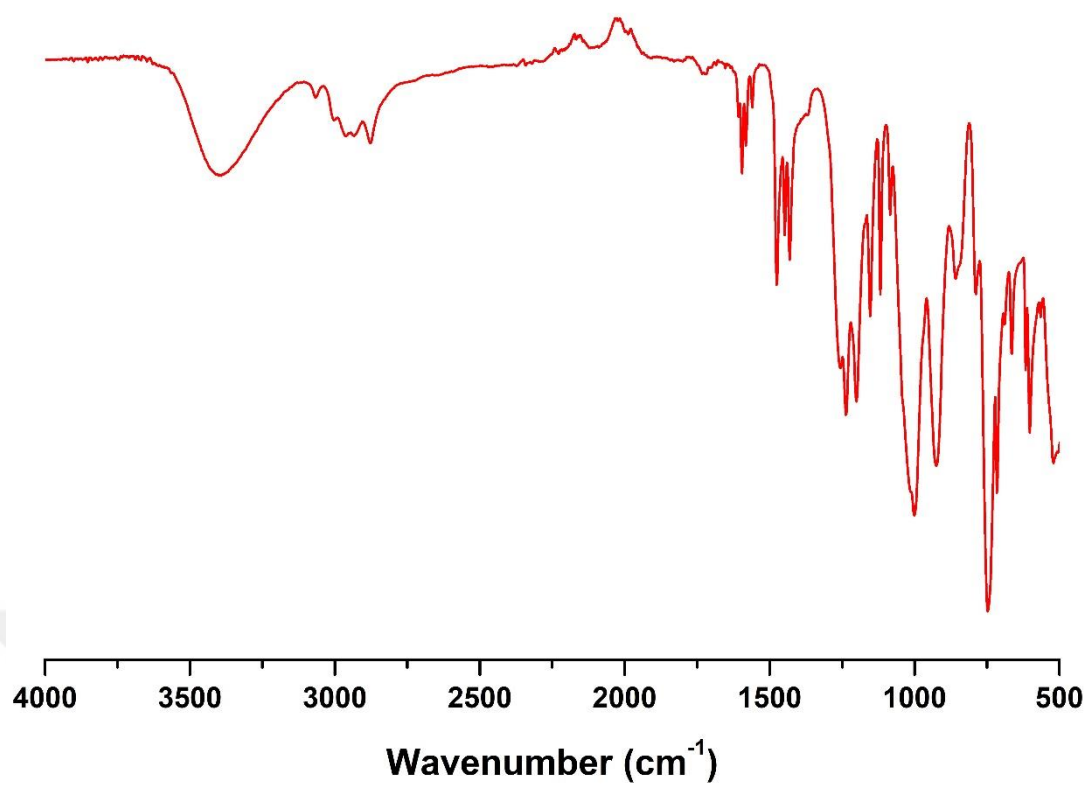


Figure 4.11 : FTIR spectrum of DOPO-diol.

¹H NMR of DOPO-dipropiolate is shown in Figure 4.12.

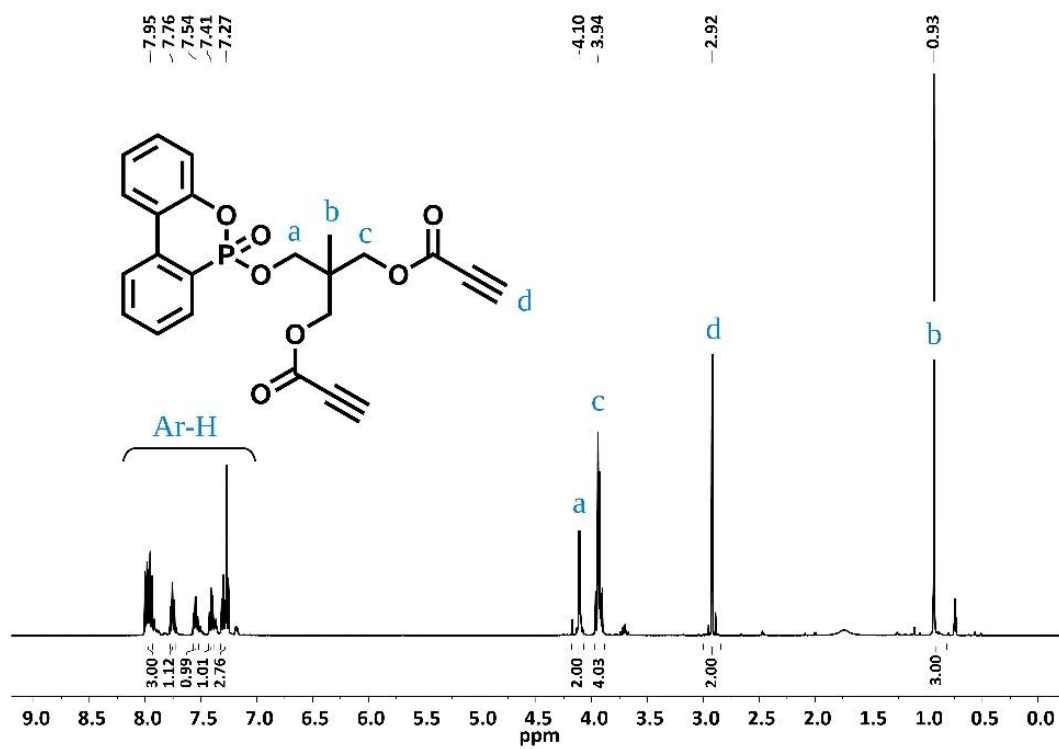


Figure 4.12 : ¹H NMR spectrum of DOPO-dipropiolate.

The aromatic hydrogens resonated between 7.95-7.27 ppm. The hydrogens of P=OOCH_2 group resonated at 4.10 ppm as a singlet peak. The protons of C=OOCH_2 group observed at 3.94 as multiplet peaks. The singlet peak at 2.92 ppm belongs to the alkyne protons. was observed at 2.82 ppm. Methyl protons formed a singlet peak at 0.93 ppm. The structure of DOPO-dipropiolate was also confirmed via ^{13}C NMR (Figure A.9), and ^{31}P NMR (Figure A.10). In addition, the FTIR spectrum of DOPO-dipropiolate is given in Figure 4.13. The signal at 1712 cm^{-1} indicates the presence of ester groups whereas at 2115 cm^{-1} indicates the presence of alkyne groups in the molecule structure. The strong signal at 922 cm^{-1} was attributed to the P-O-Ph group and 1269 cm^{-1} P=O group of DOPO. The signal at 1474 cm^{-1} attributed P-Ph group [37, 51]. The signal at 1084 cm^{-1} belongs to the P-O-C stretching. The strong C-O stretching signals were observed at 1002 and 1021 cm^{-1} . The signals at 3278 , 2976 and 2896 cm^{-1} belong to C-H stretching vibrations.

According to result of mass spectroscopy, the m/z of DOPO-dipropiolate was found as 439.0940 [M+H]^+ which corresponded to the molecular weight of DOPO-dipropiolate.

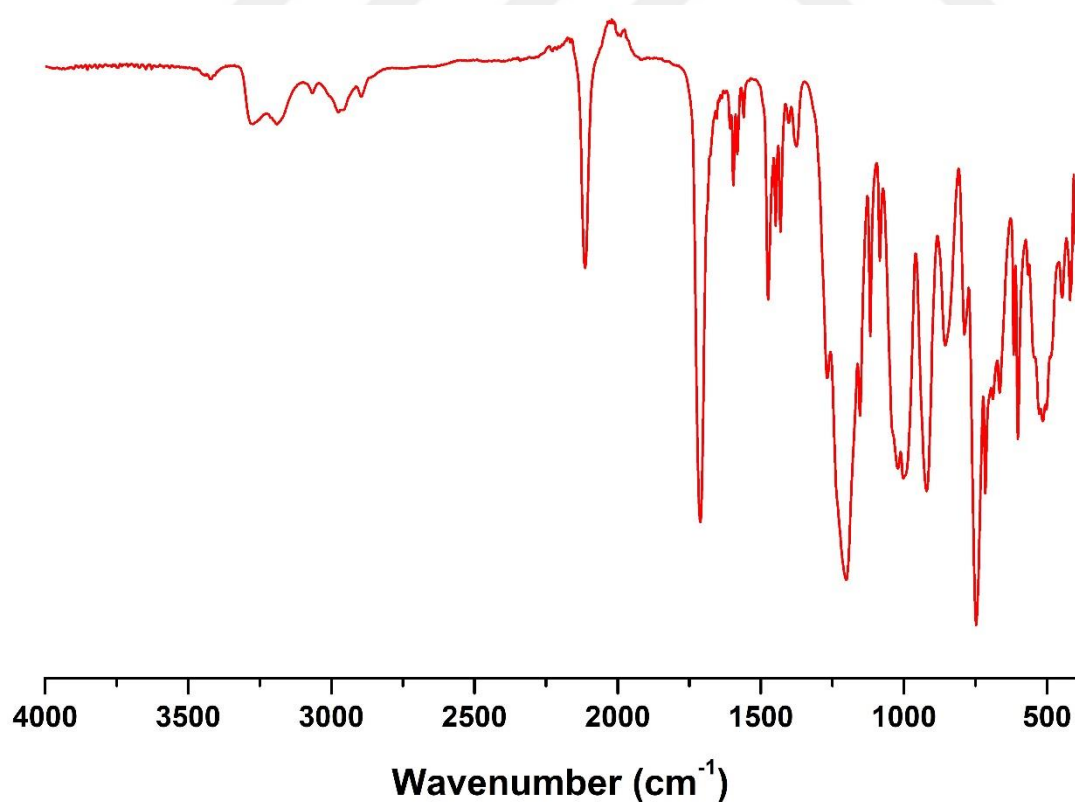


Figure 4.13 : FTIR spectrum of DOPO-dipropiolate.

P3T2 was synthesized from the reaction of DOPO-dipropiolate and DOPO-N₃. P3T2 was obtained at a yield of 73.42%.

¹H NMR of P3T2 is presented in Figure 4.14. The aromatic protons resonated between 7.99-7.13 ppm while the aliphatic hydrogens observed between 4.87-3.86 ppm. ¹H NMR spectrum of P3T2 is similar to that of P2T1 with the exception of the peak at 0.99 ppm which belongs to the hydrogens in the methyl group. While its ¹³C NMR (Figure A.11) further proved the structure of P2T3, its ³¹P NMR (Figure A.12) also indicated its high purity.

