REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

IN-SITU SYNTHESIS OF Au, Ag, MnO and Fe_2O_3 NANOPARTICLESWITH THIOXANTHONE-ANTHRACENE AND INVESTIGATION OF THE EFFICIENCY OF PHOTOINITIATOR

Uğur BAYRAK

MASTER OF SCIENCE THESIS

Department of Chemistry
Physical Chemistry Program

Supervisor

Prof. Dr. Nergis ARSU

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A thesis submitted by Uğur BAYRAK in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE is approved by the committee on 24.02.2022 in Department of Chemistry, Physical Chemistry Program

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Uğur BAYRAK

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LIST OF SYMBOLS

A	Absorbance
l	Amount of Light
C	Concentration
ΔE	Energy Gap
E	Energy of Photons
ν	Frequency
R	Gas Constant
I_0	Intensity of Light
ε	Molar absorptivity
l	Path length of the cuvette containing the sample
h	Planck's Constant
Φ	Quantum Yield
c	Speed of Light
T	Temperature
σ *	The anti-bonding orbital
π *	The anti-bonding orbital
π	The bonding orbital
σ	The bonding orbital
λ	Wavelength

LIST OF ABBREVIATIONS

A	Anthracenes
AuNps	Gold Nanoparticles
AgNps	Silver Nanoparticles
DMF	Dimethylformamide
HOMO	The highest energy occupied molecular orbital
LUMO	The lowest energy unoccupied molecular orbital
MO	Moleculer orbital
Nps	Nanoparticles
PEGDA	Poly(ethylene glycol) diacrylate
PEGMEA	Poly(ethylene glycol) methyl ether acrylate
SPR	Surface Plasmon Resonance
TX	Thioxanthone
TX-A	Thioxanthone-Anthracane
UV	Ultraviolet
VIS	Visible

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ABSTRACT

In-Situ Synthesis of Au, Ag, MnO And Fe_2O_3 Nanoparticles With Thioxanthone-Anthracene And Investigation of The Efficiency of Photoinitiator

Uğur BAYRAK

Department of Chemistry

Master Of Science Thesis

Supervisor: Prof. Dr. Nergis ARSU

A photoinitiator is a chemical that, when exposed to light, performs a photoreaction, resulting in reactive species. These are capable of starting or catalyzing chemical processes that alter the solubility and physical characteristics of appropriate formulations significantly. As a result, a photoinitiator is a substance that can convert light's physical energy into chemical energy in the form of reactive species.

Thioxanthone-Anthracene (TX-A) was used as a one-component Type II photoinitiator for preparation of Au, Ag, MnO ve Fe_2O_3 nanoparticles.

In this study, we have seen that nanoparticles (NPs) are distributed differently in solution and in polymer matrices and that the particle size also changes. The size of the AuNPs synthesized in the solution in the presence of air atmosphere is smaller than the AuNPs synthesized in the polymer matrix.

Keywords: Photoınıtıator, photopolymerızatıon, thıoxantone anthracane, nanopartıcle, metaloxides

ÖZET

Au, Ag, MnO ve Fe_2O_3 Nanoparçacıklarının Tiyokzanton Antrasen Fotobaşlatıcısı Beraberinde In-Situ Olarak Hazırlanması ve Başlatıcının Etkinliğinin İncelenmesi

Uğur BAYRAK

Kimya Anabilim Dalı

Yüksek Lisans Tezi

Danışman: Prof. Dr. Nergis ARSU

Fotobaşlatıcılar, ışık absorpsiyonu sonucunda reaktif başlatıcı radikalleri üreten, fotopolimerizasyon tekniğinin en önemli bileşenleridir. Fotobaşlatıcılar, uygun formülasyonlarda fiziksel özelliklerinde önemli değişiklikler ile sonuçlanan kimyasal reaksiyonları başlatma veya katalize etme yeteneğine sahiptir. Bu çalışmada farklı bir fotobaşlatıcı seçilerek farklı nanoparçacıkların in-situ fotokimyasal yöntem kullanılarak hazırlanması amaçlanmıştır. Au, Ag, MnO ve Fe_2O_3 nanoparçacıklarının tiyokzanton antrasen (TX-A) fotobaşlatıcısı beraberinde in-situ olarak hazırlanması ve başlatıcının etkinliğinin incelenmesi hedeflendi. Tiyokzanton antrasen'in reaktif başlatıcı radikalleri üretebilmesi için oksijene ihtiyaç duyması sebebiyle, nanoparçacıkların hazırlanmasında deneyler hem hava ortamında hem azot ortamında gerçekleştirildi.

Sonuç olarak, Au, Ag, MnO ve Fe_2O_3 nanoparçacıklarının fotokimyasal sentezinde tiyokzanton antrasen'in önemli bir fotoindirgeyici bileşik görevi gördüğüne deneysel sonuçlar neticesinde karar verildi.

Anahtar Kelimeler: Fotobaşlatıcı, fotopolimerizasyon, tiyokzanton antrasen, nanoparçacık, metal oksit

1
INTRODUCTION

1.1 Literature Review

Nanocomposites are the matter that have one of the phases shows properties in the nanometer rates. [1] These materials have high performance that exhibit uniqe property combinations and design possibilities and are thought of as the materialsof the last century. [2]

There are applications of photopolymerization from nanocoatings to dental applications [3] For these applications well suited technic is photopolymerization because of its usefull applications. In addition, the reaction that using photopolymerization may also be controlled both temporally and spatially. For that reason, When preparing nanocomposite, the most used method is photopolymerization because it lets the polymer chain form into thin films with uniqe properties [4]

Formulations that can be polymerizable have some additives, oligomers, photoinitiators and reactive parts. These incredients, the photoinitiator has uniqe role in the last properties of the nanocured coating [5]

Photoinitiators are molecules that can absorb light and create reactive initiator radicals, are the most wanted components of UV and polymerization systems. Photoinitiated radical polymerization may be initiated by bond cleavage and H-abstraction-type initiators. [5]

1.2 Objective of the Thesis

The aim of the work was to see how effective Thioxanthone anthracene (TX-A) is in preparing Au, Ag, MnO, and Fe_2O_3 Nps in solution or in a polymer matrix. Because TX-A requires oxygen to make the starting radicals, studies were carried out in both an air and nitrogen environment to examine how nanoparticles were formed. TX-A was discovered to be an exceptionally effective photoreducing agent for the preparation of Au, Ag, Fe_2O_3 and MnO Nps.

1.3 Hypothesis

The photochemical synthesis method has attracted much attention by offering several advantages e.g. convenience, speed, low cost, green and space selectivity. Photoinitiators play the most important role part of the photochemical system

We report here the use of TX-A as photoreducing agent for metal and metaloxide salts to nanoparticles. Shape, size and distribution control was achieved extremely well by using of TX-A either in solution or in polymer matrix.

2

THEROTICAL PART

2.1 Electromagnetic Radiation

Electromagnetic radiation is a kind of energy created by alternating electric and magnetic instabilities, or by charged particles moving through a vacuum or substance. Magnetoelectric fields intersect at direction perpendicular, and the merged wave travels parallel to both magnetoelectric pulsing regions. Photons are boxes of light energy that move at the speed of light as quantified waves propagating when electron radiation is emitted. The wavelength of this energy in the electromagnetic spectrum is used to categorize it. These electric and magnetic waves have properties, such as wavelength, amplitude, and frequency, and they travel perpendicular to each other. [6]

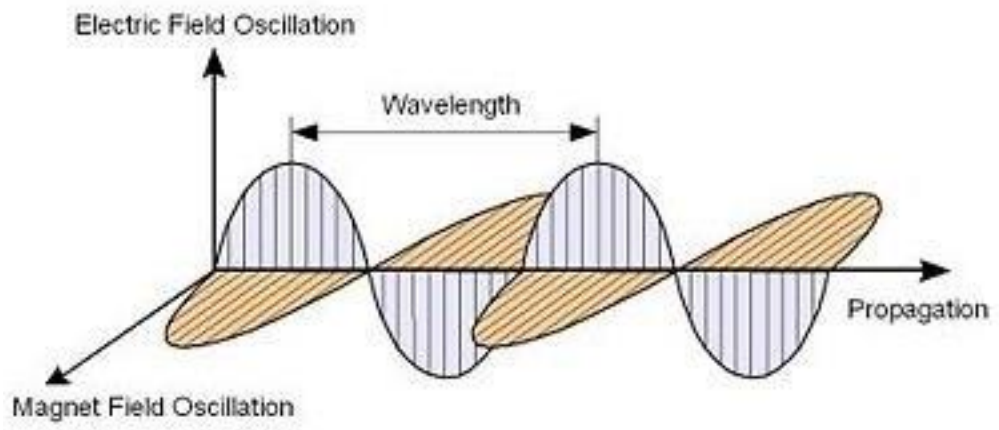

Figure 2.1 Electromagnetic wave

In model that shows wave, electromagnetic radiation is characterized by a wavelength, λ, a frequency, ν, and a velocity, c.

According to PLANCK-EINSTEIN correlation, distinction between the different classes can be shown as;

$$E = h\upsilon = hc / \lambda \quad (J.foton\text{-}1) \qquad (2.1)$$

E= Energy of photons

h = Planck's constant (6,6256x10-34 J.s.foton^{-1})

υ = frequency (s^{-1})

c = Speed of light (2,9979x10^{8} m.s^{-1})

λ = Wavelength (nm)

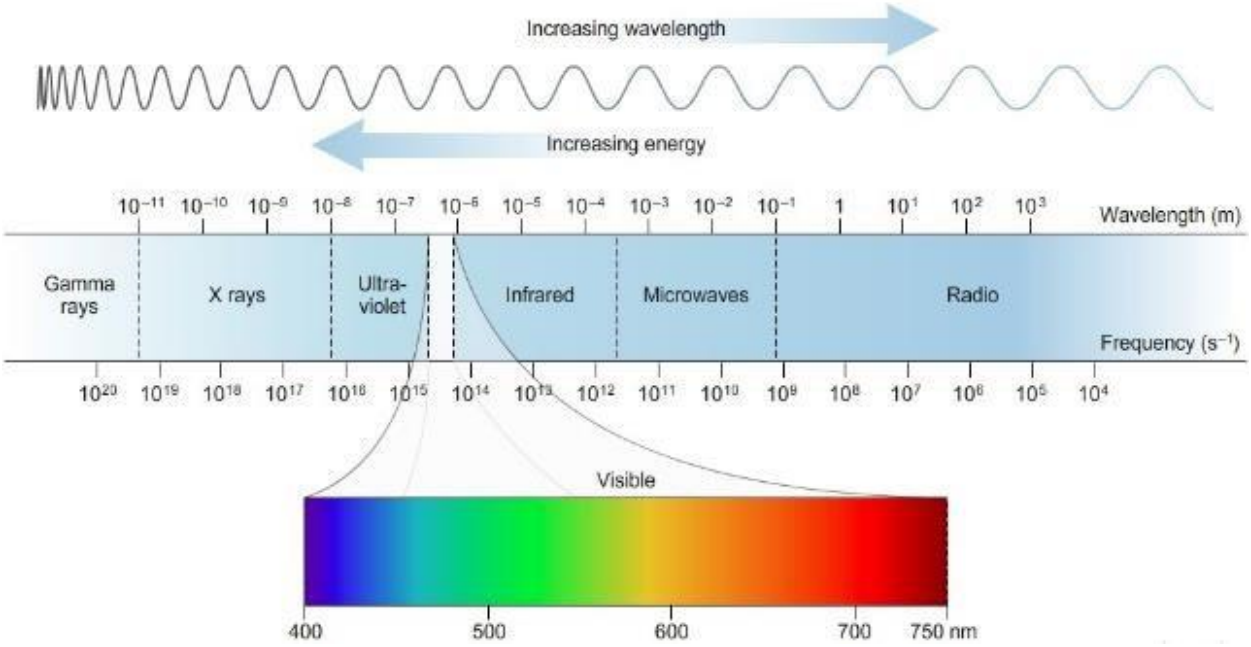

Figure 2.2 Electromagnetic spectrum

2.1.1 Excitation by Absorption

A molecule is promoted from its initial state to an electrically excited state by light excitement with a beam of sufficient energy. Because light stimulation produces changes in a molecule's electronic structure, each type of higher energy state has its own molecular orbital distinct from the ground state. The electronic structure of a molecule is affected by its chemical and physical characteristics, and that is why each exciton will have its own physical and chemical features. [7]

Light excitation with an adequate energy beam promotes a molecule from its original state to an electrically higher energy state. Because light stimulation modifies the electronic structure of a molecule, each higher energy state has its own molecular orbital that is unique from the ground state. Because a molecule's electrical structure is influenced by its physical and chemical characteristics, each exciton will have its unique physical and chemical characteristics. [8]

As a result, light excitation expands the scope of chemistry and physics. To chemistry, since as compared to the ground state, excited states can respond in a variety of ways, both qualitatively and quantitatively. To physics, since each excited state seems to have its unique absorption spectrum (color) and may be deactivated by photophysical processes, such as light emission. [9]

Photophysics and photochemistry and are the results of the interaction of electromagnetic radiation and matter. It deals with the nature of light before proceeding to describe photochemical and photophysical processes. [10]