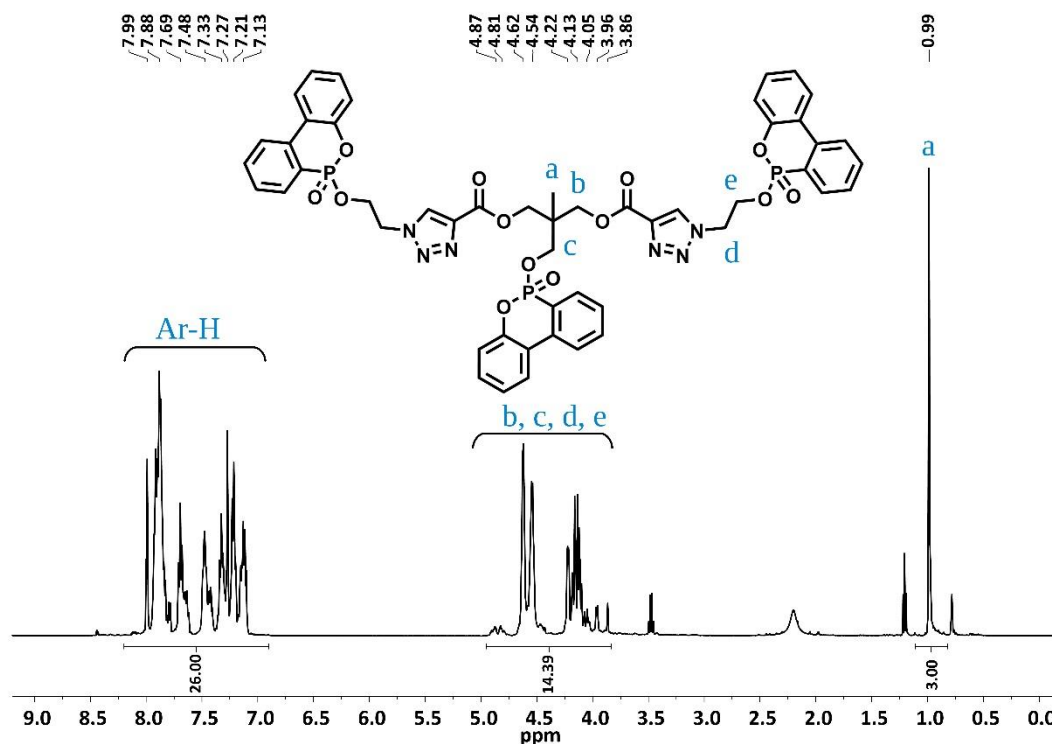


Figure 4.14 : ¹H NMR spectrum of P3T2.

The FTIR spectrum of P3T2 is given in Figure 4.15. The strong signal at 926 cm⁻¹ was attributed to the P–O–Ph group and 1239 cm⁻¹ P=O group of DOPO. The signals at 1448 and 1476 cm⁻¹ P–CH₂ and P–Ph group, respectively. [37, 51]. The strong signal at 1735 cm⁻¹ belongs to ester carbonyl group. Additionally demonstrating the success of the click reaction and the purity of the molecule is the absence of an azide stretching vibration band at around 2117 cm⁻¹ [37]. Peaks at 3065 and 2955 cm⁻¹ due to C–H and N–CH₂ stretching vibrations. The –N=N stretching peak was observed at 1595 cm⁻¹. The peak at 1431 cm⁻¹ was attributed the –C=C group [52, 53]. The signal at 1030 cm⁻¹ belongs to the P–O–C stretching.

The m/z P3T2 were found as 1041.2178 $[M+H]^+$ which corresponded to the molecular weight of P3T2.

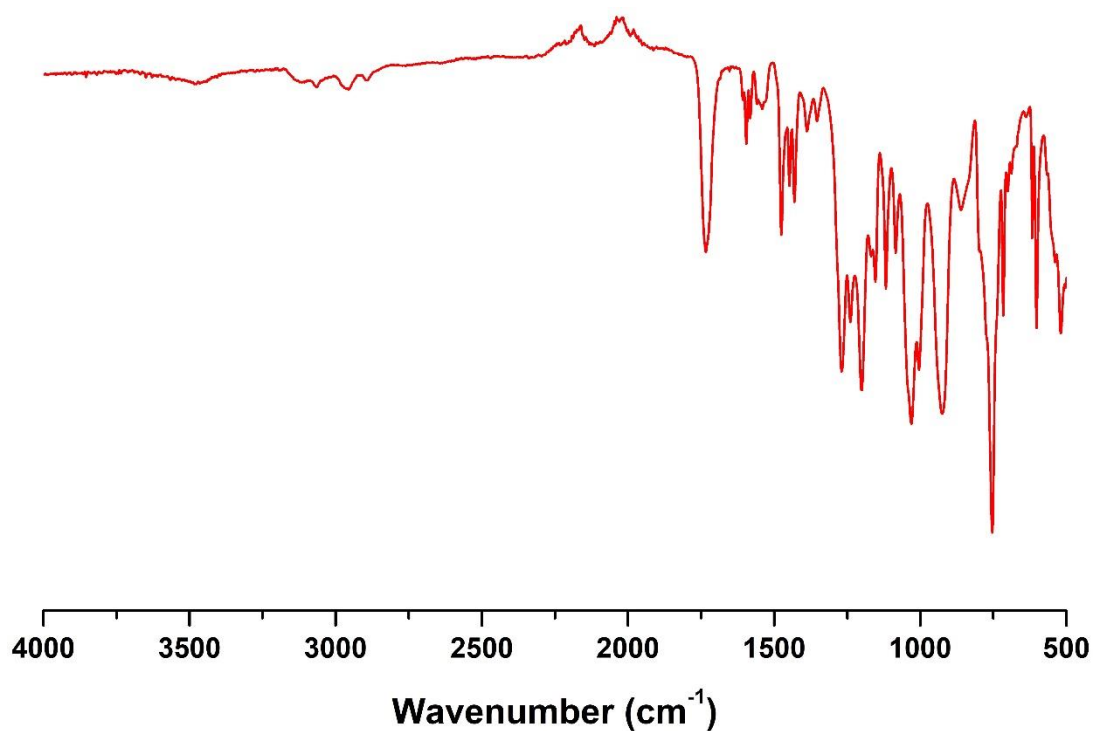


Figure 4.15 : FTIR spectrum of P3T2.

4.2 Structural Characterization and Physical Appearance of The Cured EPs

The cured EPs were characterized via FTIR spectroscopy. Figure 4.16 displays the FTIR spectrum of neat epoxy resin, DDM and the cured resin, respectively. The FTIR spectra of FR-containing films are presented in Figure 4.17 and Figure 4.18, respectively. The main characteristic vibrations bands for the epoxy resin before curing were observed at 3400 cm^{-1} , $2965\text{--}2872\text{ cm}^{-1}$, 1607 cm^{-1} , and 913 cm^{-1} , which correspond to the --OH , groups, aliphatic --CH-- bonds, aromatic carbon-carbon double bonds, and the oxirane groups (--C--O stretching vibrations), respectively [54, 55]. Additionally the band at around 827 cm^{-1} is also associated with the oxirane group (--C--O--C stretching vibrations). After curing with DDM, it can be seen that the intensity of the bands at 913 cm^{-1} and 827 cm^{-1} were declined and the intensity of the bands in region $3500\text{--}3200\text{ cm}^{-1}$ were increased due to ring opening polymerization and crosslinking of the DGEBA/F resin. Moreover, new bands appeared at 1103 cm^{-1} and 1361 cm^{-1} and they were attributed to the --C--N--C-- and --C--N-- stretching vibrations

[55]. The addition of the triazole-bearing FRs produced similar FTIR spectra and were found not to effect the FTIR spectra of the resins (Figures 4.17 and 4.18). On the other hand, the bands observed at 1232 cm^{-1} , 941 cm^{-1} and 911 cm^{-1} in the spectra of the FR-containing cured epoxy resins were attributed to the -P=O stretching vibrations, -P-O , and the -P-O-C bond vibrations [56]. Furthermore, the bands at 1031 and 1450 cm^{-1} were assigned to the triazole ring stretching frequencies [22].

The digital photographs of the cured epoxy films are given Figure 4.19. As can be seen the films are homogeneous and crack free. It must be noted that as the ratio of the FR was increased in the EP composition, the color of the films becomes darker.

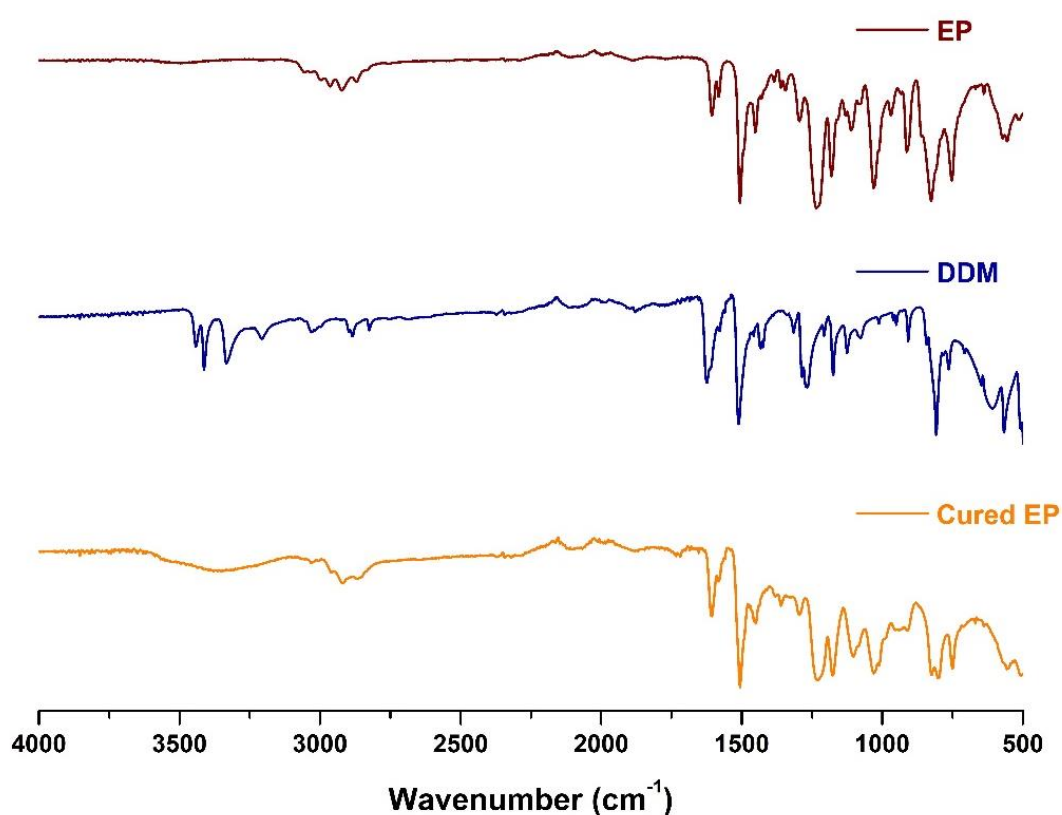


Figure 4.16 : FTIR spectra of neat EP, DDM and cured EP.