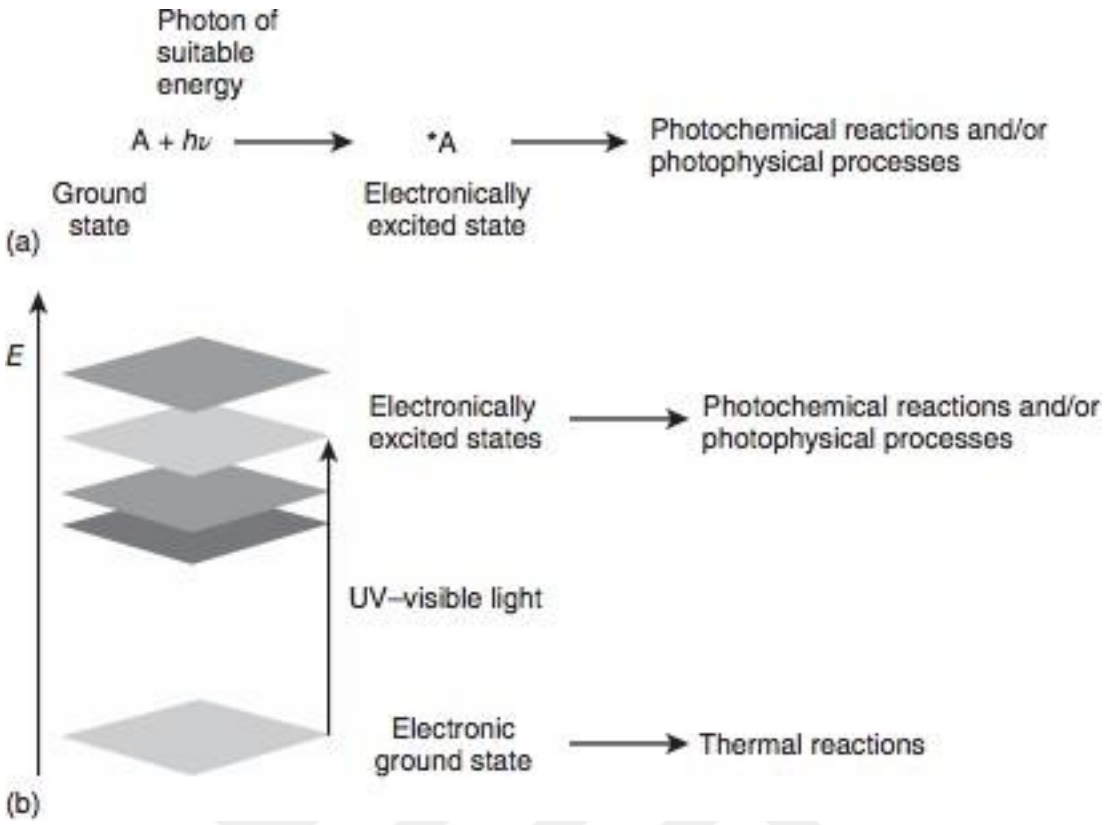

Figure 2.3 Light excitation

2.2 Photochemistry

Photochemical reactions are processes that occur when chemical systems are exposed to light, and photochemistry is the discipline that studies them. With the development of many techniques that allow direct measurements on reactive intermediates and molecules in electronically excited states over the last 20 years, the phrase photochemical reaction has carried on a rather clear definition: a photochemical reaction begins with the appearance of the first ground-state product and ends with the appearance of the first electronically excited state product (s). Photochemical reactions, in other words, are a type of electronic excited state that does not return to the original molecule. [11]

2.2.1 The Photochemical Process

When light is absorped photocemical process starts and goes with the change of electronic configurations. Some changing can be occured when the excitation is done [12]

1) The compound goes into the new energy structure for the excited state byvibronic relaxation. Energy is given into the solvent.

2) By spin inversion, intersystem crossing leads to triplet states. The new energyminimum is reached by vibrational relaxation.

3) Spreading of light and return to the ground state (luminescence, fluorescence, phosphorescence).

4) Quenching of the exited state: Energy is transferred to different molecule in themedium. Usually we observe diffusion controlled dynamic quenching by collision.

5) Radiationless deactivation. Molecule goes back to ground state by vibrational(thermal) deactivation. The energy goes to the solvent/environment of molecule [8]

2.2.2 Lambert – Beer Law

When light of a certain wavelength reaches the sample tube in a spectrophotometer, some gets to the detector, some of it is absorbed by the sample, , and some is lost due to leaving from tube surfaces, bending by the solution, or scattering from microscopic particles floating in the sample.When the concentration of the light source entering our sample (I0) is compared to the intensity of the light source departing our sample (I), the ratio I/Io is used to calculate the proportion of the light that enters the sample that was discovered exiting the sample. The Transmittance is the name given to this ratio. [13]

$$T = I / I0 \quad (2.2)$$

After obtaining absorbance, the negative logaritm of transmittance is calculated. The quantity of molecules in a solution is determined by the absorbance of light.

$$A = - \log I / I0 \quad (2.3)$$

The Beer-Lambert law describes the relationship between a solution's concentration and the quantity of light absorbed by the solution.

$$A = \varepsilon l C \quad (2.4)$$

Which are;

C = Concentration of the compound in the solution (mol L^{-1})

l = Path length of the cuvette containing the sample (cm)

ε = Molar absorptivity (L mol^{-1} cm^{-1})

A = Absorbance

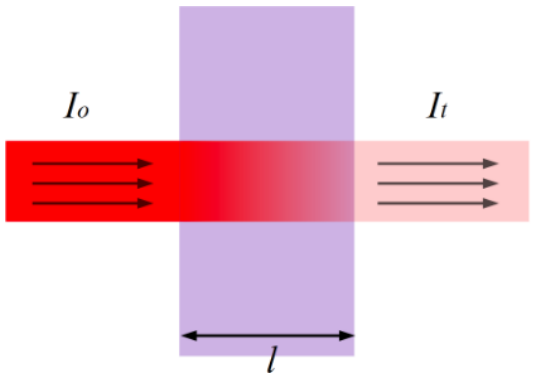

Figure 2.4 Schematic representation of Lambert-Beer law

2.2.3 Quantum Yield

The reaction's quantum yield is significant quantitative measurements of a reactions that goes under the photochemistry [14]

If we divided number of seperated photons by number of taken photons it gives the quantum yield.

Calculated from reacted electrons divided by the absorbed photons is the actual quantum efficiency. However,determinations of absorbed photons by photocatalystin a dispersed system is hard because of emitted and lost light [15].

For a photochemical reaction, quantum yield can be defined as:

$$\Phi(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}} \qquad (2.5)$$

2.2.4 Molecular Orbital Theory

The distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals is described as molecular orbital theory. Using quantum mechanics, the behavior of an electron ina molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin. The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals.[16]

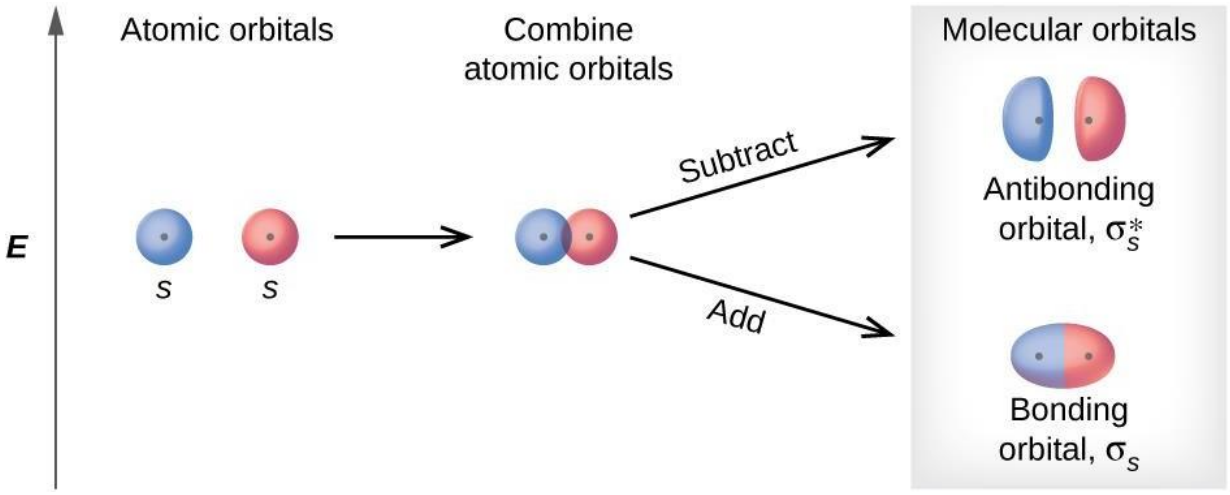

Figure 2.5 Formation of moleculer orbitals from atomic orbitals

The wavelike properties of an electron is described as the wave function. Molecular orbitals are mixtures of atomic orbital wave functions. Integrated waves can lead to constructive interference or devastating interference here are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The in-phase combination creates a lower energy σ_s molecular orbital in which most of the electron concentration is directly between the nuclei. The out-of-phase addition generates a higher energy $\boldsymbol{\sigma_s^*}$ molecular orbital molecular orbital in which there is a node between the nuclei. The asterisk means that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable than they would be in the isolated atoms. Bonding orbitals are created by putting electrons to these orbitals to produce a force that holds the two nuclei together. Electrons in the σ_s^* orbitals are well placed away from the area between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals [17]

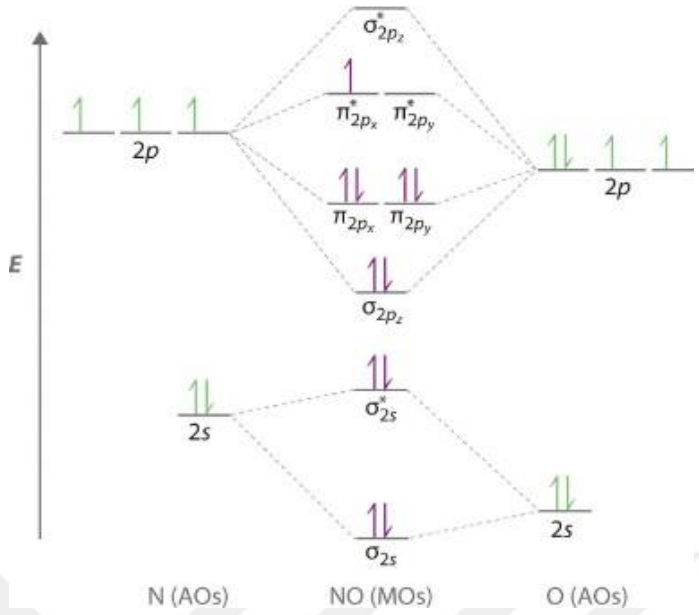

Figure 2.6 MO scheme of NO

2.2.5 Electronic Transitions

Light absorption is highly influenced by the chemical structure of the molecule. The two functionalities of a chemical substance that significantly influence the nature of a molecule's absorption spectrum are functional groups and conjugated π-systems. For both elements absorption of light corresponds to a transition of electron from an n-, σ- or π-orbital to a $\sigma*$ - or $\pi*$ - orbital. For light absorption in the UV-Vis range following electron transitions are possible: $n \rightarrow \pi*$, $n \rightarrow \sigma*$, $\sigma \rightarrow \sigma*$, $\pi \rightarrow \pi*$ [18]

n → σ $*$ transitions usually occur if solution has heteroatoms such as O, N and S. In this case, electrons of heteroatom's lone pairs are excited to the $\sigma*$ orbital which can already be observed at wavelengths $\lambda > 200$ nm. [19]

n → π $*$ transitions can be observed in unsaturated molecules comprising heteroatoms. For these transitions electrons, which are located in the heteroatom's n-orbitals, are excited to the anti-bonding orbital of a π-bond. Important examples possessing $n \rightarrow \pi*$ transitions are aldehydes and ketones.

For saturated aldehydes and ketones n $\rightarrow \pi *$ transitions can be observed at wavelengths of λ= 270 nm to300 nm [20]

$\sigma \rightarrow \sigma *$ This transitions are required higher excitation energies. For saturated hydrocarbons these are the only observed transitions. Thereby $\sigma \rightarrow \sigma *$ transitionsof C – H bondings are excited more easily than $\sigma \rightarrow \sigma *$ of C – C-bondings due to small differences in the bond energy. These transitions occur in a wavelength region of 100 nm to 200 nm [21]

$\pi \rightarrow \pi *$ Every molecule that contains a π-bonding system or π- electrons can made this transitions (e.g. chromophores, polyenes, etc.). During this transition electrons from the π-orbital are raised to a anti-bonding $\pi *$ orbital. A crucial parameter forthe amount of energy required for excitation is the extent of the conjugated π- system. In order to induce $\pi \rightarrow \pi *$ transitions in ethylene, possessing an isolated π- bonding, a wavelength of λ = 193 nm is needed due to a high The difference in energy between HOMO and LUMO. [21]

Because the energy difference between the HOMO and LUMO depends on the number of conjugated π-bondings, light with longer wavelengths can induce $\pi \rightarrow \pi *$ transitions in conjugated π-systems. [21]

As a consequence of the tuneability of the energy difference between the HOMO and LUMO, linear or cyclic conjugated π-systems are often used as basic chromophores. Chromophoric groups takes light in the UV-VIS area and are essential for the functionality of a molecule e.g. as a dye. When the extent of a π-system exceeds a certain value, absorption of light in the visible range is observed. [14] In order to induce $\pi \rightarrow \pi *$ transitions in ethylene, possessing an isolated π- bonding, a wavelength of λ = 193 nm is needed due to a high The difference in energy between HOMO and LUMO. [21]

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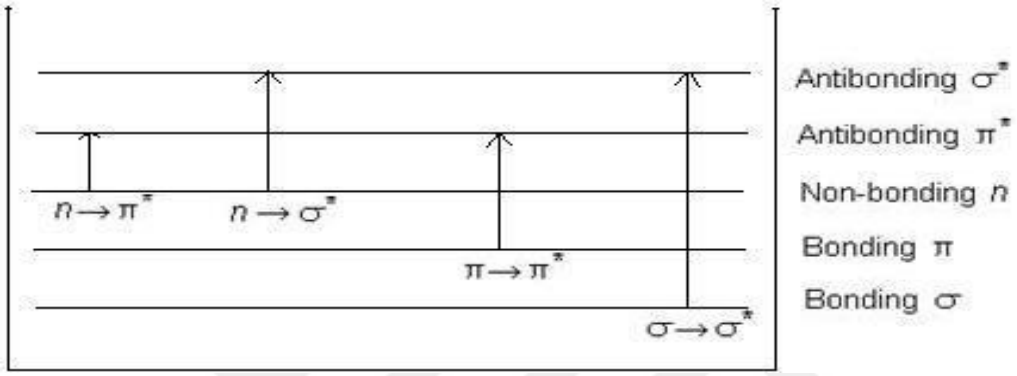


Figure 2.7 Electronic transition

2.3 Photoinitiated Polymerization

Photopolymerizations are the use of light as a power source to induce the conversion of tiny unsaturated compounds in the liquid form to rigid polymers. The term "photoinitiated polymerization" refers to a series of reactions that is started by light and involves radicals or cations as both the starting species and the developing chain ends. Conversely, the photoinitiated copolymerization method, which involves the step-growth addition of lowmolecular-weight components to produce a macromolecule, is still in its infancy. The photocondensation process is most commonly based on the oligomerization of nonconjugated olefins via singlet and triplet excited states, and the resulting macromolecules do not have the traditional polycondensate structure of polyamides, polyesters and polyurethanes. [23]