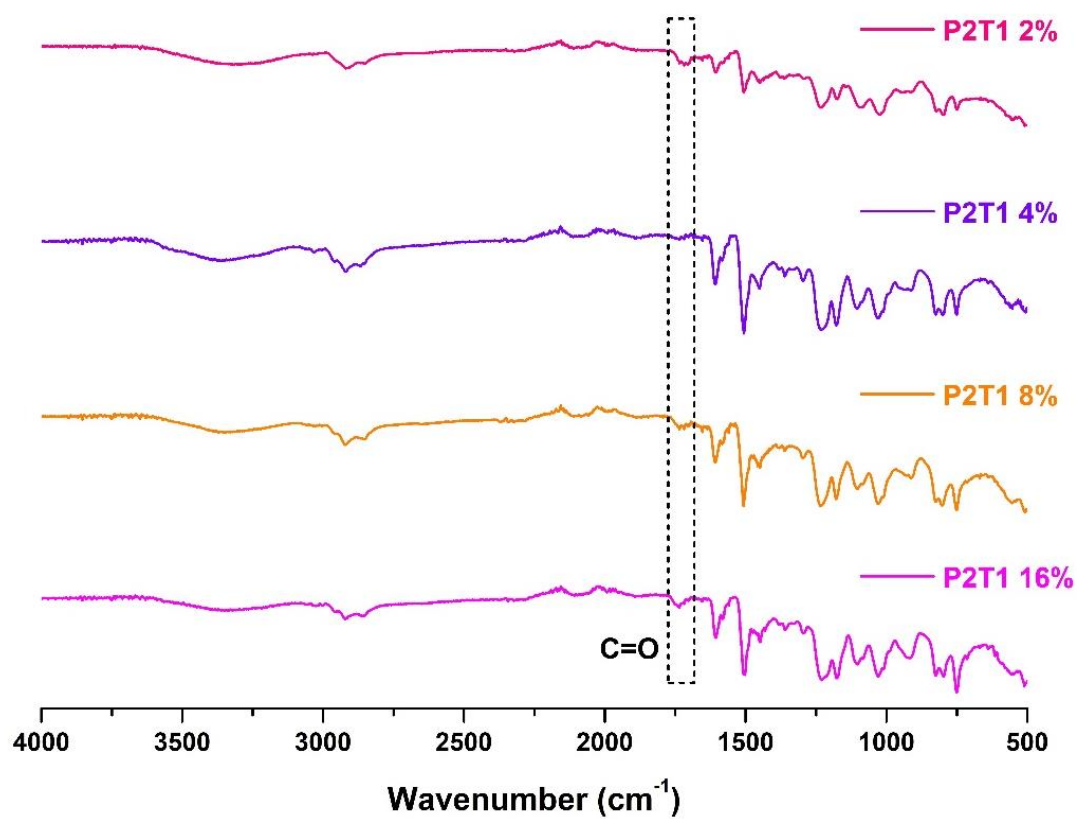


Figure 4.17 : FTIR spectra of P2T1-containing EPs.

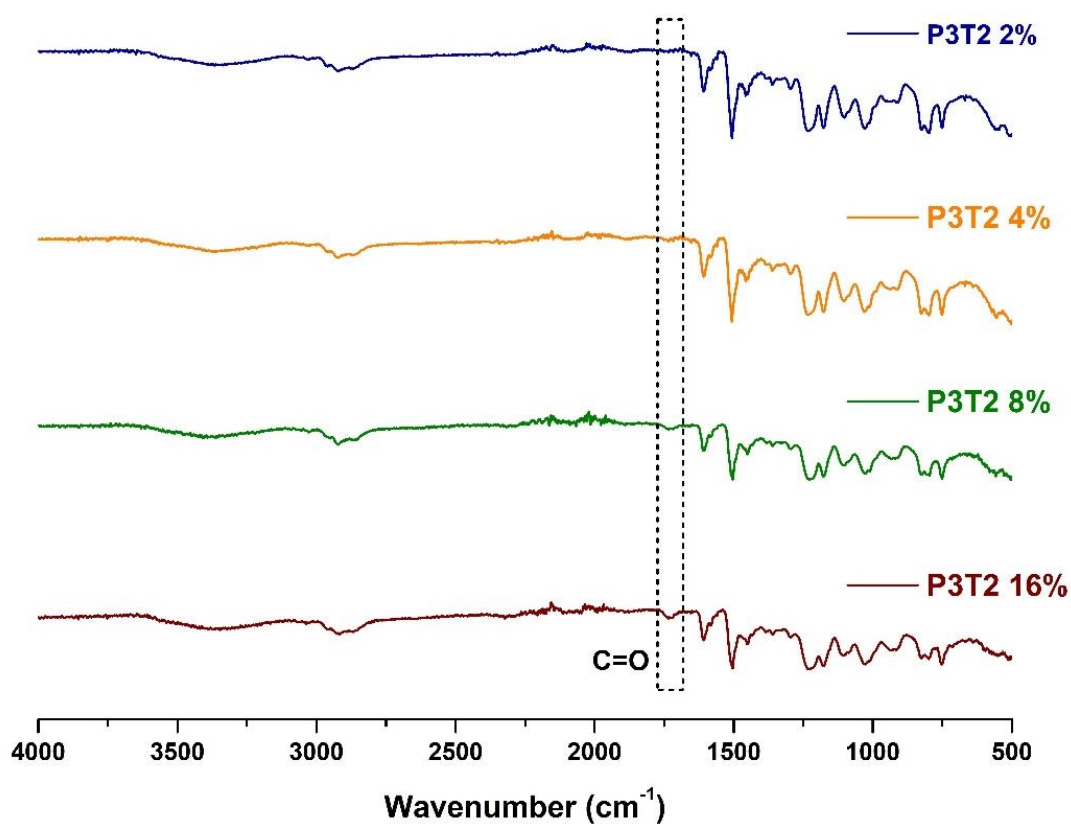


Figure 4.18 : FTIR spectra of P3T2-containing EPs.



Figure 4.19 : Digital images of the neat EP and the FR-containing EPs.

4.3 Thermal Decomposition Characteristics of The Synthesized FRs

The thermal stability of the synthesized FRs were determined by TGA under nitrogen atmosphere. TGA thermograms of P2T1 and P3T2 are given in Figure 4.20 and 4.21, respectively. Structurally similar P2T1 and P3T2 gave similar decomposition profiles and displayed two maximum weight loss temperatures. The first maximum weight loss temperature was attributed to the decomposition of the ester groups while the second temperature was due to the decomposition of the DOPO and triazole units [22]. While the first maximum weight loss temperatures of P2T1 and P3T2 were found to be same and 332 °C, the second maximum weight loss temperature of P2T1 (467 °C) was found to be 36 °C higher than that of P3T2 (431 °C). On the other hand the earlier decomposition of P3T2 compared to P2T1 resulted to higher char yield. The char residue percentage for P2T1 was 11.9% while P3T2 produced the highest amount of char among the studied FRs as 15.4%.

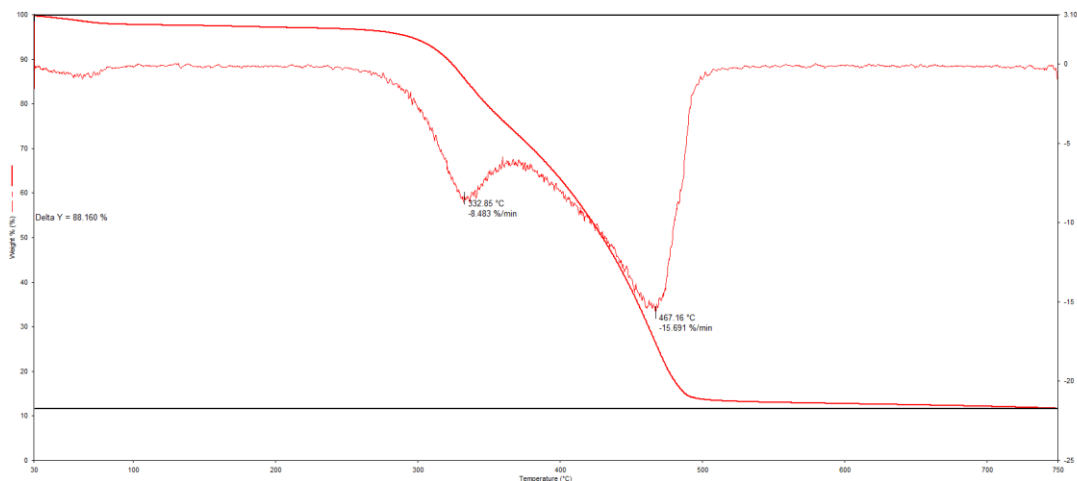


Figure 4.20 : TGA thermogram of P2T1 under nitrogen atmosphere.

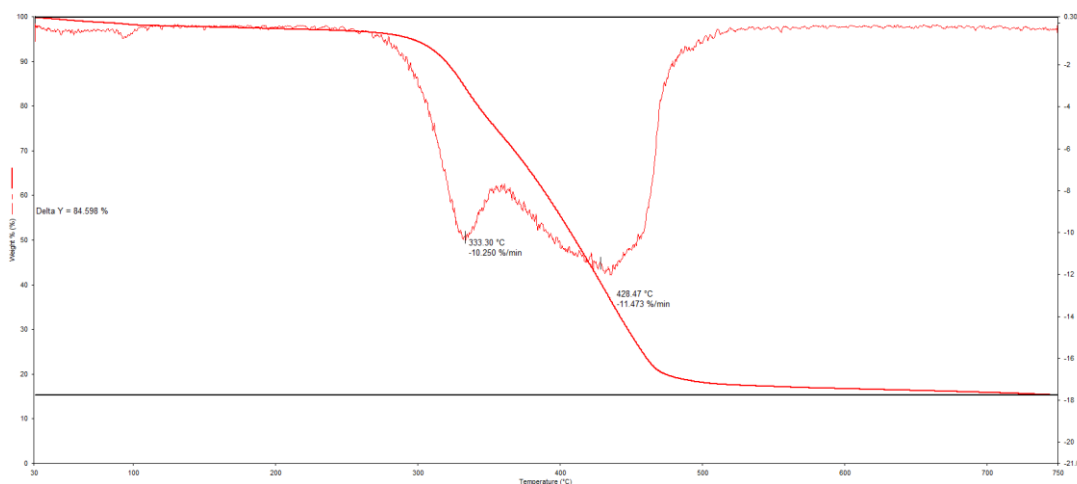


Figure 4.21 : TGA thermogram of P3T2 under nitrogen atmosphere.

4.4 Thermal Properties of The EPs

The glass transition temperatures (T_g s) of the EPs were determined by DSC measurements. The DSC curves of the EPs are given in Figure 4.22 and Figure 4.23. The T_g s are listed in Table 4.1. The T_g of the cured DGEBA/F+DDM system was measured as 127 °C. Different T_g values were reported previously in the literature for DGEBA+DDM and diglycidylether bisphenol F (DGEBF)+DDM systems [57-59]. The different reported values can be attributed to the use of different instruments, different curing temperatures, and different epoxy resins (different molecular weights), etc. When only 2% P2T1 and P3T2 were added, the T_g values significantly increased to 150 °C and 157 °C, respectively. This situation was attributed to the higher crystallinity and rigidity. As it can be seen from Table 4.1 the T_g values were often found to decrease or fluctuate with further FR additions. We attributed these

fluctuations in T_g values to the reduced degree of curing upon rigid FR additions. The maximum temperature we applied to cure the epoxy resins was 160 °C. Therefore, as the T_g values started to get closer to this temperature, it became difficult for the epoxy end groups to react with the remaining amine functionalities. Thus, it is thought that the degree of crosslinking was slightly decreased as the ratio of the FR compound was increased in the formulations, leading to decrease in the observed T_g values.

The thermal degradation properties of the prepared EPs were investigated both under nitrogen and air atmospheres. TGA thermograms under nitrogen and air atmospheres of the neat EP and FR-containing EPs are presented in Figure A.13, Figure A.14, Figure A.15 and Figure A.16, respectively. The results of TGA are given in Table 4.1.