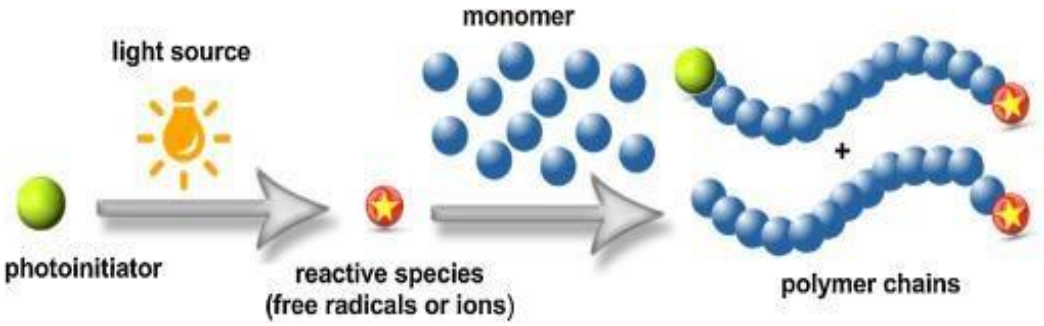


Figure 2.8 Photoinitiated polymerization

2.3.1 Photoinitiators

The molecules that can have ability to absorb the light are called as photoinitiators. They undergo photochemical separation upon light absorption, producing reactive radicals that will bind to the active ingredients in formulations. In another meanings, photoinitiators are molecules that can absorb light energy and convert it into chemical energy to initiate chemical reactions. [24]

We may state that the materials will be well cured after the emission of the light source utilized for curing. The photopolymerization mechanism is divided into two types: free radical and cationic. Because the reactive species generated in each process are different, it's also important to pick a photoinitiator that can induce the proper sort of photopolymerization. [25]

2.3.2 Free Radical System

Type I and Type II UV photoinitiators are two types of free radical UV photoinitiators. Type I photoinitiators are based on molecules whose triplet excited states are reacted with a hydrogen donor to produce an initiating radical. Type II photoinitiators are based on compounds whose triplet excited states are

coupledwith a hydrogen donor to produce an initiatingradical.[16] Compounds containing benzoyl groups are commonly used as Type I initiators. The initiator's carbonyl group absorbs a photon and converts it to an excited singlet state. The excited α-carbon bond is then homolytically cleaved into two radical pieces. [26]

Type II initiators consume UV light to produce excited molecules that then steal an electron or hydrogen atom from an electron donor. After that, the donor molecule combines with a monomer to start the polymerization process. Benzophenone and its derivatives, as well as isopropyl thioxanthone in conjunction with a synergist such as tertiary amines, are common type II photoinitiator systems. For the excited photoinitiators, the amines operate as active hydrogen donors. The removal of hydrogen results in the formation of highly reactive alkyl-amino radicals, which then begin polymerization.[27]

Free radical polymerization consists of three fundamental steps. These are initiation, which involves the formation of radicals followed by the radical's reaction with a vinyl monomer; propagation, which is the rapid and progressive addition of monomers to the growing polymer chain without a change of the active center; and termination, which is the destruction of the growth active center, usually by combination or coupling of the radicals of two growing polymer chains or by disproportionation. In addition to these three processes, chain transfer might occur, which is the transfer of the growth active site from the active chain to a previously inactive one. [28]

2.3.2.1 Initiation

Radicals or radicals ions produces from excited molecules . The free radical attacksto a vinyl monomer, it gives to one of the electrons of the double bond of the vinyl monomer and the left electron creates the new free radical.

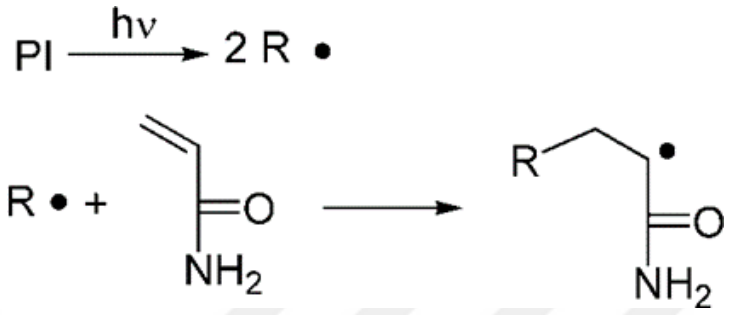


Figure 2.9 Initiation step

2.3.2.2 Propagation

As the second step, propagation, active polymer chains are growing by integratingother monomer molocules into it.

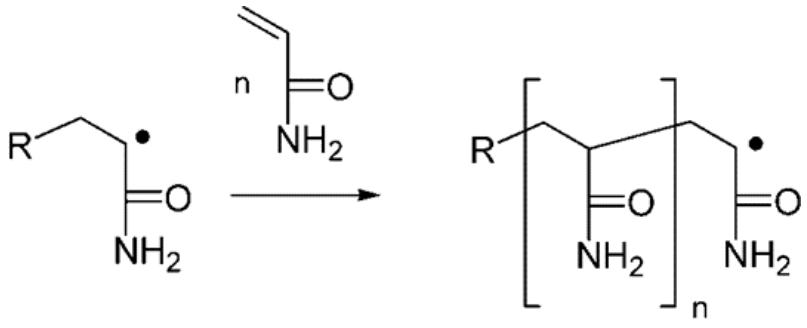


Figure 2.10 Propagation step

2.3.2.3 Termination

When all monomers have been utilized, the propagation stage is said to be complete. Pairs of radicals, on the other hand, have an ability to react with one another, effectively annihilating their activity. Combination or disproportionation might lead to termination. Two developing polymer molecules react with each other to generate a single chemically inert polymer network in the event of combinationor coupling.

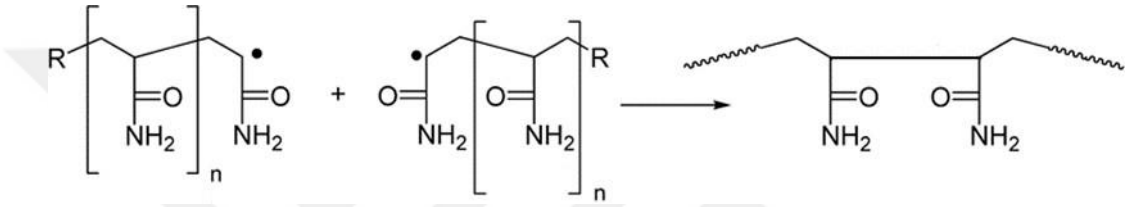


Figure 2.11 Termination step via combination

And in the case of disproportionation, a hydrogen atom is transferred from one radical to the other resulting in two polymers, one with a saturated end and the other with an unsaturated end and each with an initiator fragment.

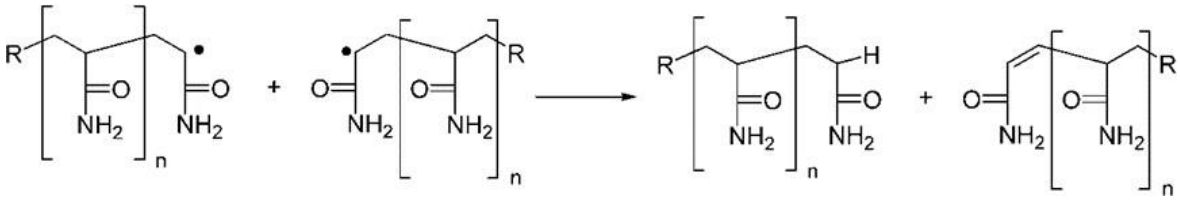


Figure 2.12 Termination step via disproportionatioN

2.3.3 Type I Photoinitiators

Type I photoinitiators are unimolecular free-radical producers, in which a particular bond within the initiator's structure undergoes homolytic cleavage to form free radicals when UV light is absorbed. A bonded pair of electrons even scission into free radical products is known as homolytic cleavage. [29]

Molecules make “α-cleavage” to generate free radicals by absorping light, some examples are α-hydroxyalkyl ketones, benzoin and derivatives, aminoalkyl phenones, benzil ketals, acetophenones, O-acyl-α-oximino ketones, and acyphosphine oxides [30]

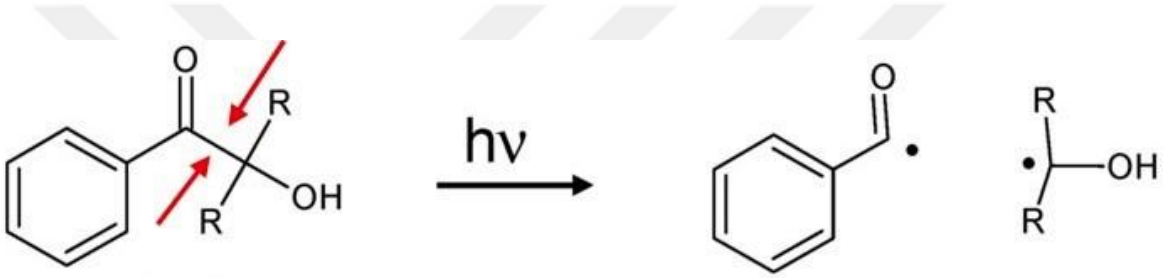


Figure 2.13 Photolytic α-cleavage

2.3.4 Type II Photoinitiators

In addition to the photoinitiator, type II photoinitiators require a co-initiator to activate the reaction. These photoinitiators are commonly an alcohol or amine, functional groups that may easily have hydrogens abstracted. When the UV light is absorbed by the type-II photoinitiator, it creates an excited state form in the photoinitiator, which abstracts a hydrogen from the co-initiator while separating a bonding pair of electrons. [31] These systems are more susceptible to the photoinitiators' excited triplet states, which are the reactive intermediates of light-induced chemical reactions in carbonyl compounds, being quenched. When type I photoinitiators are used, quenching by monomers with low triplet energy or oxygen is common and can result in poor curing rates. [32]

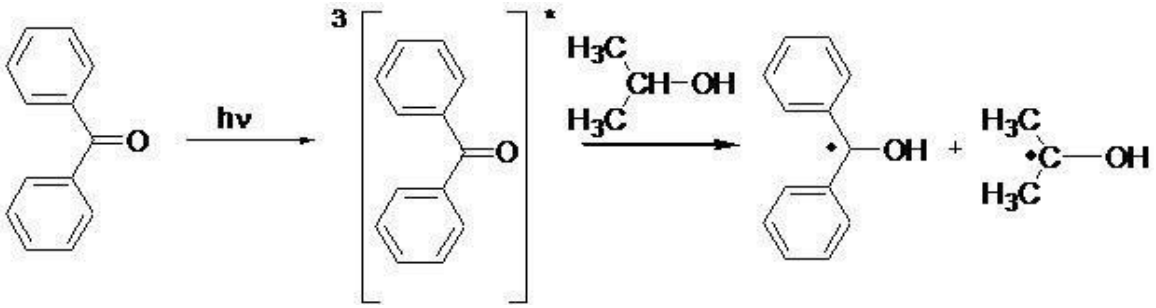


Figure 2.14 Benzophenone's photoinitiation mechanism as Type II

2.3.5 One-component Type II photoinitiators

Numerous thioxanthone derivatives have been developed as a novel class of Type II photoinitiators for free radical polymerization of olefinic compounds. Because these compounds include both light absorption and hydrogen giving sites in one molecule, they have a high starting capacity. They are classified as one-component Type II photoinitiators based on how free radicals are formed. [33]

2.3.5.1 Thioxantone-Anthracene

The light-absorbing and hydrogen-donating sites are contained in the photoinitiator molecules. Notably, these one- component photoinitiators initiate the polymerization much more efficiently than two-component systems in which the related functions are composed in independent molecules. As part of our continuing interest in photoinitiating systems, herein it is reported a new photoinitiator possessing two photochromic groups, anthracene (A) and Thioxantone (TX) [34]

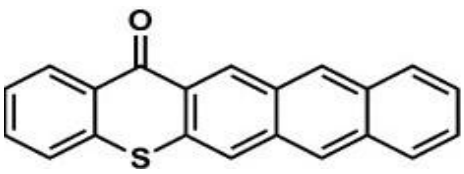


Figure 2.15 Thioxantone-Anthracene

It is known that life of triplet state of anthracene is longer than singlet state.In the presence of oxygen, Anthracene can form endoperoxide

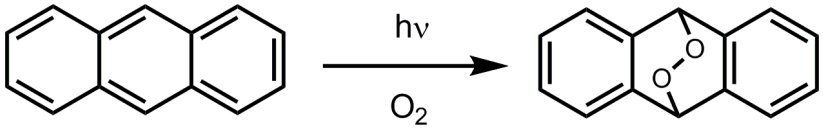


Figure 2.16 Formation of endoperoxide by anthracene in the presence of air andlight

This photoinitiator creates radicals that can be used as initiator without needed hydrogen donor and so can be considered also as a one-component photoinitiator [35] Also, TX-A can form endoperoxide as anthracene and initiate polymerization.[35]