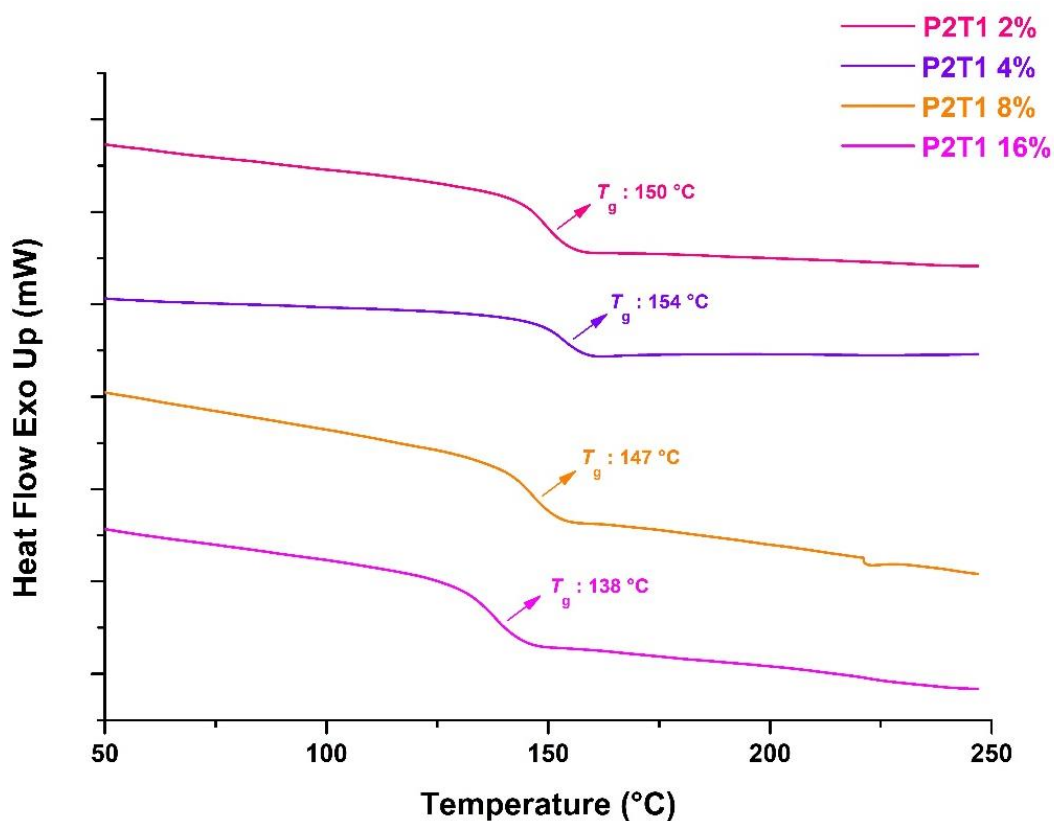


Figure 4.22 : DSC thermograms of P2T1-containing EPs.

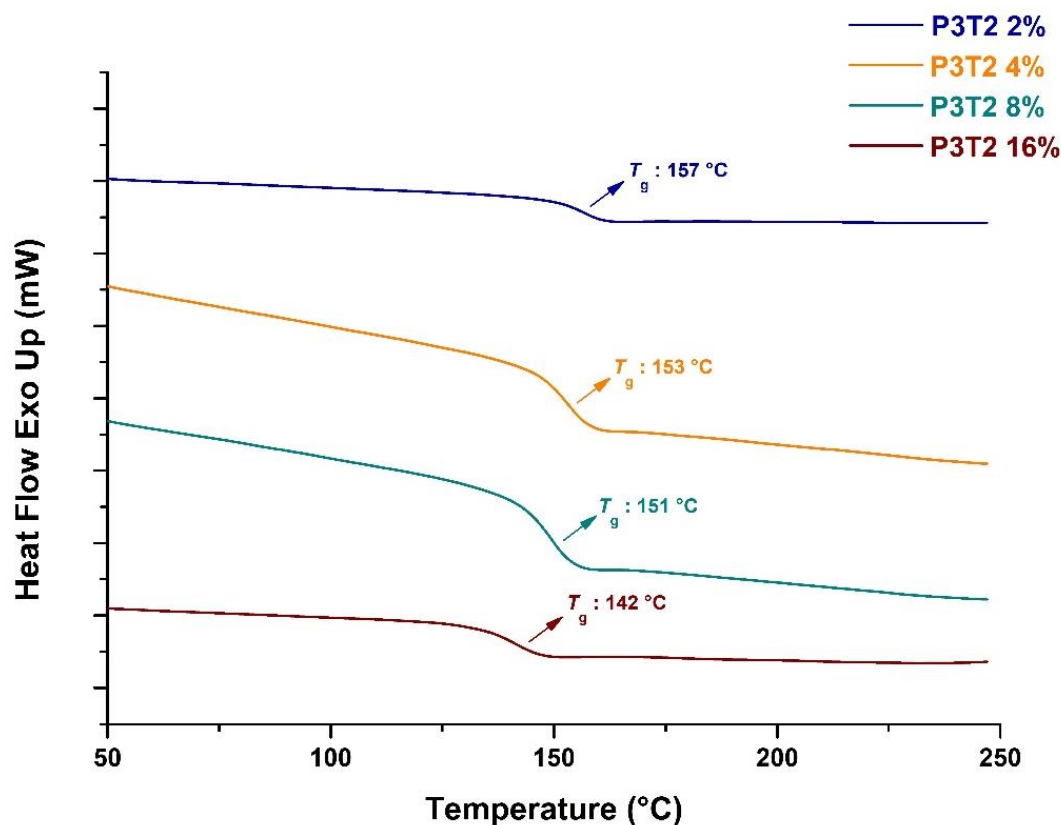


Figure 4.23 : DSC thermograms of P3T2-containing EPs.

Table 4.1 : Thermal properties of the EPs.*

	NITROGEN				AIR				
	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Char %	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Char %	T_g (°C)
DGEBA/F+DDM	384	391	399	19.6	393	399	406	13.1	127
P2T1-2	367	380	394	20.4	367	384	395	12.5	150
P2T1-4	355	366	378	22.4	355	368	382	15.8	154
P2T1-8	335	351	367	20.7	330	347	372	14.4	147
P2T1-16	331	340	360	21.3	325	343	365	18.2	138
P3T2-2	367	377	392	20.5	365	376	388	11.4	157
P3T2-4	354	364	375	22.0	352	365	378	9.7	153
P3T2-8	336	349	364	21.7	335	352	366	13.3	151
P3T2-16	321	336	355	21.0	323	338	353	18.8	142

* T_5 : 5% weight loss temperature, T_{10} : 10% weight loss temperature, T_{max} : maximum weight loss temperature obtained from the corresponding derivative curves, Char percentages were obtained at 750°C, T_g was obtained from DSC measurements.

Neat EP was found to be highly stable under nitrogen atmosphere and did not lose weight almost up to 350 °C. The T_5 and T_{10} temperatures of DGEBA/F+DDM under nitrogen atmosphere was measured as 384 °C and 391 °C, respectively. DGEBA/F+DDM produced as high as 19.6% char yield at 750° C under non-oxidative conditions. The addition the synthesized FRs to the neat epoxy resin lowered the T_5 ,

T_{10} , and T_{max} temperatures. The gradual decrease in these temperatures were attributed to the early decomposition of the FR. The early decomposition of the P-containing flame retardants is a well-documented phenomenon [12, 14, 60].

The addition of P2T1 or P3T2 improved the char yields under N_2 atmosphere but the increases in the char yield values did not follow a trend. Nevertheless, the results clearly proved that the thermal stability of the neat DGEBA/F+DDM was improved with the addition of the synthesized FRs. With respect to the produced char residues under N_2 atmosphere P2T1 and P3T2 displayed the similar performance. The char yields obtained under oxidative conditions did not follow a trend. Similar to the results in the nitrogen atmosphere, T_5 , T_{10} , and T_{max} temperatures also decreased gradually in the air atmosphere as the amount of the FR compounds increased. Under air atmosphere 16% P3T2-containing EP displayed the highest char yield as 18.8%. The char yields under air atmosphere are in good accordance with the theoretical P and N percentages (see Table 4.2) within the FR-containing EPs. Overall, it can be said that all the synthesized FRs in this work improved the thermal stability of the neat DGEBA/DDM system.

4.5 Flame Retardant Properties of The EP

Flame retardancy of the EPs were investigated via UL-94 measurements and LOI tests. The results are collected in Table 4.2. According to UL-94 test, neat EP was classified as V1 while all other studied compositions resulted to V0 classification, indicating a good level of flame retardancy. No dripping was observed in any of the test specimens for all studied compositions and thus the cotton did not ignite. The LOI values were found to correlate with the amount of P and N percentages. In all cases the LOI values increased with increasing amount of the FR. The LOI value for the neat DGEBA/F+DDM system was found as 26%. The addition of only 2-4% of the synthesized FRs were enough to increase the LOI value to above 30%. Recently Zhang et al, prepared triazole-containing phosphorus FRs for epoxy resins and the LOI value of the neat epoxy resin was raised from 25% up to 33.5% (7.5% FR containing specimens) [15].

The maximum LOI value was reached for the 16% P3T2-containing composition and it was as high as 47.4%. The high LOI values obtained in this work are due to the synergistic effect of P and N. It is known that N-containing FRs mostly act in the gas

phase; upon combustion they decompose, release gases like ammonia, and thereby dilute the gas phase and decrease the oxygen concentration in the gas phase [12, 24, 58, 60]. Whereas P-containing FRs generally lead to early decomposition upon ignition and generate species like phosphoric acid which catalyze the formation of a carbonaceous char. This char impedes the transfer of heat and oxygen to the rest of the material and thus the propagating flame extinguishes [60]. Furthermore, when P and N atoms are present, the FR compound can exhibit a feature known as intumescent property. Intumescent FRs swell upon combustion and lead to the formation of a foam like carbonaceous char which is very effective for fire-protection. Figure 4.24 displays the digital images of the selected test specimens after the LOI test. As can be seen from these images P2T1-16 and P3T2-16 have the intumescent character. The elemental N/P ratios of P2T1 and P3T2 are 0.68 and 0.90, respectively. As can be seen from these ratios the P3T2 has the highest N/P ratio. P3T2 whose N/P ratio is almost 1, displayed the best flame retardant performance to the P2T1 studied herein.

Table 4.2 : UL-94 and LOI test results.

	%P	%N	LOI	UL-94
DGEBA/F+DDM	-	3.11	26.0	V1
P2T1-2	0.1786	0.1402	28.4	V0
P2T1-4	0.3572	0.2804	32.7	V0
P2T1-8	0.7144	0.5608	40.6	V0
P2T1-16	1.4288	1.1216	42.5	V0
P3T2-2	0.206	0.1614	30.2	V0
P3T2-4	0.4132	0.3228	34.3	V0
P3T2-8	0.8264	0.6456	45.6	V0
P3T2-16	1.65	1.2912	47.4	V0

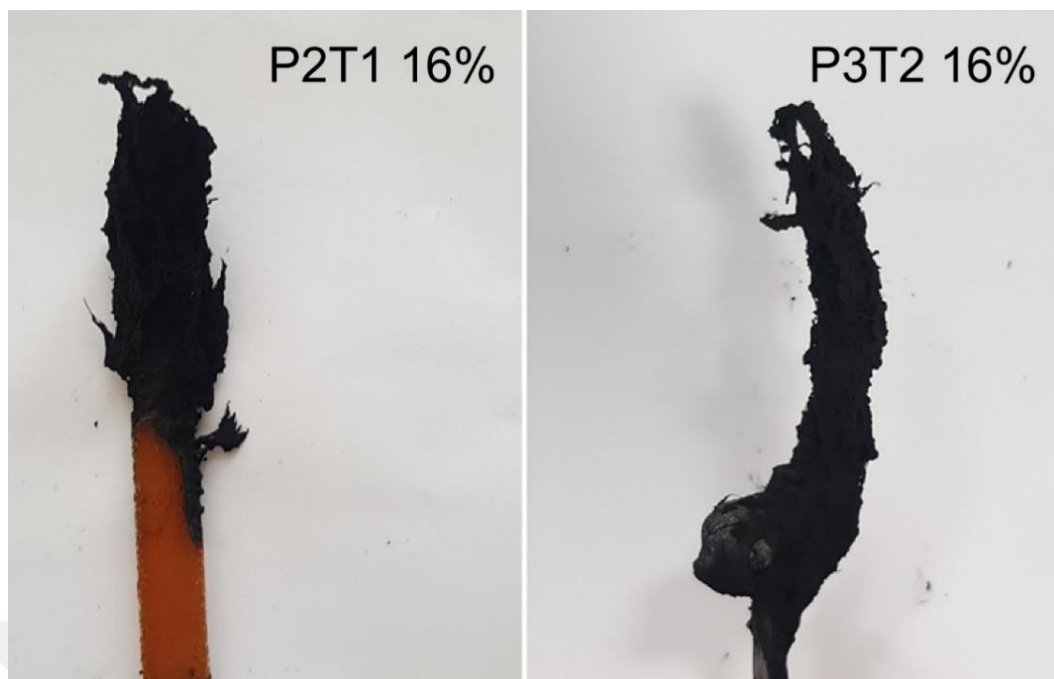


Figure 4.24 : Digital images of the FR-containing EPs after the LOI test.