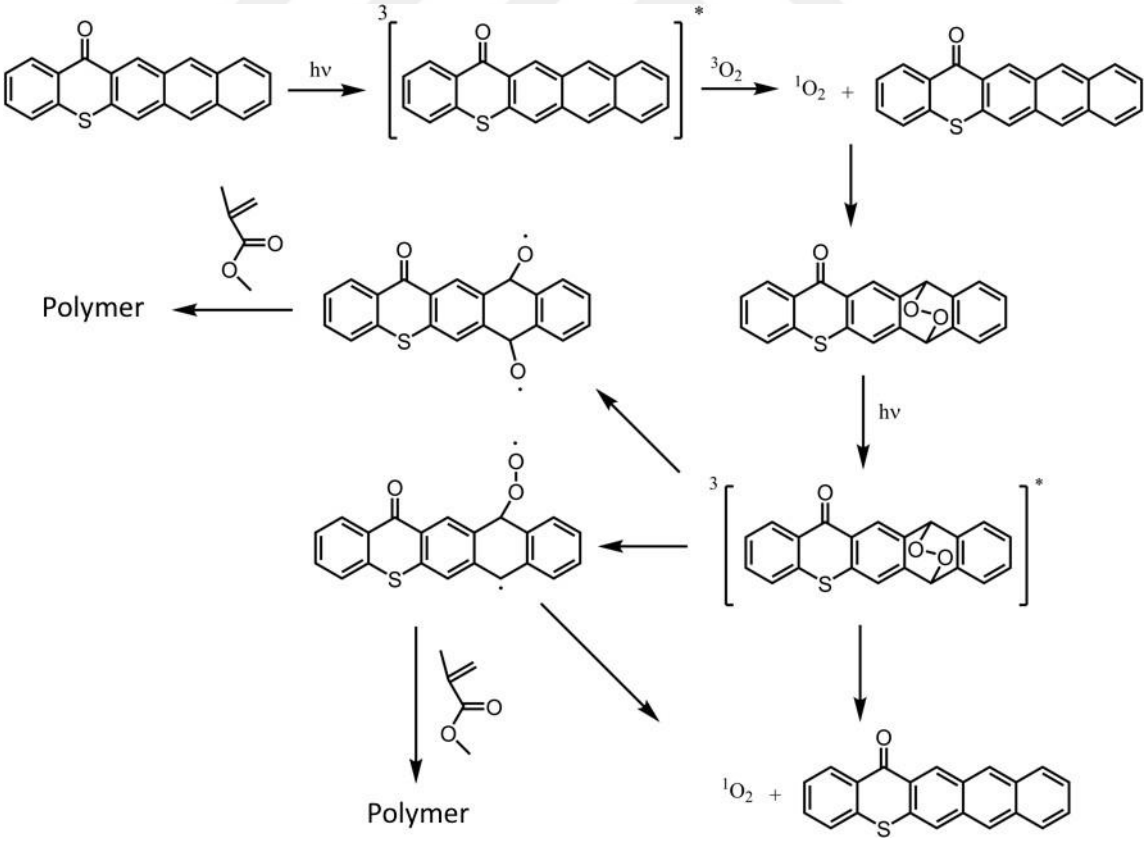


Figure 2.17 Polymer formation mechanism by TX-A

2.3.6 Oxygen Inhibition

In the presence of molecular oxygen,any free radical can easily reacts with it, including the initiator molecules. This quenching results in the initiator losing its radical and reactive state, which subsequently lowers the number of free radicals produced by the initiator, less initiated polymer chains, and of course a fewer number of final polymer chains produced. The reaction of the initiator with molecular oxygen also produces an oxygen free radical. This oxygen free radical reacts with already existing propagating radicals, converting the propagating chains to oxygen based free radicals. This resulting type of radical is less reactive, which further inhibits the polymerization process by producing lower molecular weight polymers [36]

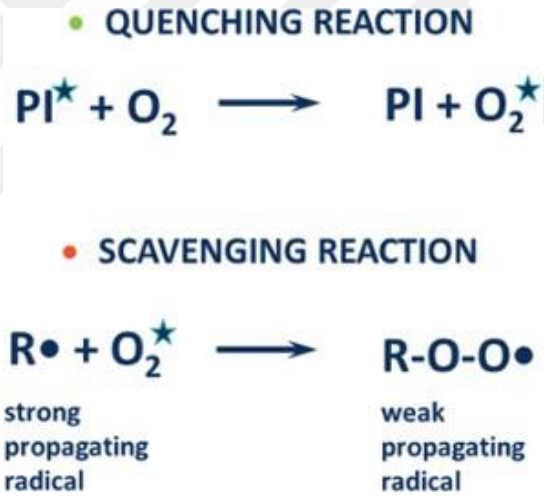


Figure 2.18 Quenching of oxygen

As the presence of oxygen greatly prevents free radical polymerization, oxygen inhibition has long since been considered to be a problem for polymers such as coatings that are cured through free-radical polymerization. In cases like this, an oxygen inhibition layer forms on the surface of these polymers, mainly composed of uncured monomers, which is why it is frequently referred to as a surface cure problem. [37]

There are several techniques to reduce oxygen inhibition in UV-curing. A general differentiation of these techniques in physical and chemical methods is commonly used. The most efficient and commonly deployed physical method is the application of an inert gas atmosphere, usually nitrogen or in rare cases carbon dioxide is used. The main requirement for these methods is a continuous flow of inert gas over the surface of the polymerizing monomer film, which involves high expenditures for materials and is in some cases not executable [38]Free radical curing adhesives and sealants can be formulated to contain thiols, amines, or ethers, all of which contain easily abstractable hydrogen atoms that will react with the peroxy radicals formed by oxygen, reducing scavenging.A very frequently used chemical method is the formation of new propagating centers by aminebased hydrogen donors like N- methyldiethanolamine. a-Hydrogen atoms of these amines react with peroxy radicals to form new a-aminoalkyl radicals which initiate more efficiently than radicals of tertiary carbon groups. Cyclic N-vinylamides which are applied as reactive diluents for photocuring formulations have been proposed to function similar to tertiary amines as hydrogen donors [39]

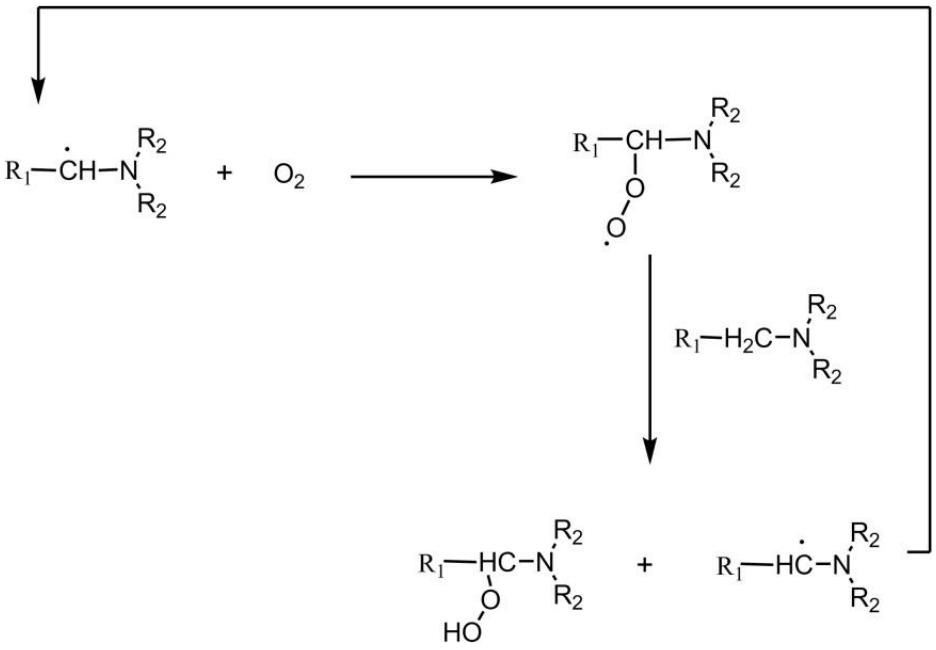


Figure 2.19 Using of amines to reducing of oxygen inhibition

2.4 Nanotechnology

Nanotechnology is interested in materials that has nano sizes. If matters are sizedone billionth of a meter or in nanometers that matters are called as nano level particles. Using various techniques, nano scale particles can be created. If production of nanoscale particles starts with material has larger scale and removes portions, this methos is known as top-down nano production. Bottom-up nanofabrication, wherein specific atoms or molecules are combined to generate nanomaterials, is the second way.[40]

The aim of nanotechnology is to produce materials that behave differently at the nanoscale, less than 100 nm in size by doing this, surface area of materials is larger than before.

2.5 Synthesis Methods of Nanoparticles

Nanotechnology is an interdisciplinary field based above all on findings of chemistry, physics, materials engineering, electronics, and biology. Especially electronics is a driving force of development of nanotechnology. The needed structures can be created by manipulation with atoms and molecules, possibly various chemical processes can be used. [41]

Metal nanoparticles can be prepared by two basic methods

- Mechanical separation of metal aggregates (physical methods) and
- Nucleation and growth of a “nucleus” (chemical methods)

2.5.1 Chemical Method

Chemical methods belong among the most widely used methods for preparation of nanoparticles. Nanoparticles of the demanded shapes and sizes can be prepared using appropriate conditions. Reduction of salts of transition metals in a solution isthe most widely used method for the preparation of colloid suspensions of metals. [42]

Monodisperse nanoparticles in amounts in order-of-magnitude of grams originate. Various reducing agents are used for the preparation of colloid matters, such as hydrides and salts or even oxidizable agents, e.g. alcohols [43]

2.5.2 Physical Method

Most organometallic molecules are thermally decomposable to their zero-valent components. The pressure (> 20 MPa), higher temperature (>5000 K), and the cooling rate (> 107 K·s -1) reached by ultrasound made unique properties to the solution. Those unique conditions were used to produce gold, iron and other nanoparticles. By warming some metal compounds by microwave radiation Ag, Au and Pt nanoparticles with a low relative standard deviation of particle diameters can be obtained. Hydrothermal synthesis is carried out in a supercritical liquid environment, which serves as a dissolvent. Ni, Co and Fe nanoparticles were prepared this way. By the latter method nanoparticles of Pt, Au, Pd and Ag were prepared, whereas it was found out that UV-Vis irradiation provides smaller nanoparticles with a low relative standard deviation of diameters [44]

Photochemically manufactured nanomaterials can be made either by reducing transition metallic ions with a radiolytically generated reduction agent or by radiolytically degrading an organometallic compound. [45]

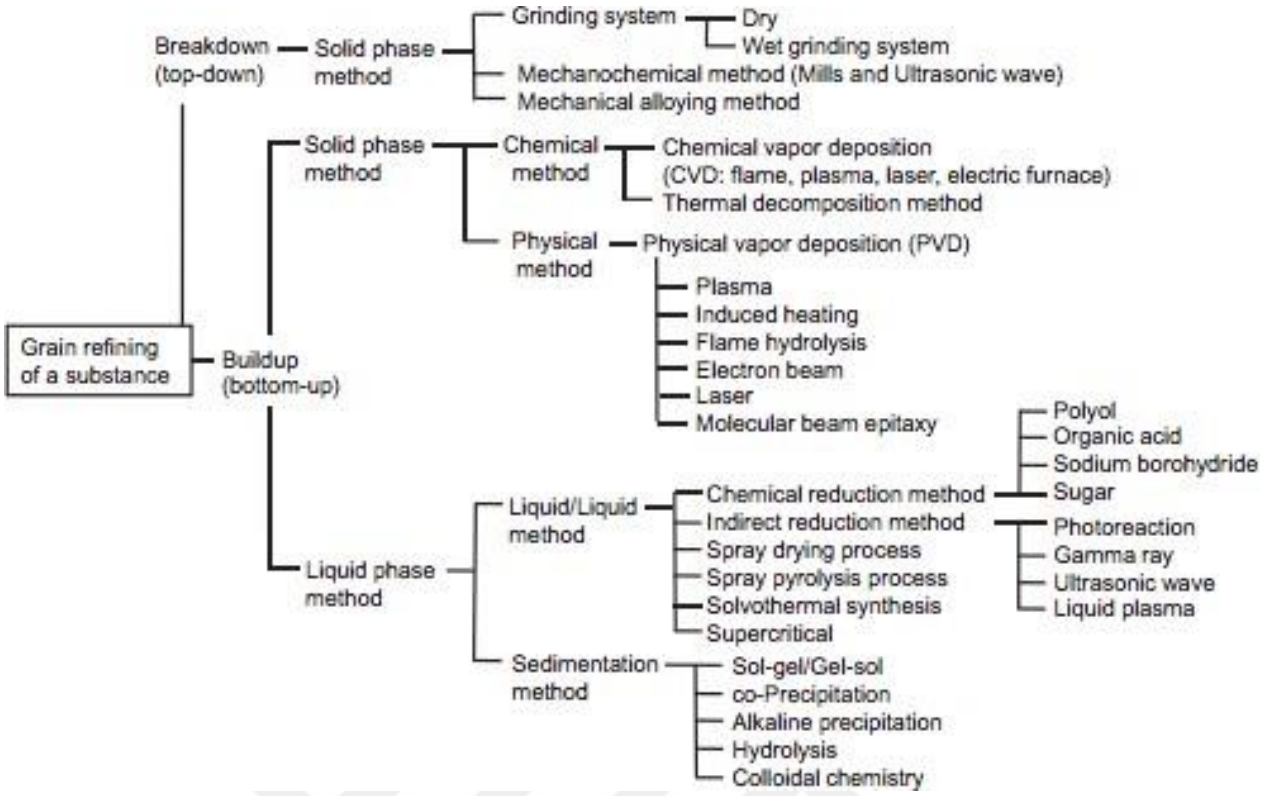


Figure 2.20 Typical synthetic methods for nanoparticles

2.6 Applications of Nanoparticles

2.6.1 Smart Materials

Smart materials react in ways that are suited to the stimuli or circumstance they areexposed to. Integrating smart materials with nanostructured materials, for example,might allow scientists to develop medications that react when they come into contact with certain viruses or illnesses. They might also be used to alert users to issues with several other technologies, such as nuclear power plants. [46]

2.6.2 Medical Uses

The potential uses of nanoscale materials in the field of medicine are of particular interest to researchers. Theoretically, nanorobots could be programmed to perform functions that would eliminate the possibility of infection at a wound site. They could also speed healing. Smart materials could be designed to dispense medication in appropriate doses when a virus or bacteria is encountered. Sensors could be used to alert physicians to the first stages of malignancy. There is great potential for nanomaterials to meet the needs of aging populations without intrusive surgeries requiring lengthy recovery and rehabilitation. [47]

2.6.3 Energy

Nanomaterials also hold promise for energy applications. With nanostructures, components of heating and cooling systems could be tailored to control temperatures with greater efficiency. This could be accomplished by engineering the materials so that some types of atoms, such as oxygen, can pass through, while others, such as mold or moisture, cannot. With this level of control, living conditions could be designed to meet the specific needs of different categories of residents.[48]

2.7 Silver Nanoparticles

In recent years, nanoparticles of noble metals such as gold, silver and palladium have drawn immense attention due to the wide range of new applications in various fields of industry. Particularly, silver nanoparticles have significant interest in medical applications such as very effective antibacterial agents without the toxic effects, and industry application such as inkjet inks containing well uniform dispersions of nano-sized silver particles that are useful for producing electronic circuits. It is important that the silver nanoparticles require not only the particles to be of nano-size, but also synthesis of the nanoparticles to be produced easily and at low cost. Over the past few decades, many synthetic methods of silver nanoparticles have been studied [49]

2.8 Gold Nanoparticles

Gold nanoparticles are widely used in many fields as preferred materials for their unique optical and physical properties, such as surface plasmon oscillations for labeling, imaging, and sensing. Recently, many advancements were made in biomedical applications with better biocompatibility in disease diagnosis and therapeutics. AuNPs could be prepared and conjugated with many functionalizing agents, such as polymers, surfactants, ligands, dendrimers, drugs, DNA, RNA, proteins, peptides and oligonucleotides. It is working on the use of gold nanoparticles and the surface functionalization with a wide range of molecules, expanding and improving gold nanoparticles in targeting drugs for photothermal therapy with reduced cytotoxic effects in various cancers, gene therapy and many other diseases. Overall, AuNPs would be a promising vehicle for drug delivery and therapies [50]

2.9 Manganese Nanoparticles

Owing to its high physicochemical qualities, manganese oxides may be used in batteries, catalysts, molecular sieves, ion-sieves, magnetic materials, and other applications such as imaging contrast agents and water treatment. One of the most essential elements is MnO_2. Due to the obvious properties of ferrite materials, scientists are interested in the effect of MnO2 addition on several methods for preparing nanoscale MnO_2 have been designed, including self-reacting micro emulsions, hydrothermal methods, precipitation, room temp solid reactions. [51]

2.10 Iron Oxide Nanoparticles

Metal oxide NPs have important role in a lot of chemical and physical areas because of their physicochemical properties. Iron oxide is important one of them due to their magnetic properties.