4.6 Wettability of The EPs

EPs are widely used as adhesives or matrix materials for preregs (composites). Glass or carbon fibers are used for epoxy preregs and it is essential for the epoxy resin to easily spread and adhere on the fiber surface. The wettability of the epoxy resin can be assessed by measuring the WCA values of the cured epoxy resins. The WCA values of the EPs studied in this work are plotted in Figure 4.25 and the representative contact angle images are presented in Figure 4.26. The WCA of the neat DGEBA/F+DDM system was found as $74^{\circ} \pm 2$. The addition of the FR compounds led to a gradual decrease in the WCA values. This was attributed to the presence of polar triazole and phosphorus groups which lead to more hydrophilic surfaces [37, 38]. From Figure 4.25 it can be seen that P3T2 and P2T1 gives almost similar results up to 16% of FR addition however, the highest amount of FR-containing samples are compared, P3T2-16 leads to a more hydrophilic surface than P2T1-16.

Finally, it can be said that the FR-containing EPs become much more polar which is beneficial for composite preparation.

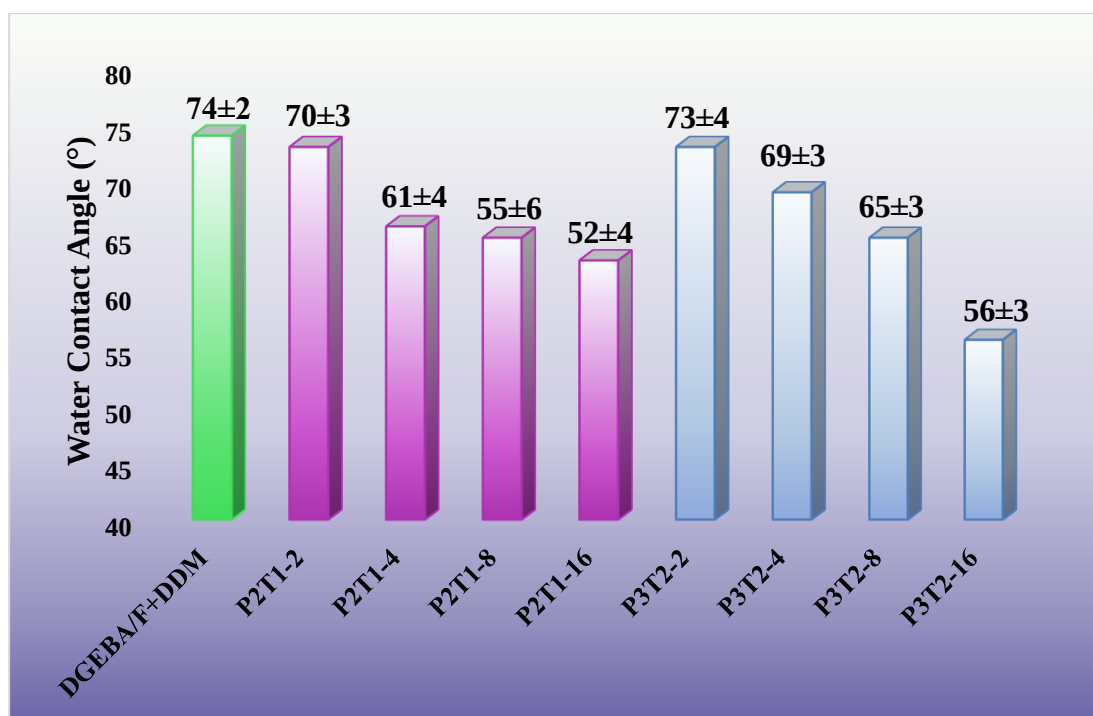


Figure 4.25 : WCA values of FR-containing EPs.

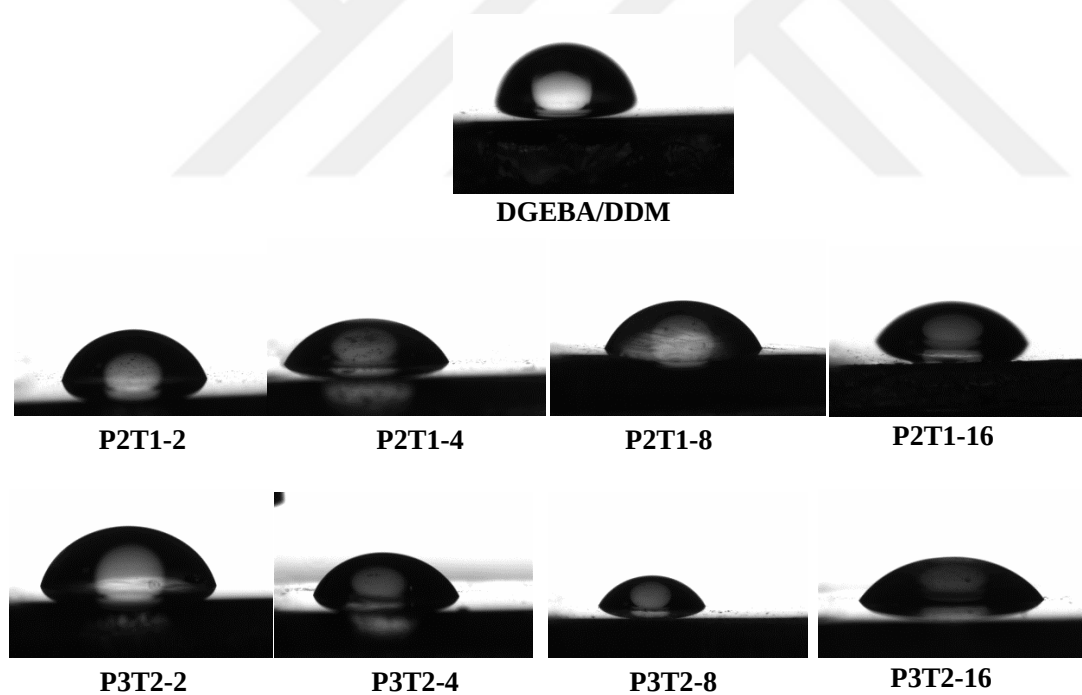


Figure 4.26 : WCA images of the epoxy thermosets.

5. CONCLUSION

In summary, triazole- and P-containing FRs via metal-free click reactions of activated alkynes. The synthesized FRs were characterized via FTIR, ^1H NMR, ^{13}C NMR, and ^{31}P NMR. The synthesized FRs led to early decomposition temperatures but significantly improved the char yields of the epoxy resins. FR-containing EPs exhibited superior flame retardancy values and intumescent behavior. The LOI values were found to increase with increasing amount of the FRs. The highest LOI value was 47.4% and it was achieved with 1.65% P- and 1.29% N- containing thermosets (P3T2-16). The presence of polar triazole and phosphorus units led to hydrophilic surfaces.

With this study, a new chapter in the synthesis of flame-retardants for epoxy resins has been opened. This study is believed, the use of activated alkynes and metal-free click chemistry will lead to new horizons in the future and enable the emergence of new flame retardants.



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APPENDICES

APPENDIX A: ^{13}C Spectra, ^{31}P NMR Spectra and TGA Thermograms



APPENDIX A

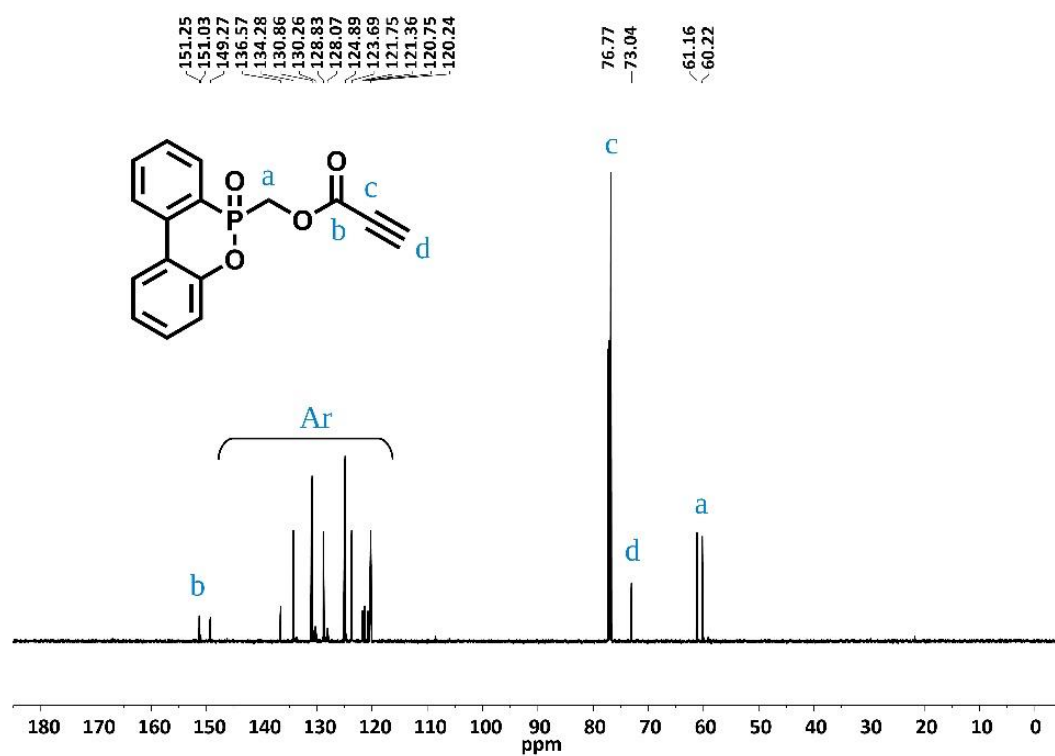


Figure A.1 : ^{13}C NMR spectrum of DOPO-propiolate.