There are three allotropic forms of iron nanoparticles known as alpha, beta and gamma. Iron NPs can rapidly form oxides. When NPs reacts with air /oxygen, it forms Fe_2O_3which is named as hematite (alpha Fe_2O_3).

There are many applications area of Iron oxide NPs. It is mostly used for medical and biomedical applications for instance delivery of drug, thermal ablation therapy, magnetic resonance imaging (MRI), and magnetic separation of cells or molecules. [52]

3

EXPERIMENTAL PART

3.1 Instrumentals and Chemicals

N,N-Dimetilformamide (Merck-103053), Methanol (Merck-480112), Hydrogen tetrachloroaurat(III) (HAuCl4, Acros OrganicsAC41107-0010), Silver nitrate ($AgNO_3$, Merck Trace Metals Basis 99%), Manganese (II) Chloride ($MnCl_2$, Merck Trace Metals Basis 99%), Iron (III) chloride hexahydrate ($FeCl_3 * 6 H_2O$, Merck Trace Metals Basis 99%) , Iron (II) chloride hexahydrate ($FeCl_2 * 6 H_2O$, Merck Trace Metals Basis 99%), Poly(ethylene glycol) diacrylate (PEGDA, Mn=700, Sigma Aldrich-455008), Poly(ethylene glycol) methyl ether acrylate (PEGMEA, Mn=550, Sigma Aldrich-202487), Thioxantone Anthracane (synthesized by prescribed procedure ref [53])

To see the size of particle in the samples, DLS Method via Zetasizer Nano ZS device (Malvern Instruments, UK) is used. The Instrument is equipped with 4.0 mV He-Ne laser lamp (633 nm) at 25 0.1 C using 0.8872 cP of viscosity and 1.330 refractive index for the solutions. The number of runs and run durations was chosen automatically. All analyses were performed in triplicate.

The equipments used in this study are UV-Vis spectrophotometer Varian Cary 50 Conc, HAMAMATSU Lightningcure LC8 was used for irradiation, PRIMARC UV-Technology Mini-UV Cure Unit was used for coating, SEM imaging results were obtained from the Philips XL30 ESEM-FEG / EDAX instrument at Arge Central Laboratory of Advanced Technologies at Boğaziçi University. DLS analyzes were carried out at Yıldız Technical University.

4

RESULTS AND DISCUSSION

4.1 Photoinduced Synthesis of Au Nanoparticles with TX-A in DMF Solution

HAuCl4 (40 mg, 4 wt %) and Thioxanthone-Anthracene (0,5 mg, 5 wt %) were dissolved in 10 ml DMF and then, the mixture were placed during 5 mins in a ultrasonic bath at the room temperature. As the irradiation source, HAMAMATSU Lightningcure LC8 was used. Formation of AuNps was followed by UV-Vis absorption spectroscopy at room conditions. Colorless solution turned violet color after 600 secs of irradiation and then color was changed to dark purple after 1800 secs of irradiation. The change of absorption spektrum and color changing depending on the irradiation time was given in Figure 4.1

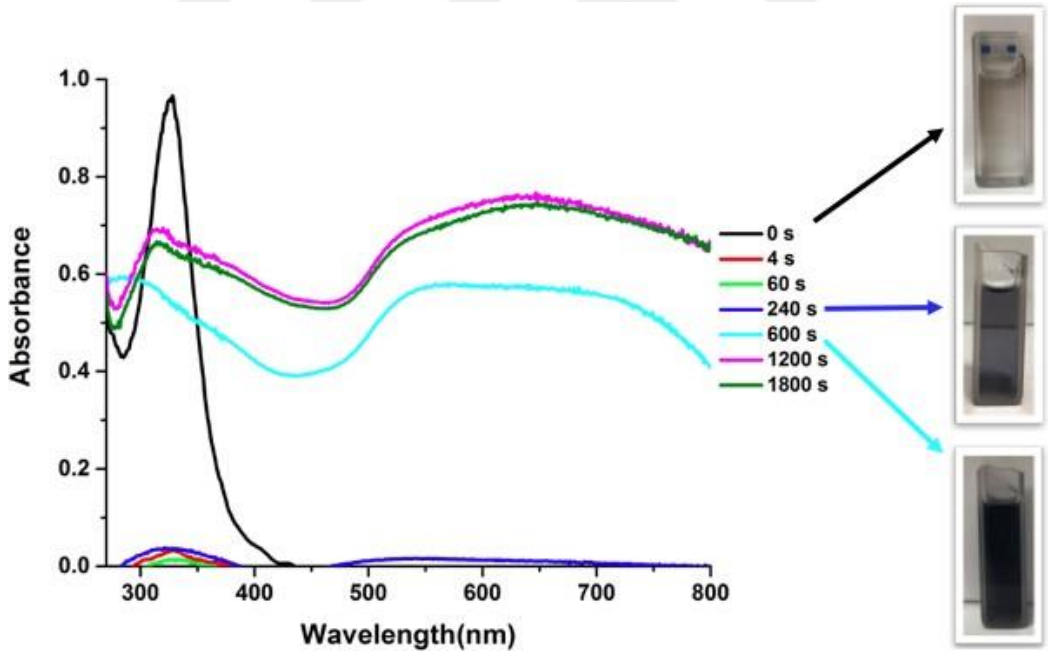
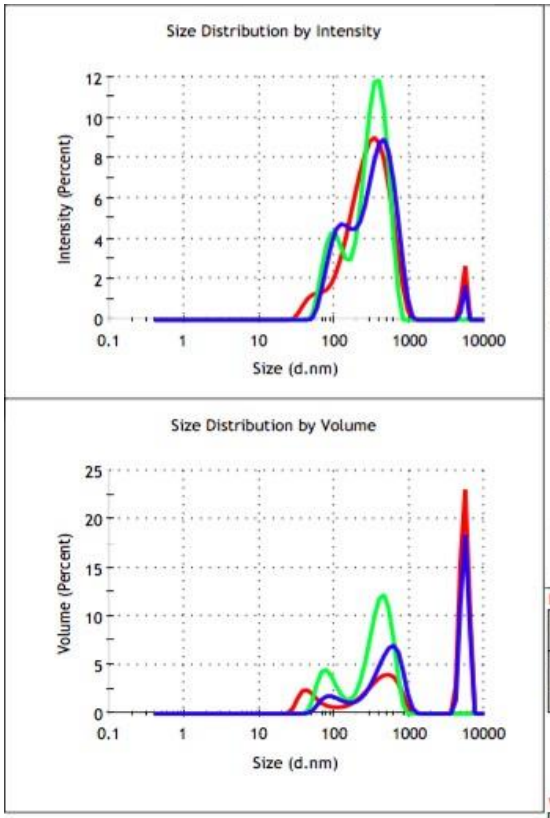
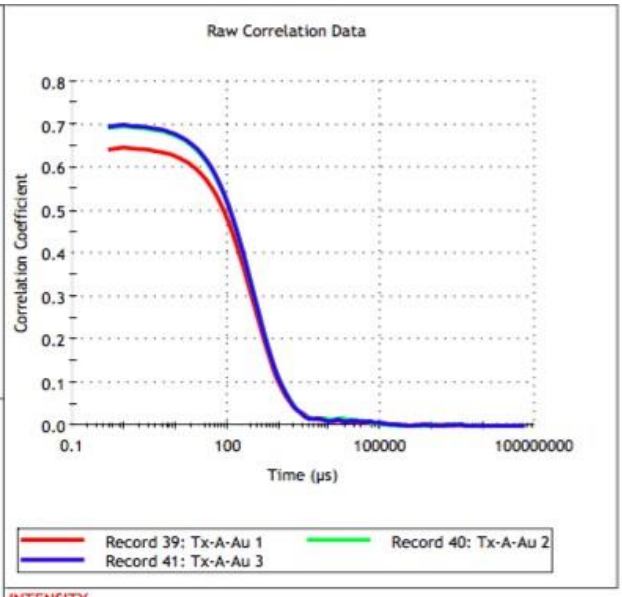


Figure 4.1 In-situ photochemical preparation of AuNps with TX-A in DMF followed by UV-Vis absorption spectroscopy

Surface Plasma Resonance (SPR) shapeless absorption band of AuNps formed after 600 secs of irradiation two absorption band was seen one of at 540 nm and theother was at 720 nm. Unusual color changes was also determined, usually color of AuNps was pink and turns dark pink but in our case color was violet and turned dark purple when irradiation prolonged 1800 secs. The changes of color and absorption wavelengths of nanoparticles generally indicates the changes of shape,size and distribution.





INTENSITY

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
39	318,5	96,4	185,0	5354	3,6	346,2	0,000	0,0	0,000
40	367,1	74,9	126,2	106,1	25,1	31,57	0,000	0,0	0,000
41	436,7	68,0	180,5	127,0	30,1	38,57	5427	1,9	288,1

VOLUME

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
39	52,54	13,7	20,01	449,3	35,1	208,8	5424	51,3	648,6
40	423,7	75,3	142,7	89,53	24,7	30,17	0,000	0,0	0,000
41	529,3	49,6	209,2	100,6	11,4	32,37	5484	39,1	627,6

No	Z-Ave d.nm	PdI	PdI Width d.nm	MCR kcps	DCR kcps	At	MeIntercept	Intercept	In Range	CumFitEr
39	269,9	0,511	193,0	373,4	7649,1	8	0,647	0,802	94,7	0,00303
40	287,5	0,409	183,8	356,9	7310,4	8	0,695	0,832	96,4	0,00635
41	274,1	0,474	188,8	364,5	7465,6	8	0,698	0,833	94,6	0,00360

Figure 4.2 DLS results of photochemically synthesized of Au Nanoparticles with TX-A in DMF solution

30 mins irradiated DMF solution which consist of AuNps were examined by DLS measurement. According to the DLS measurements results the size of AuNps were around 270 nm with a good correlation.

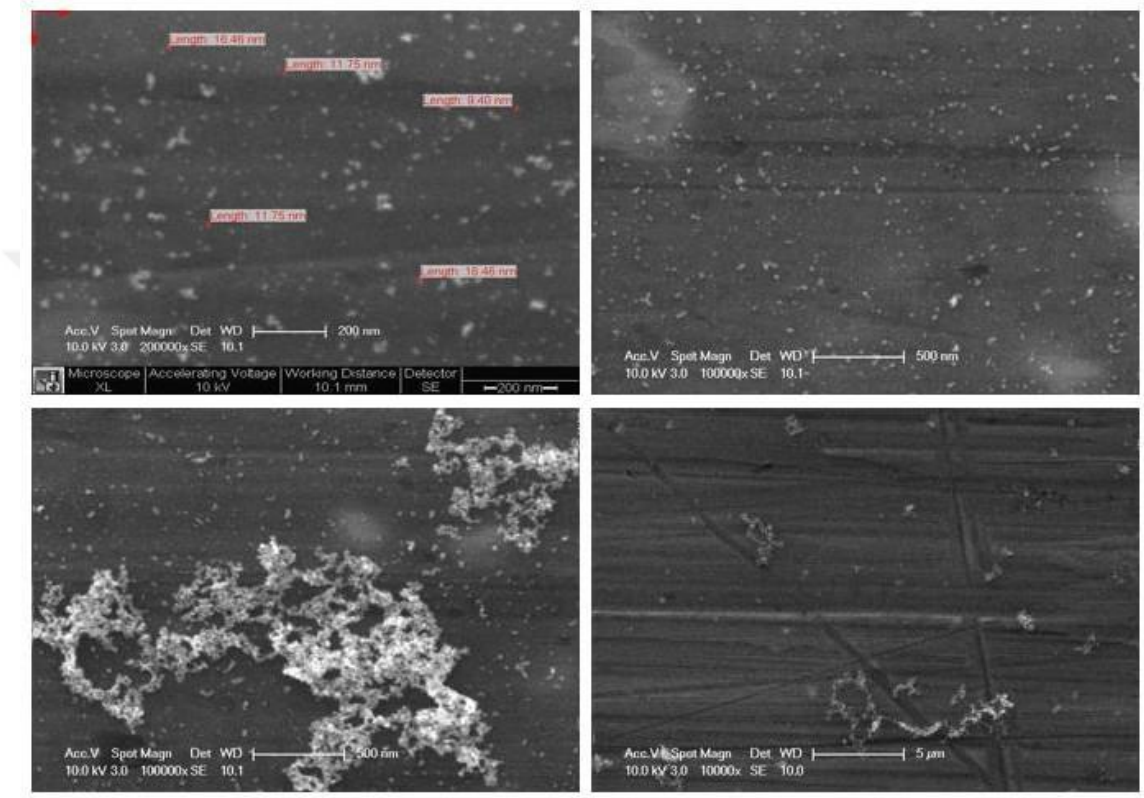


Figure 4.3 Sem images of AuNPs in DMF solution

The irradiated DMF solution of $HAuCl_4$ and TX-A examined by SEM to get information about the size changes of formed AuNps. Although aggregation was observed but this could be the reason of evaporation of solvent. The measured sizes were varied from 8-16 nm as given in Figure 4.3

4.2 In-situ Photoinduced Synthesis of Au Nanoparticles with TX-A in Polymer Matrix

Thioxanthone-Anthracene (0,5 mg, 5 wt %) and HAuCl4 (40 mg, 4 wt %) were dissolved in DMF and PEGMEA/PEGDA were added to the solution. Ultrasonic probe is used for 5 min to mix the last prepared formulation in order to obtain the metal salts nicely placed, and degassed in ultrasonic bath. At the end, they were placed on the aluminum plate surface using roller-coater (40 μm) and passed through mini UV-Cure unit.

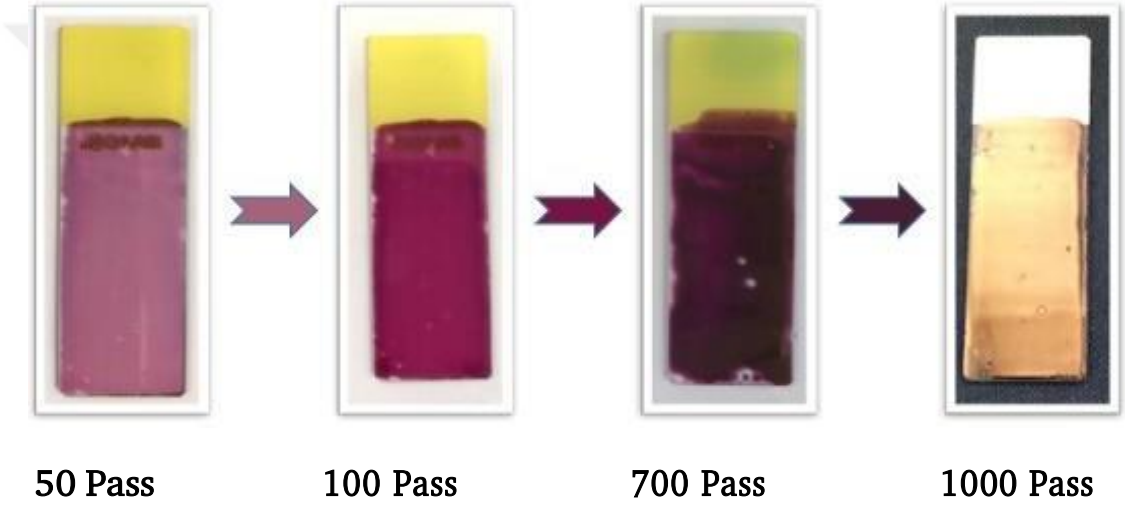


Figure 4.4 The changes of color AuNps containing PEGDA/PEGMEA nanocompsite films depending on the irradiation time

UV-Cured AuNps containing nanocomposite film's SEM images were given in Figure 4.5 Well distributed and small AuNps formation through the nanocomposite film was observed. Although the shape of nanoparticles were not determined exactly but there are both spherical and edge shape nanoparticles were seen. Size of AuNps varied from 18-25 nm even smaller size of AuNps was seen but could not be measured

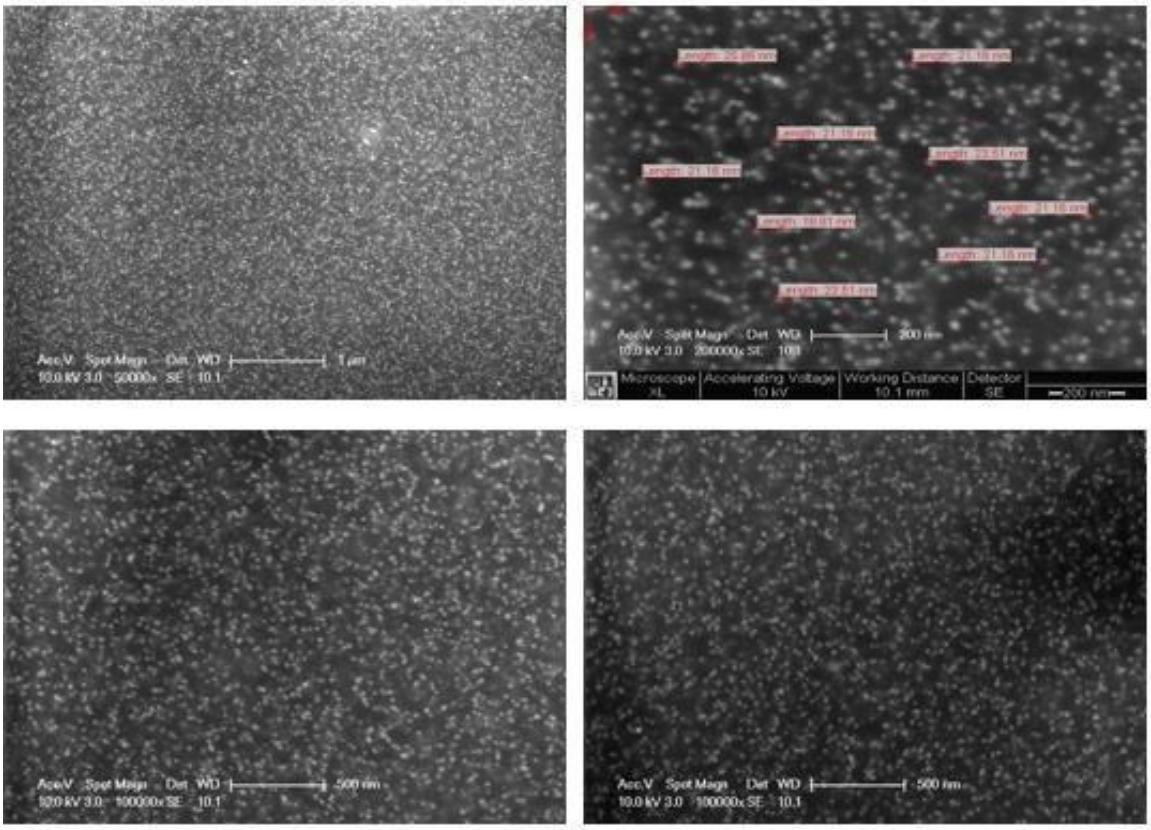


Figure 4.5 SEM images of AuNps prepared in PEGMEA/PEGDA polymer matrix

4.3 Photoinduced Synthesis of MnO Nanoparticles with TX-A in DMF Solution

Thioxanthone-Anthracene (0,5 mg, 5 wt %) and $MnCl_2$ (40 mg, 4 wt %) were dissolved in 10 ml DMF and then, the mixture were placed during 5 mins in a ultrasonic bath at the room temperature. HAMAMATSU Lightningcure LC8 was used as the irradiation source and formation of MnO Nps was followed by UV-Vis absorption spectroscopy at room conditions. After 15 min, colorless solution was obtained from light yellow color. End of the 120 min final color was brown. The change of absorption spectrum and color changing depending on the irradiation time was given in Figure 4.6

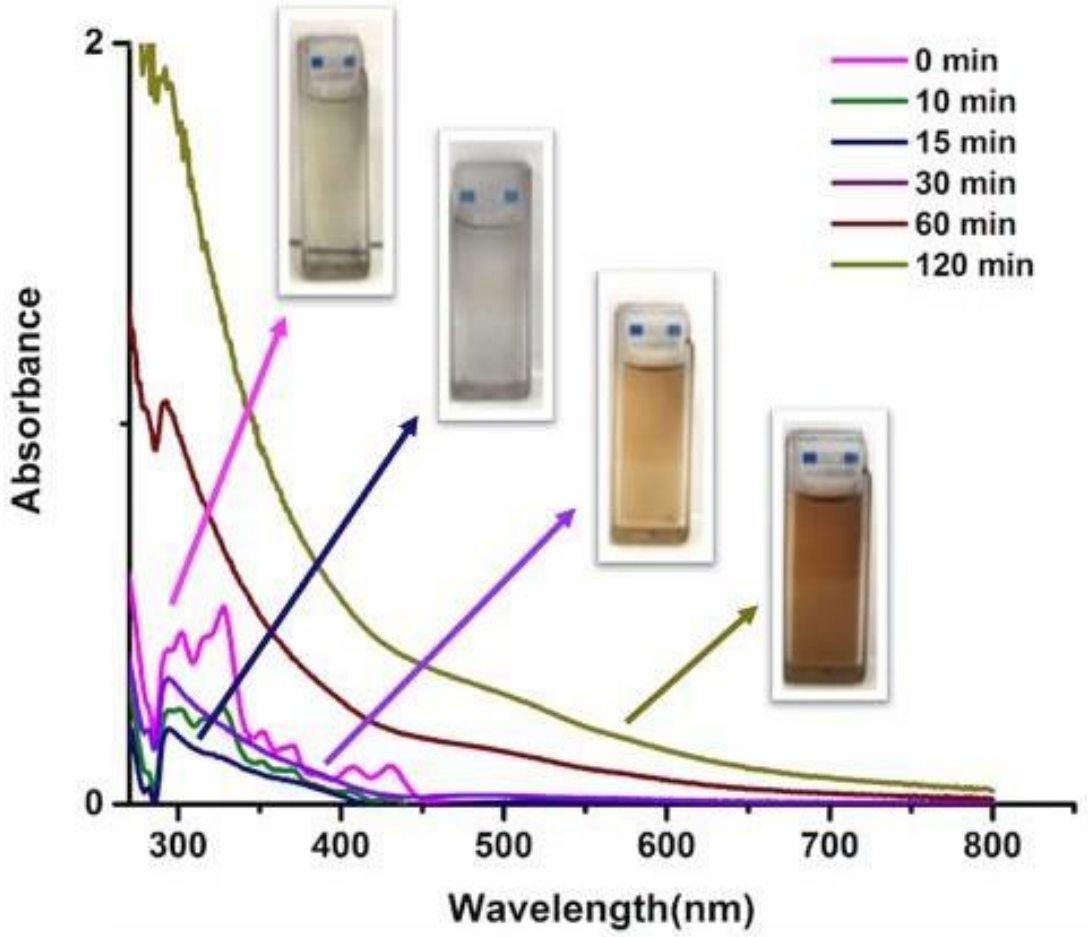
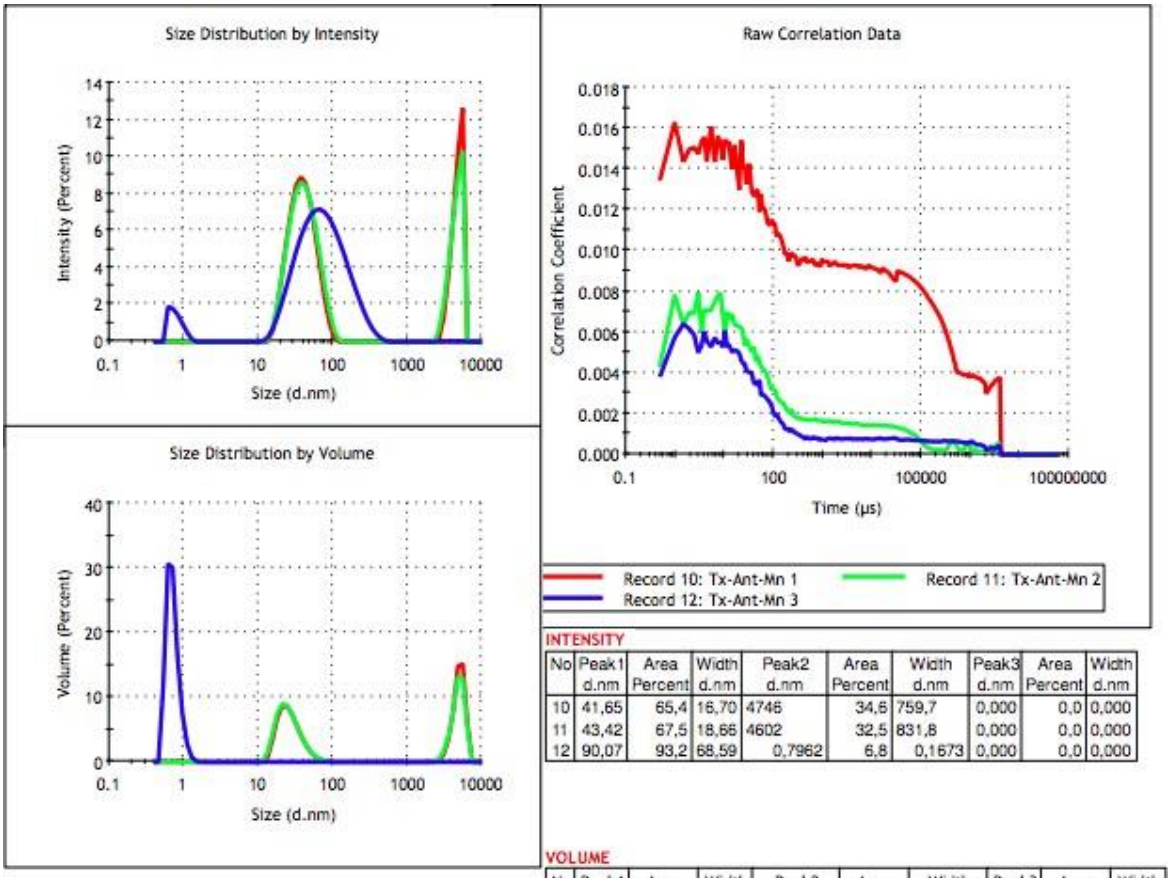


Figure 4.6 In-situ photochemical preparation of MnO Nps with TX-A in DMF followed by UV-Vis absorption spectroscopy.

In DMF solution the photoreduction of $MnCl_2$ salt was achieved by TX-A in air atmosphere. TX-A photoinitiator was bleached and the absorption band started to appear after 120 min irradiation at 505 nm.



INTENSITY

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
10	41,65	65,4	16,70	4746	34,6	759,7	0,000	0,0	0,000
11	43,42	67,5	18,66	4602	32,5	831,8	0,000	0,0	0,000
12	90,07	93,2	68,59	0,7962	6,8	0,1673	0,000	0,0	0,000

VOLUME

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
10	27,78	51,4	10,89	4983	48,6	861,0	0,000	0,0	0,000
11	27,43	54,8	11,44	4887	45,2	908,0	0,000	0,0	0,000
12	31,34	0,0	28,84	0,7223	100,0	0,1460	0,000	0,0	0,000

No	Z-Ave d.nm	PdI	PdI Width d.nm	MCR kcps	DCR kcps	At	MeIntercept	Intercept	In Range	CumFitEr
10	537,7	0,457	363,3	239,1	16464,0	7	0,015	0,0864	26,6	0,00982
11	378,2	0,397	238,4	368,4	25367,7	7	0,007	0,0799	82,7	0,00879
12	51,13	0,327	29,22	405,8	27949,7	7	0,006	0,0719	75,4	0,00168

Figure 4.7 DLS results of photochemically synthesized of MnO Nanoparticles withTX- A in DMF solution

4.4 In-situ Photoinduced Synthesis of MnO Nanoparticles with TX-Ant in Polymer Matrix

Thioxanthone-Anthracene (0,5 mg, 5 wt %) and $MnCl_2$ (40 mg, 4 wt %) were dissolved in DMF and PEGMEA/PEGDA were added to the solution. In order to make the metal salts well distributed, the final formulations were mixed by ultrasonic probe for 5 min and degassed in ultrasonic bath. At the end, they were coated on the aluminum plate surface using roller-coater (40 nm) and cured by mini UV-Cure unit.