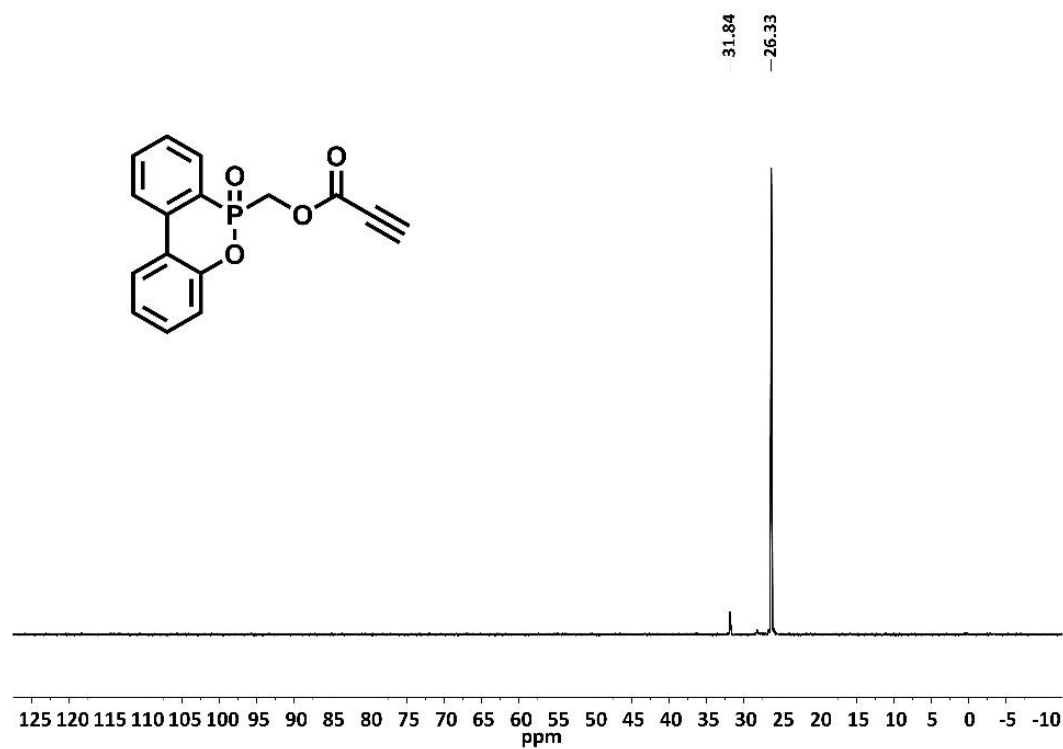


Figure A.2 : ^{31}P NMR spectrum of DOPO-propiolate.

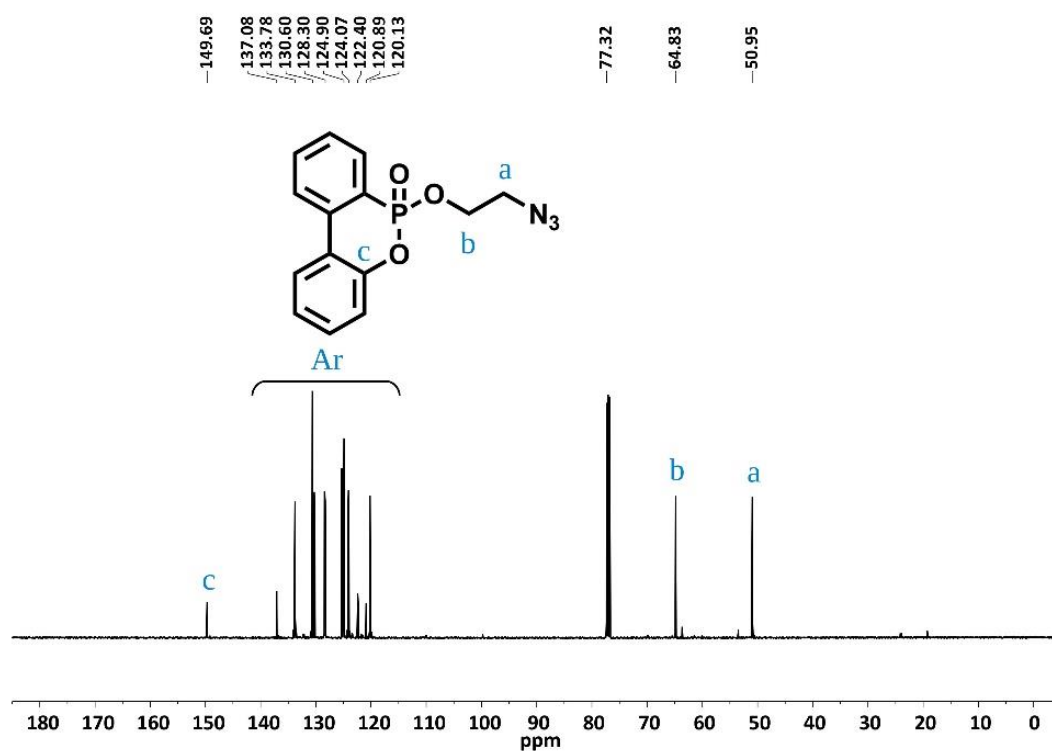


Figure A.3 : ¹³C NMR spectrum of DOPO-N₃.

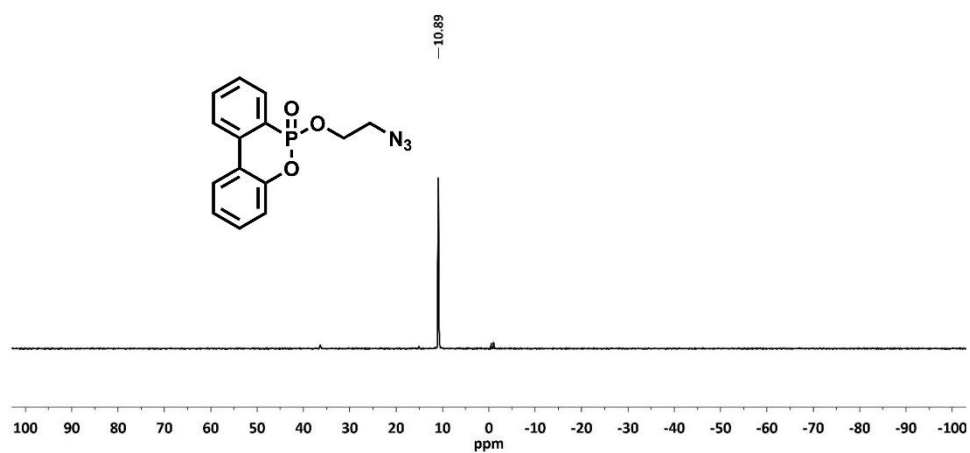


Figure A.4 : ³¹P NMR spectrum of DOPO-N₃.

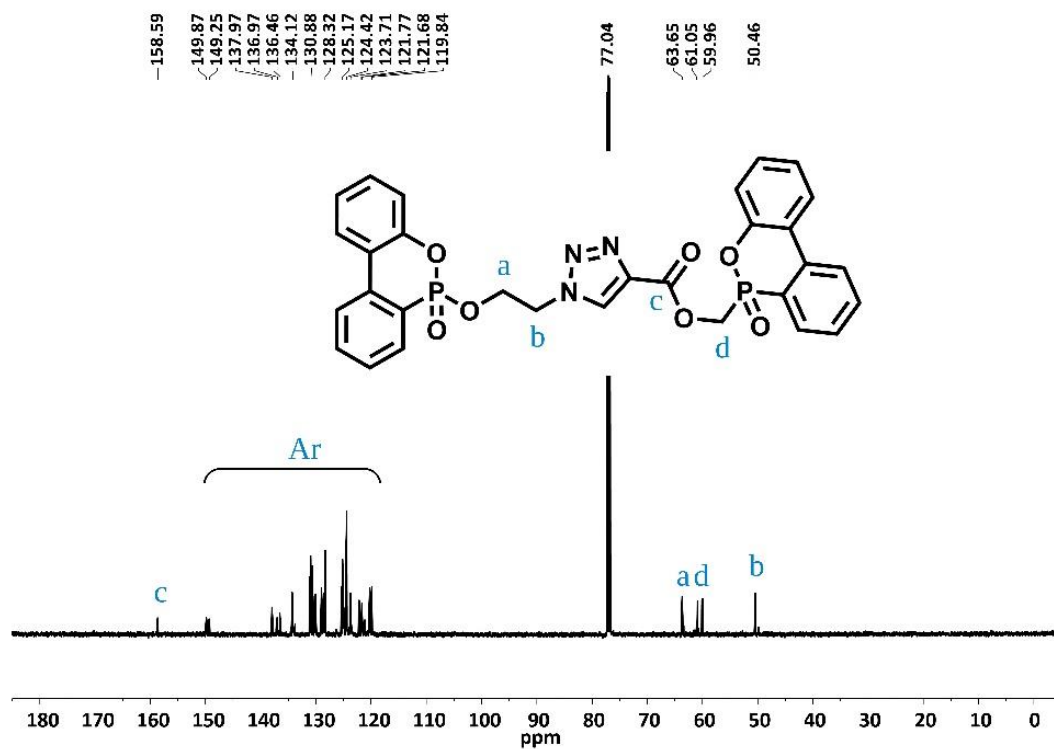


Figure A.5 : ¹³C NMR spectrum of P2T1.

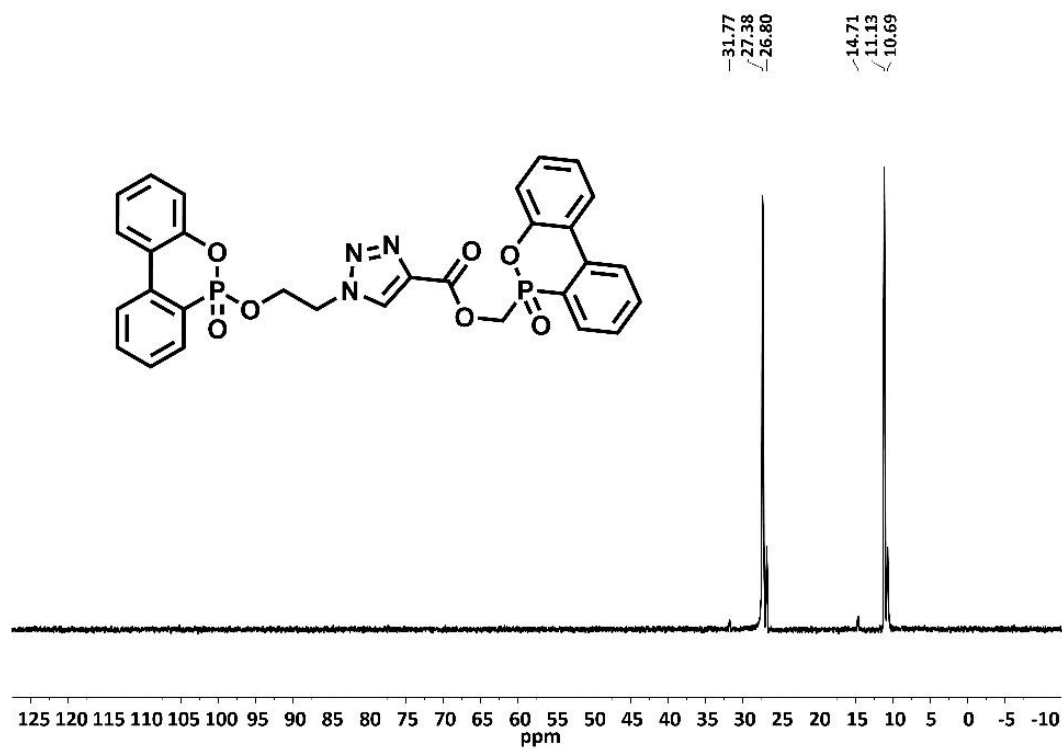


Figure A.6 : ³¹P NMR spectrum of P2T1.