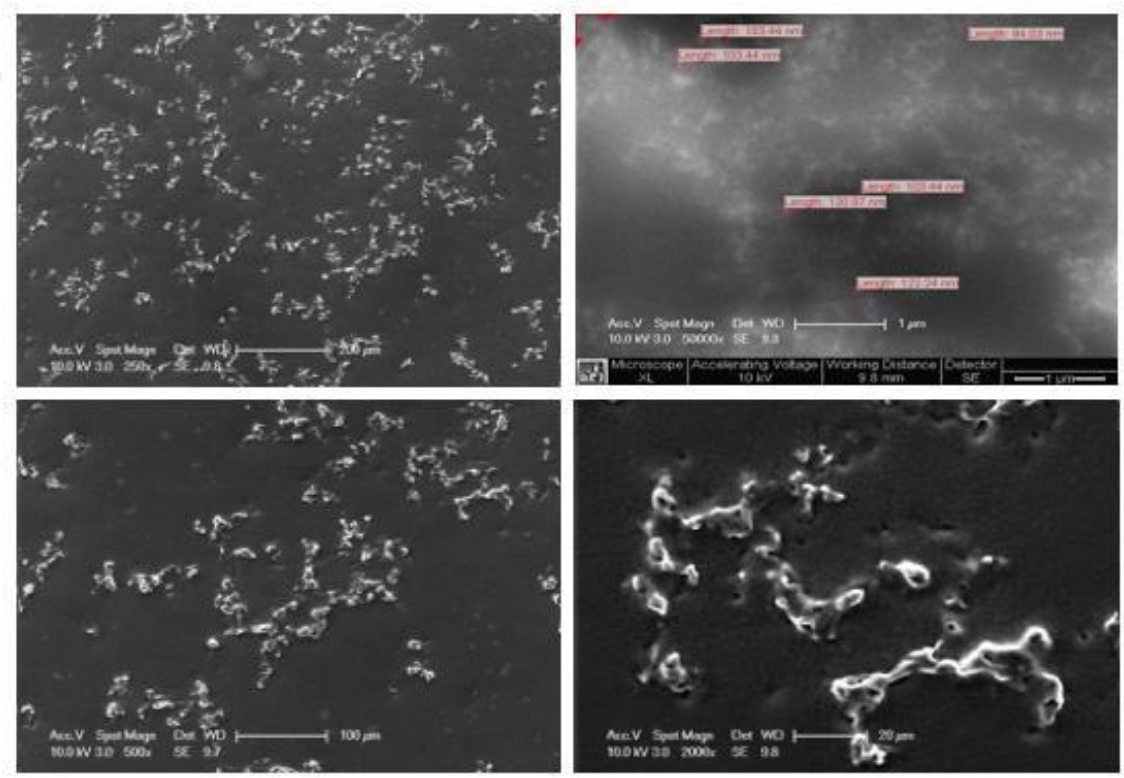


Figure 4.8 SEM images of MnO Nps prepared in PEGMEA/PEGDA polymer matrix

SEM images of UV-Cured MnO Nps containing PEGMEA/PEGDA nanocomposite films were given in Figure 4.8. The formation of MnO Nps was clearly seen and sizes of MnO Nps varied 94-130 nm. Nanorod shape of MnO Nps was observed from SEM images.

4.5 Photoinduces Synthesis of Fe_2O_3 Nanoparticles with TX-Ant in Methanol

Thioxanthone-Anthracene (0,5 mg, 5 wt %) , $FeCl_3.6H_2O$ (20 mg) and $FeCl_2.6H_2O$ (20 mg) were dissolved in 10 ml methanol and then, the mixture were placed during 5 mins in a ultrasonic bath at the room temperature. As the irradiation source HAMAMATSU Lightningcure LC8 was choosed. Formation of Fe_2O_3 Nps was followed by UV-Vis absorption spectroscopy at room conditions. After 600 secs, yellow solution was obtained from dark brown color. End of the 3100 secs solution was colorless. The change of absorption spectrum and color changing depending on the irradiation time was given in Figure 4.9

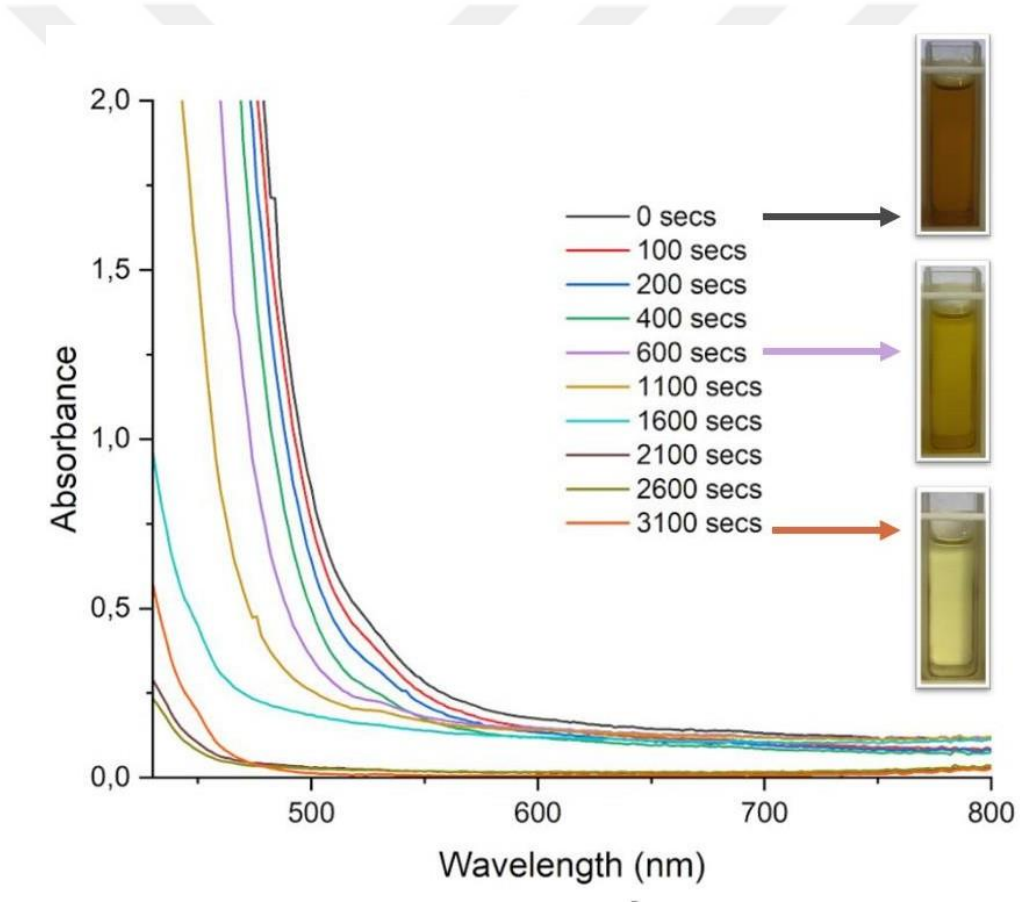


Figure 4.9 In-situ photochemical preparation of Fe_2O_3 with TX-A in methanol followed by UV-Vis absorption spectroscopy.

4.6 Photoinduced Synthesis of Ag Nanoparticles with TX-Ant in DMF Solution

4.6.1 In Air Atmosphere

In-situ metal or metaloxide nanoparticle formation by using photochemical method was conducted in air atmosphere so far. Experiments were conducted both in air and nitrogen atmosphere due to initiation mechanism of TX-A which requires oxygen to initiate or formation of endoperoxide via singlet oxygen.

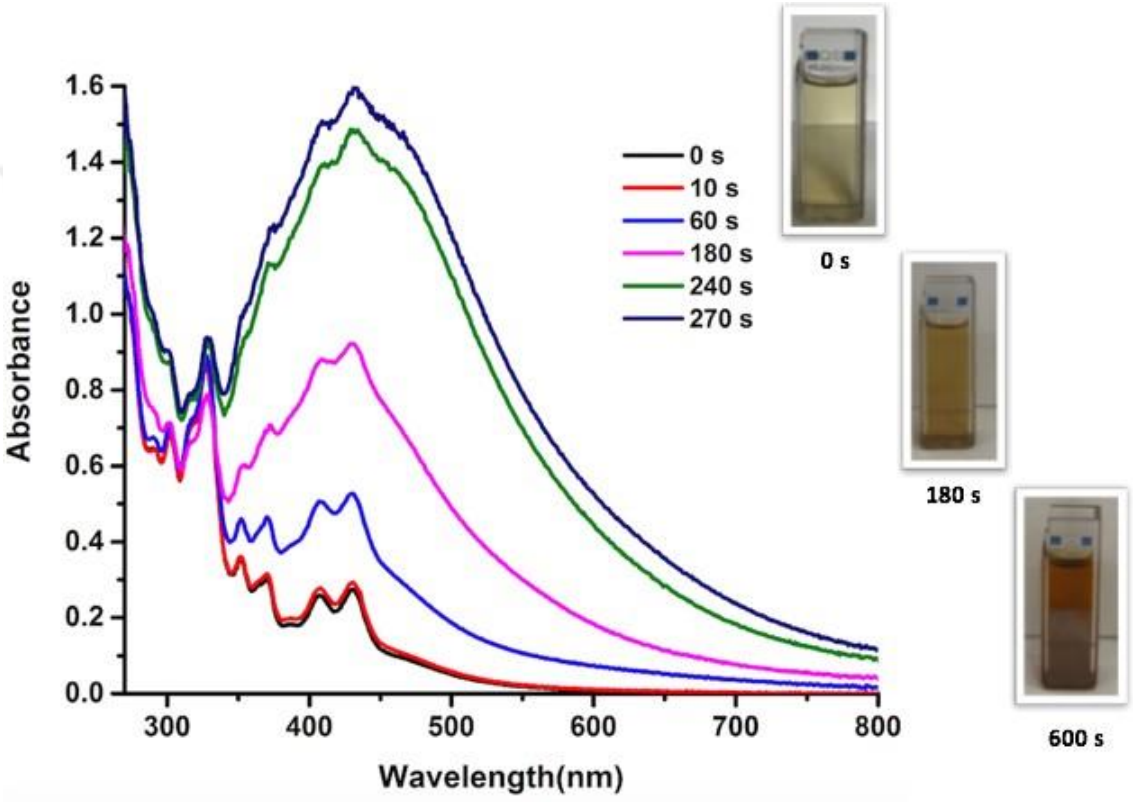
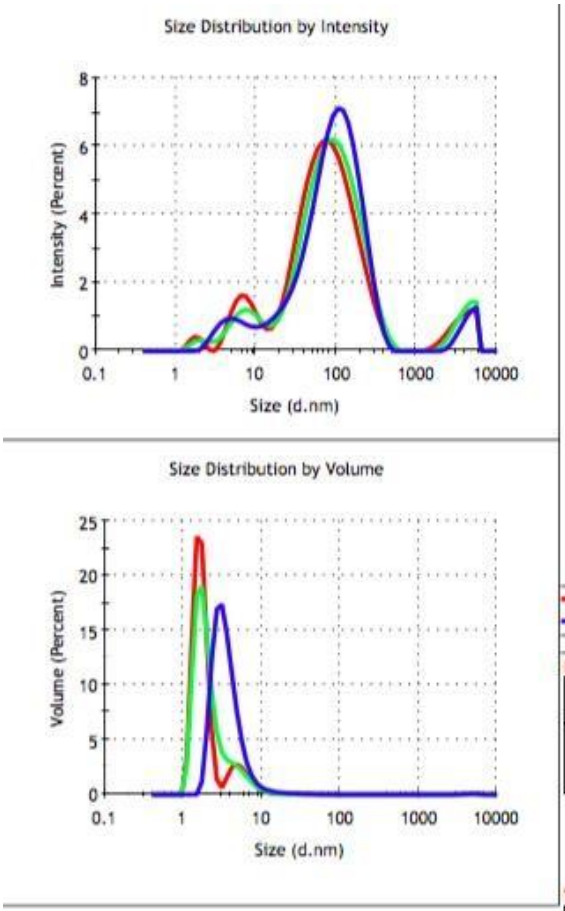
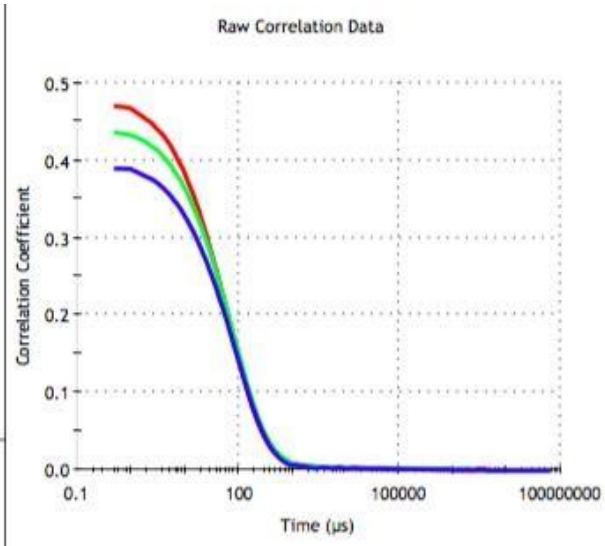


Figure 4.10 In-situ photochemical preparation of AgNps with TX-A in DMF followed byUV-Vis absorption spectroscopy in air atmosphere

As given in Figure 4.9, as a result of AgNps formation two SPR absorption band was seen and SPR absorption bands at 432 nm and 456 nm was attributed to the AgNps formation. The color changed from light brown to dark brown and after 10 min of irradiation and even one side of quartz cuvette turned to silver color due coated by silver nanoparticles.