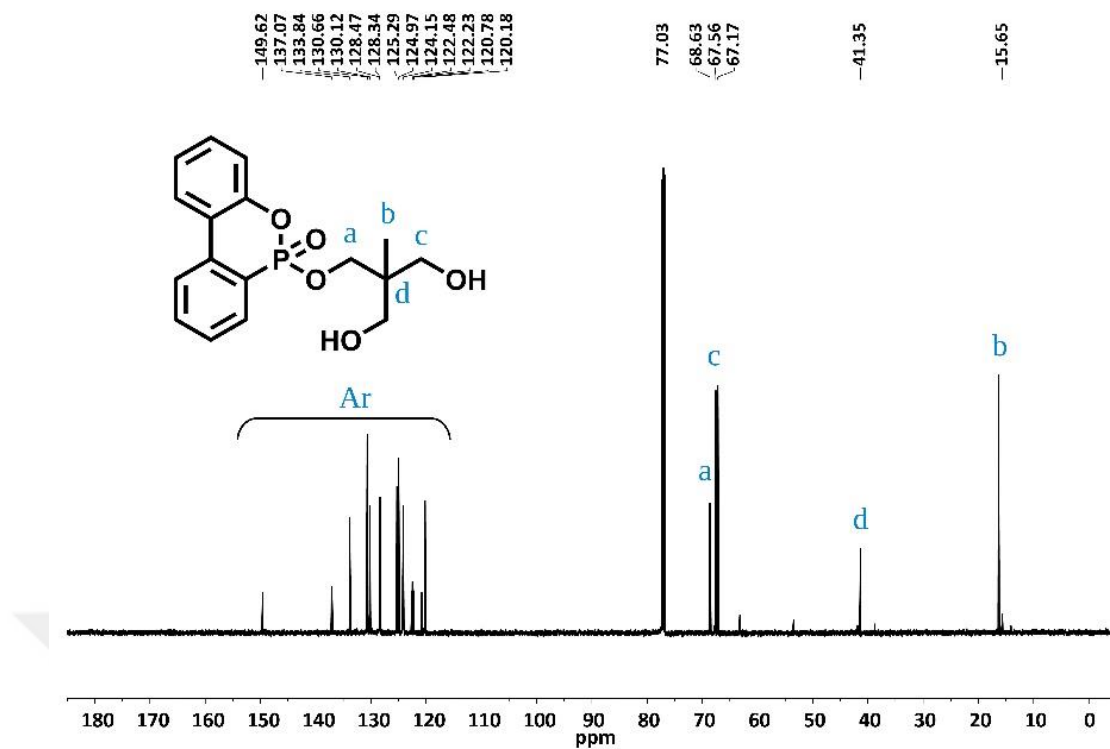


Figure A.7 : ¹³C NMR spectrum of DOPO-diol.

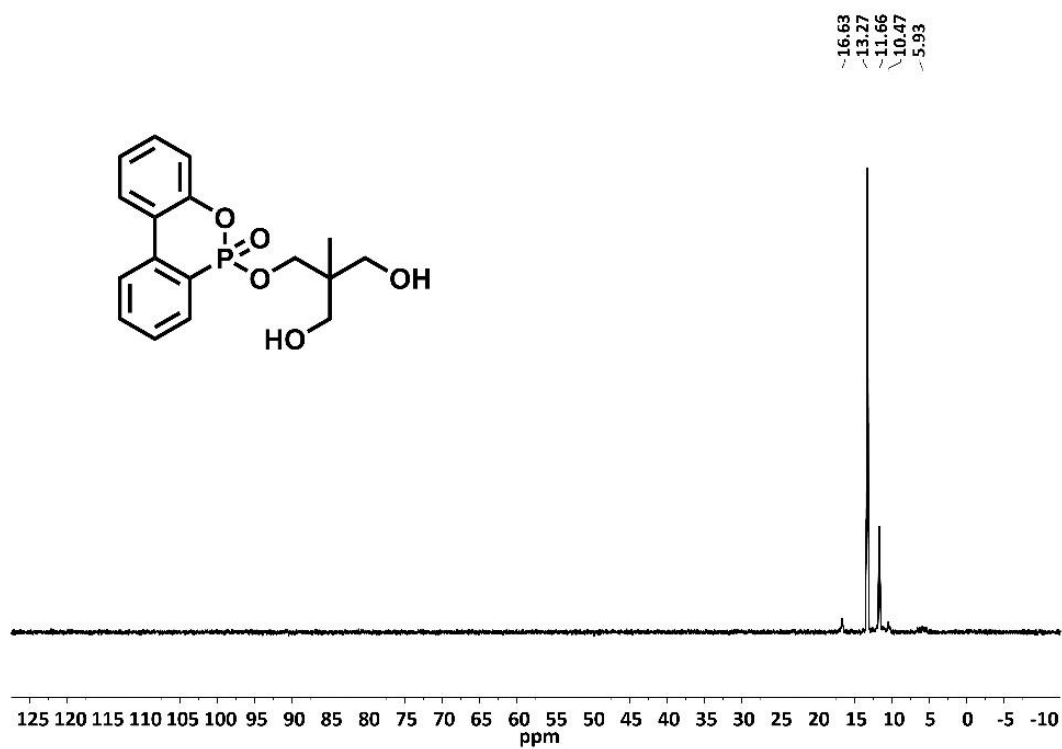


Figure A.8 : ³¹P NMR spectrum of DOPO-diol.

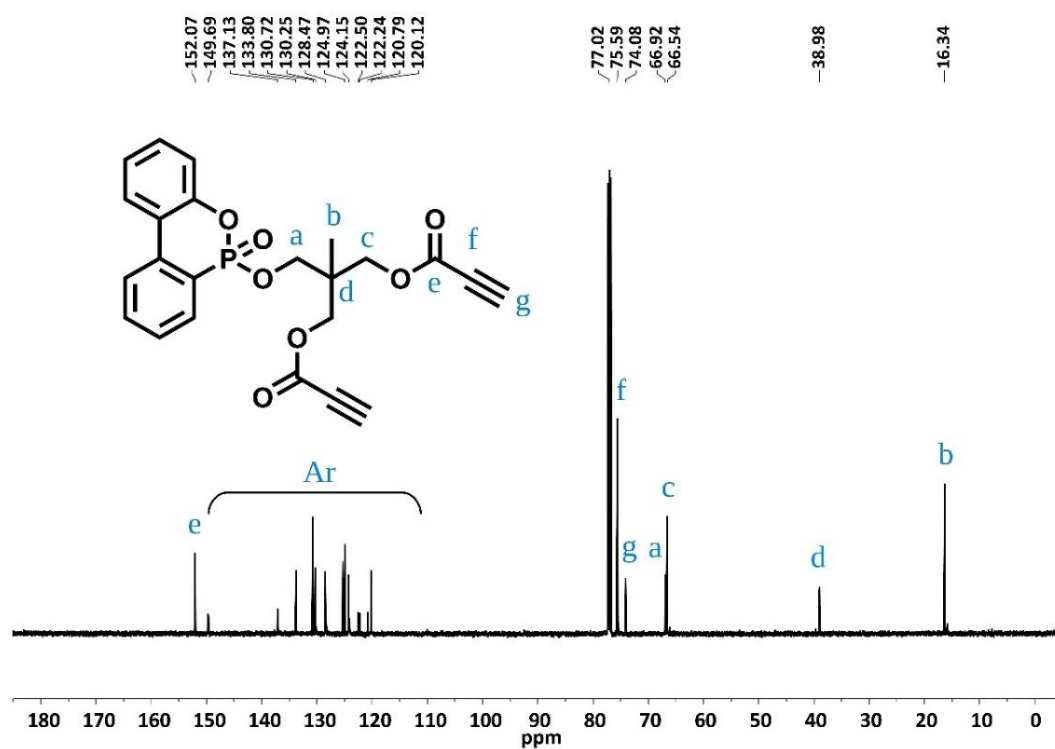


Figure A.9 : ^{13}C NMR spectrum of DOPO-dipropiolate.

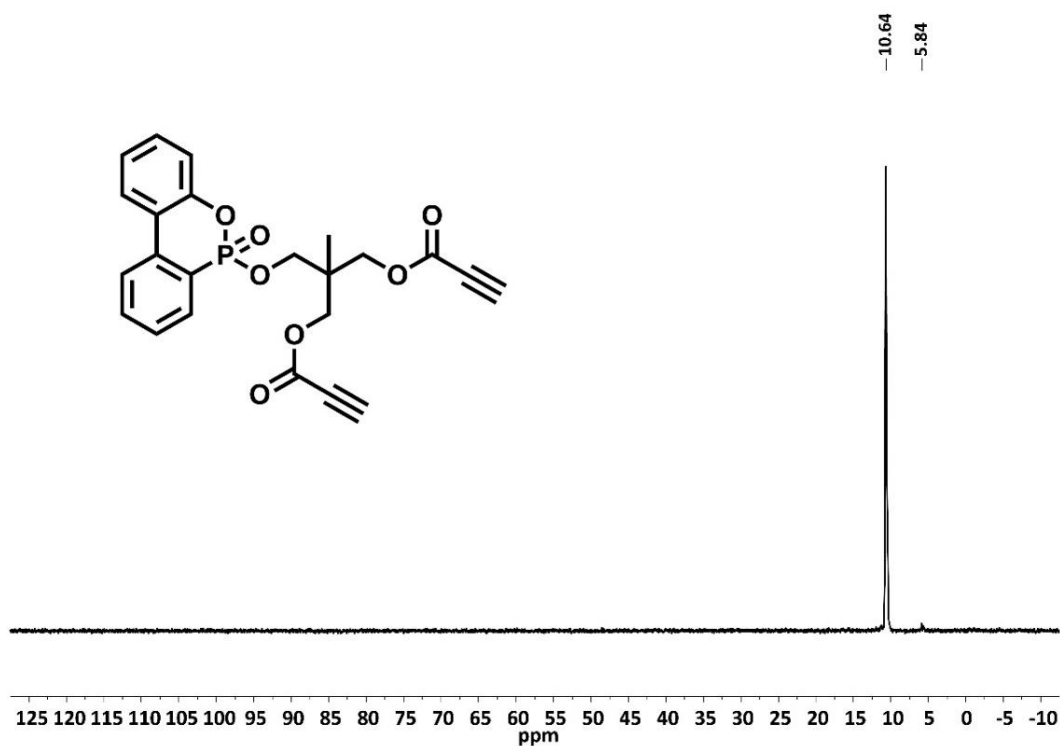


Figure A.10 : ^{31}P NMR spectrum of DOPO-dipropiolate.

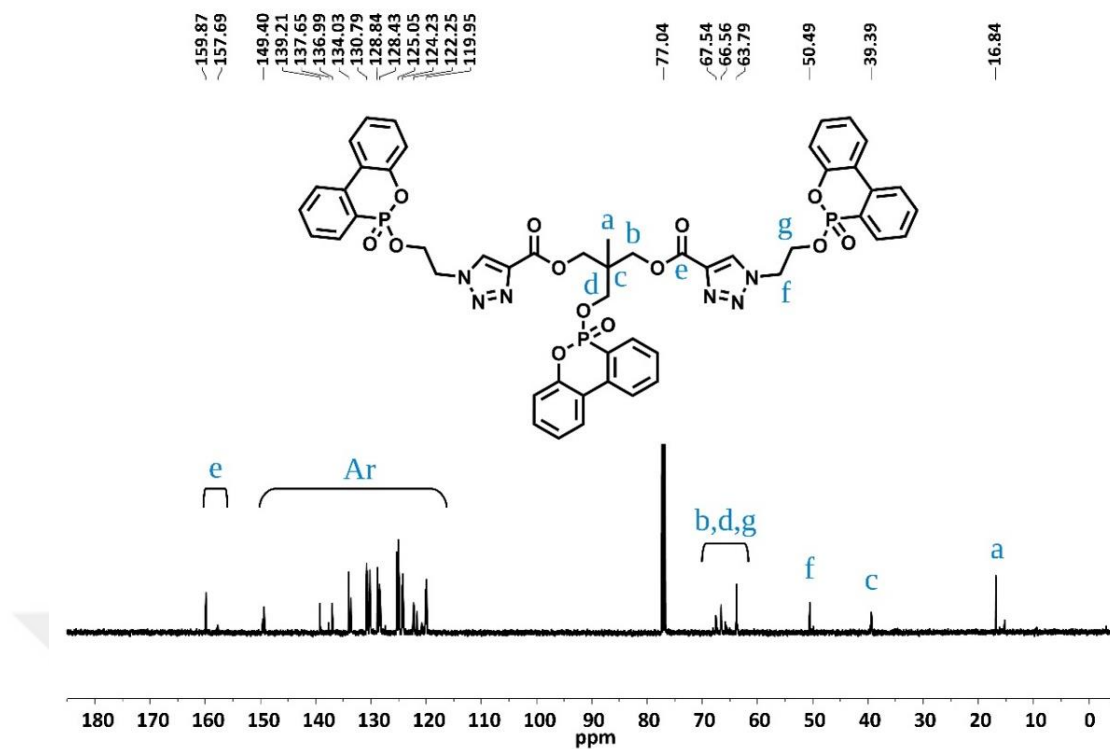


Figure A.11 : ¹³C NMR spectrum of P3T2.

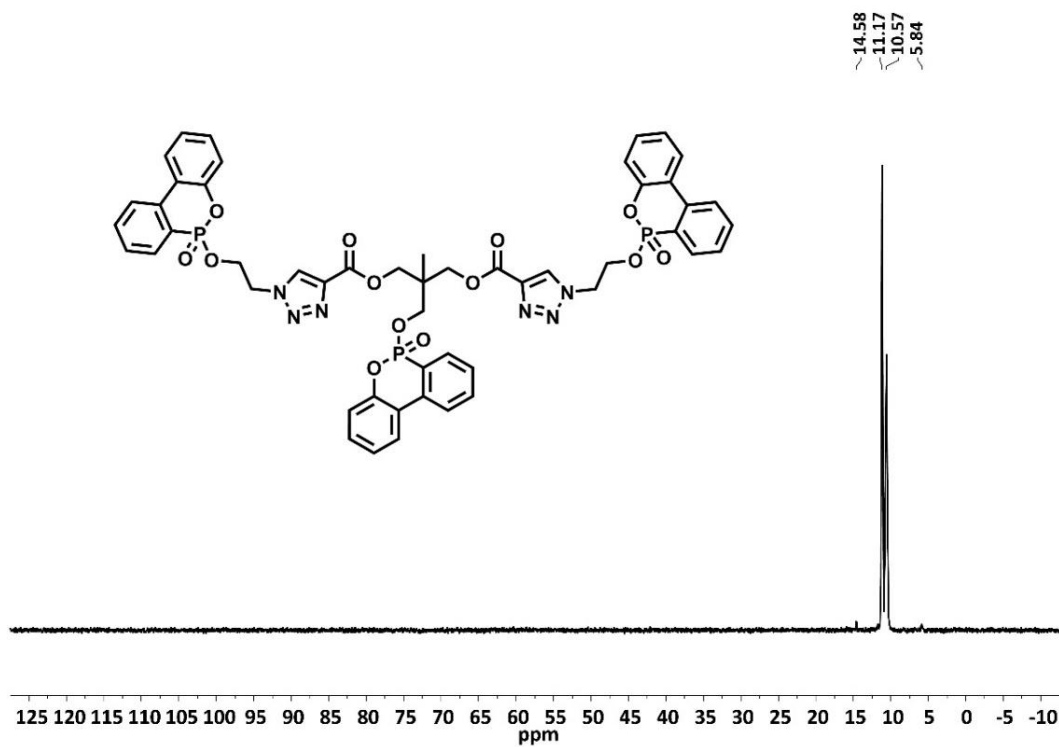


Figure A.12 : ³¹P NMR spectrum of P3T2.

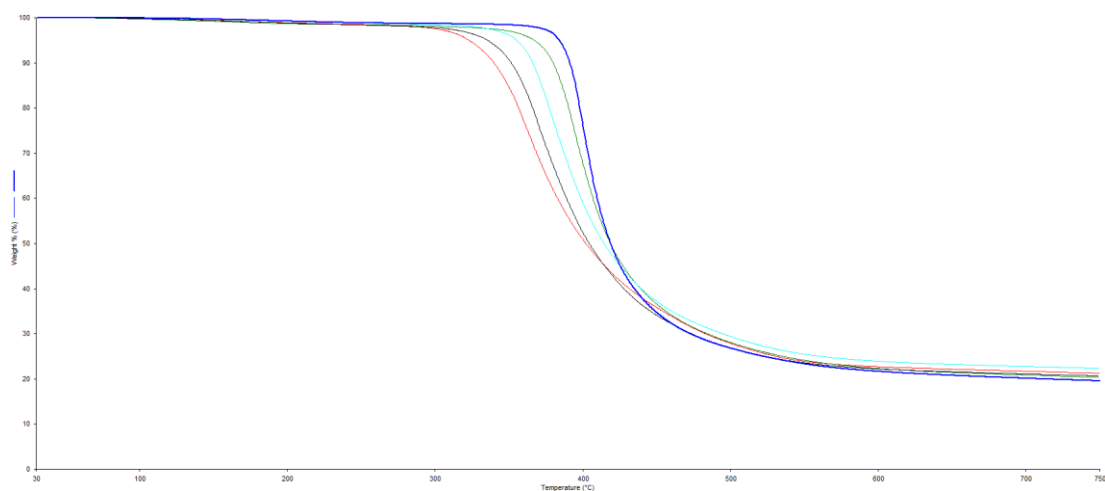


Figure A.13 : TGA thermograms of neat EP and P2T1-containing thermosets in nitrogen atmosphere.

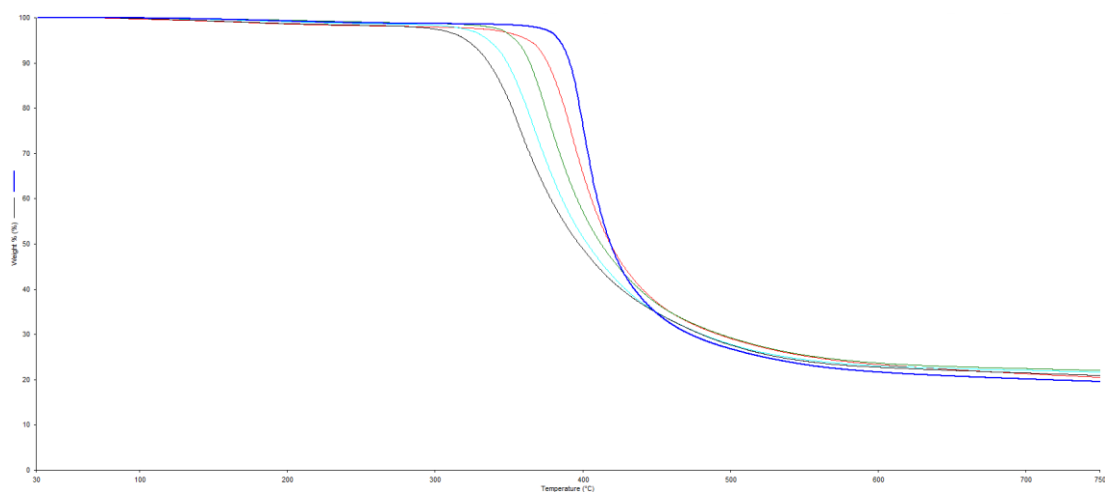


Figure A.14 : TGA thermograms of neat EP and P3T2-containing thermosets in nitrogen atmosphere.

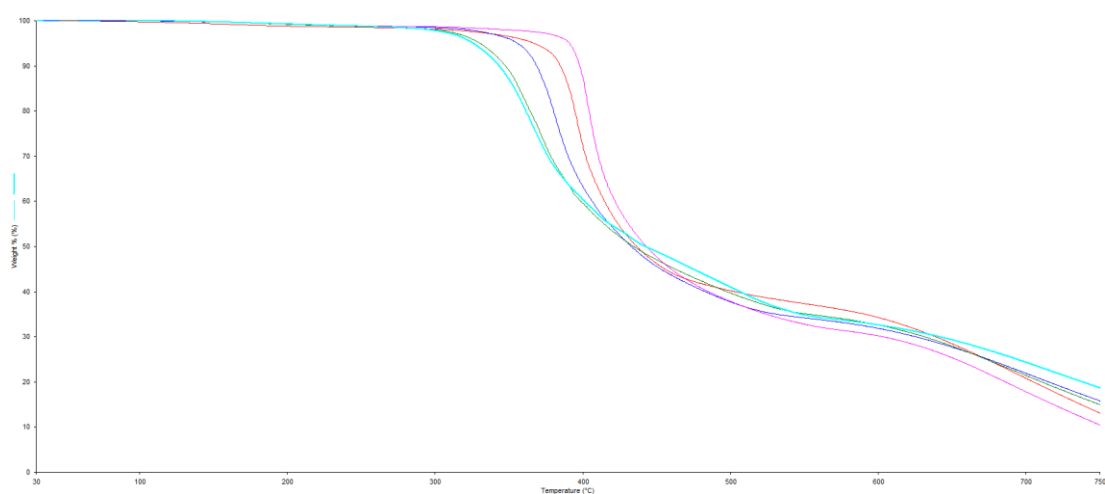


Figure A.15 : TGA thermograms of neat EP and P2T1-containing thermosets in air atmosphere.

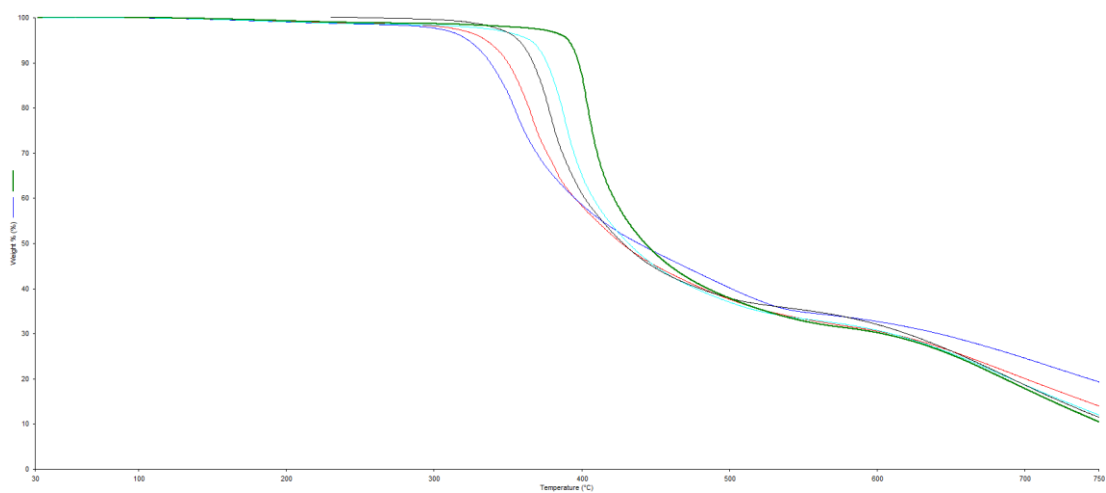


Figure A.16 : TGA thermograms of neat EP and P3T2-containing thermosets in air atmosphere.



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