INTENSITY

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
26	100,6	81,0	77,60	7,628	10,5	2,620	3803	7,1	1167
27	112,8	81,4	83,87	8,213	10,2	3,555	4120	7,0	1049
28	112,9	87,3	76,75	5,665	7,9	2,248	4414	4,8	918,3

VOLUME

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent
26	1,687	85,5	0,3535	6,307	14,5	7,648	4417	0,1
27	2,536	99,9	3,853	4593	0,1	1056	0,000	0,0
28	3,969	99,8	5,251	4766	0,2	966,6	0,000	0,0

No	Z-Ave d.nm	PdI	PdI Width d.nm	MCR kcps	DCR kcps	At	MeIntercept	Intercept	In Range	CumFitEr
26	45,00	0,725	38,31	210,9	14526,5	7	0,471	0,684	95,2	0,00538
27	52,89	0,706	44,43	267,8	18443,2	7	0,439	0,661	95,2	0,00573
28	53,59	0,807	48,15	379,4	26128,4	7	0,392	0,625	95,8	0,00447

Figure 4.11 DLS results of photochemically synthesized of Ag Nanoparticles withTX- A in DMF solution prepared in air atmosphere

Due to importance of oxygen for TX-A initiator, it is worth to investigate the DLS analysis of irradiated solution. DLS measurement confirmed SEM analyis results and nearly monodispers Ag Nanoparticles formation was obtained in DMF solution. The size was changing between 45-53 nm.

4.6.2 In Nitrogen Atmosphere

Nitrogen gas flowed from the prepared solution of TX-A and $AgNO_3$ in DMF during 10 mins. The UV-Vis absorption spectrum depending on the irradiation time was given in Figure 4.11

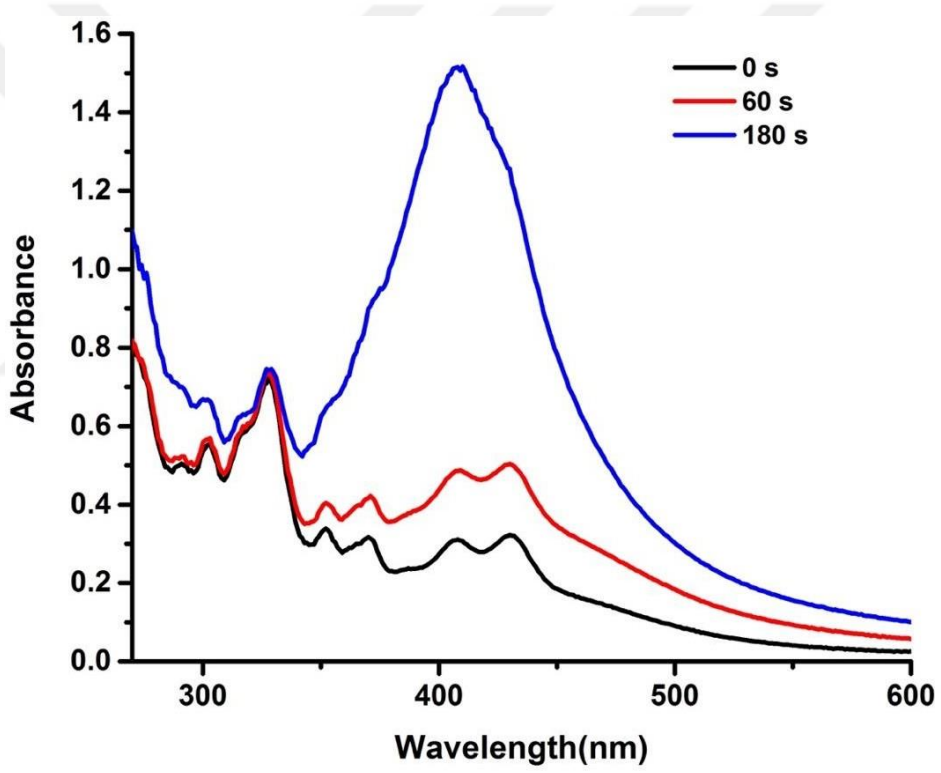
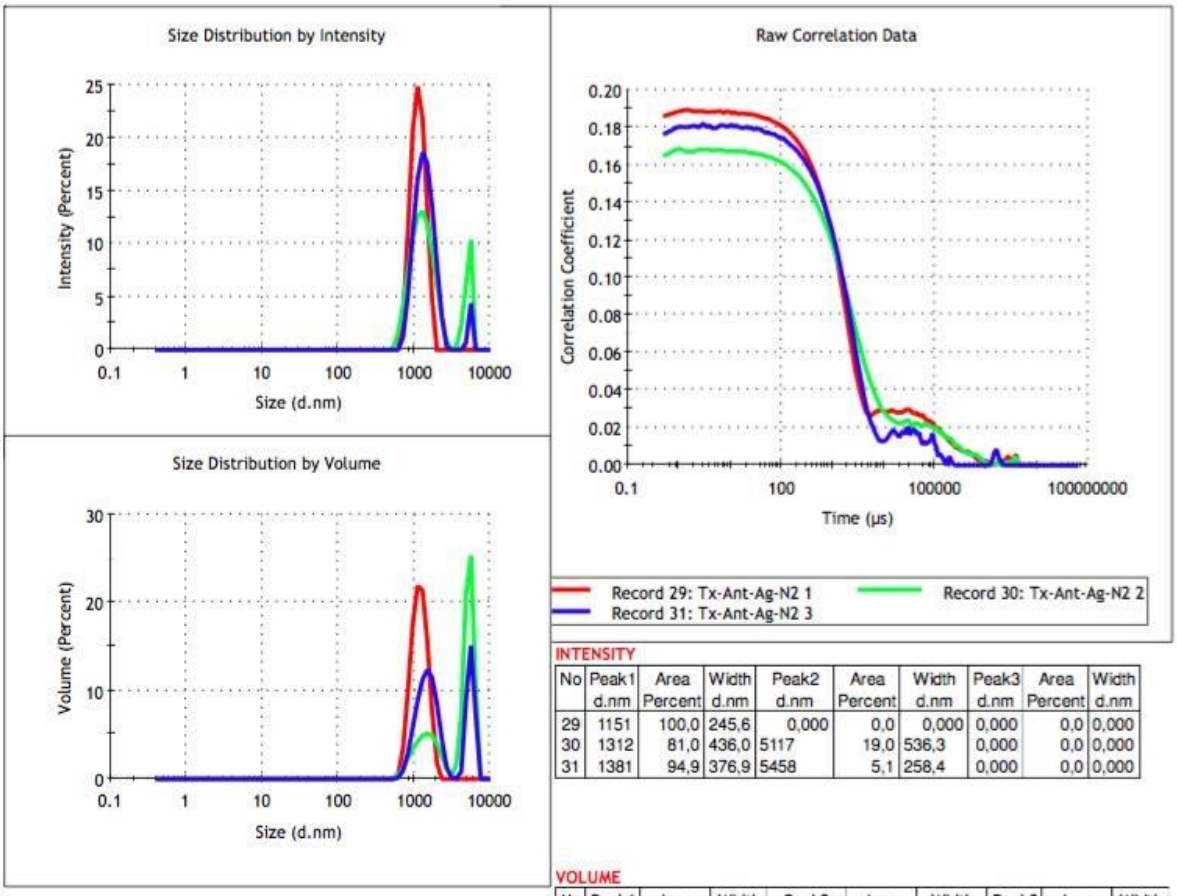


Figure 4.12 In-situ photochemical preparation of AgNps with TX-A in DMF followed by UV-Vis absorption spectroscopy in nitrogen atmosphere

The shape of absorption band of AgNps was narrow compare to spectrum obtained in air atmosphere and SPR band of AgNps appeared at 410 nm and 430 nm. Infact, the most signifigance role of oxygen was differentiated by DLS measurement results. Compare to air atmosphere huge sizes of AgNps was occured and sizes of AgNps were varied from 1500-1900 nm.



INTENSITY

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
29	1151	100,0	245,6	0,000	0,0	0,000	0,000	0,0	0,000
30	1312	81,0	436,0	5117	19,0	536,3	0,000	0,0	0,000
31	1381	94,9	376,9	5458	5,1	258,4	0,000	0,0	0,000

VOLUME

No	Peak1 d.nm	Area Percent	Width d.nm	Peak2 d.nm	Area Percent	Width d.nm	Peak3 d.nm	Area Percent	Width d.nm
29	1196	100,0	287,7	0,000	0,0	0,000	0,000	0,0	0,000
30	1476	34,5	521,1	5237	65,5	743,2	0,000	0,0	0,000
31	1500	68,1	442,9	5509	31,9	618,1	0,000	0,0	0,000

No	Z-Ave d.nm	PdI	PdI Width d.nm	MCR kcps	DCR kcps	At	MeIntercept	Intercept	In Range	CumFitEr
29	1587	0,398	1001	481,8	224152,4	5	0,189	0,414	77,9	0,00150
30	1832	0,485	1276	528,0	245637,6	5	0,167	0,389	76,5	8,70e-4
31	1941	0,359	1163	502,7	233865,1	5	0,184	0,412	79,7	7,00e-4

Figure 4.13 DLS results of photochemically synthesized of Ag Nanoparticles withTX- Antresane in DMF solution prepared in Nitrogen atmosphere

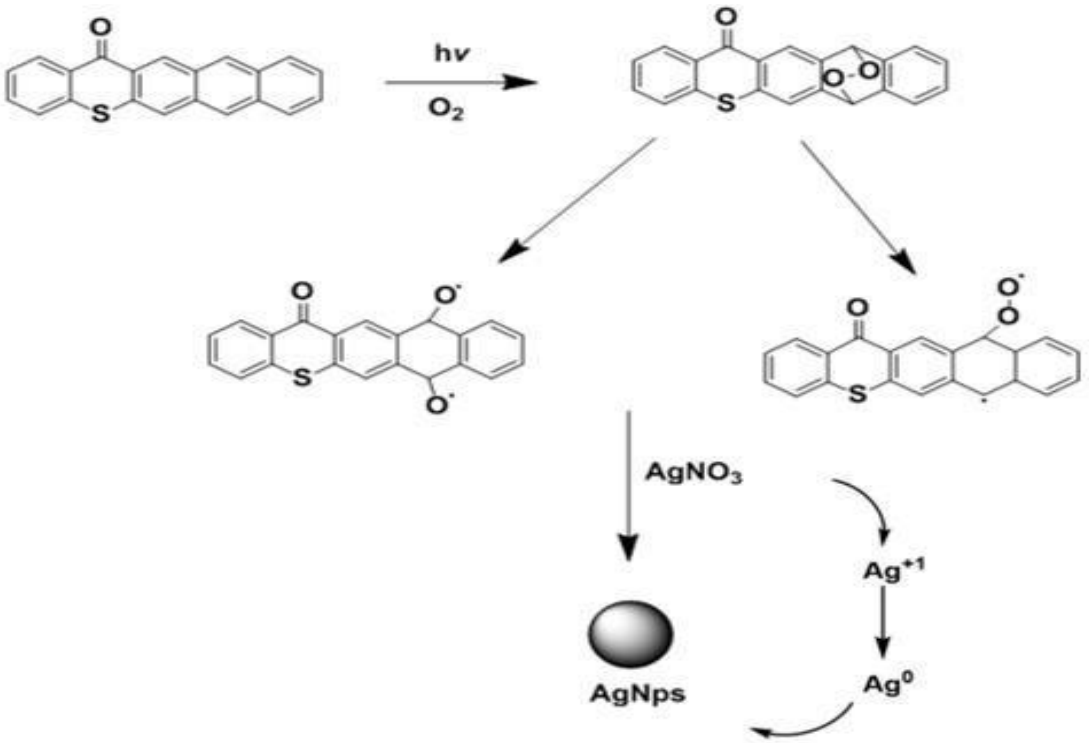


Figure 4.14 Formation mechanism of AgNps with TX-A in air atmosphere

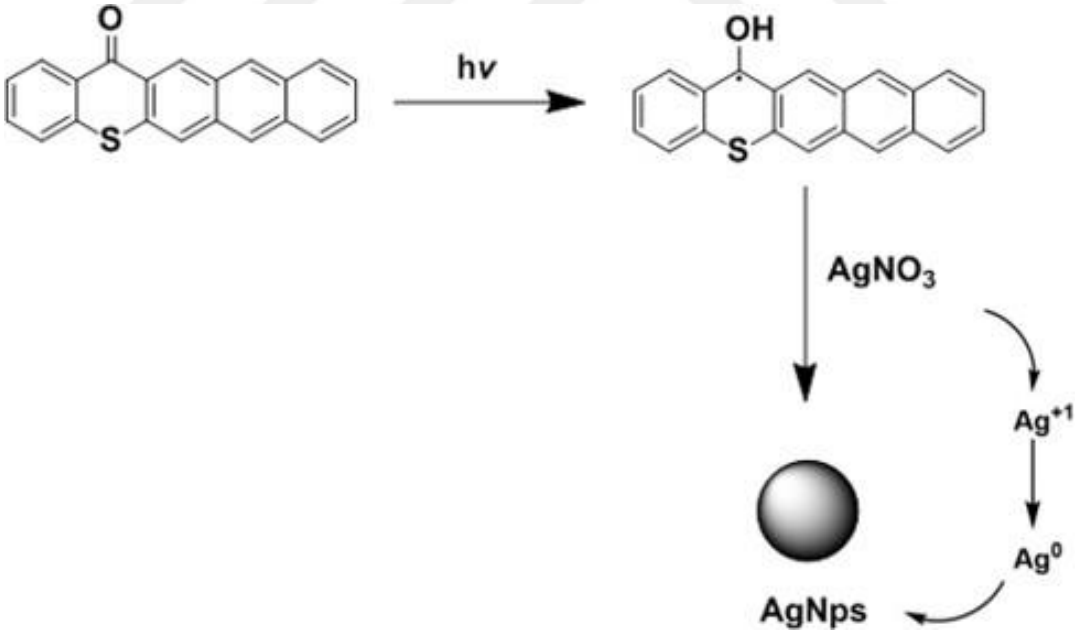


Figure 4.15 Formation mechanism of AgNps with TX-A in nitrogen atmosphere

4.7 In-situ Photoinduced Synthesis of Ag Nanoparticles with TX-A in Polymer Matrix

Thioxanthone-Anthracene (0,5 mg, 5 wt %) and $AgNO_3$ (40 mg, 4 wt %) were dissolved in DMF and PEGMEA/PEGDA were added to the solution. By using ultrasonic probe for 5 min we aim to obtain the salts as nicely distributed at the final formulations and degassed in ultrasonic bath. At the end, they were coated on the aluminum plate surface using roller-coater (40 μm) and cured by mini UV-Cure unit.

The color changes and silver mirror formation was observed as given Figure 4.15 depending on UV exposure time

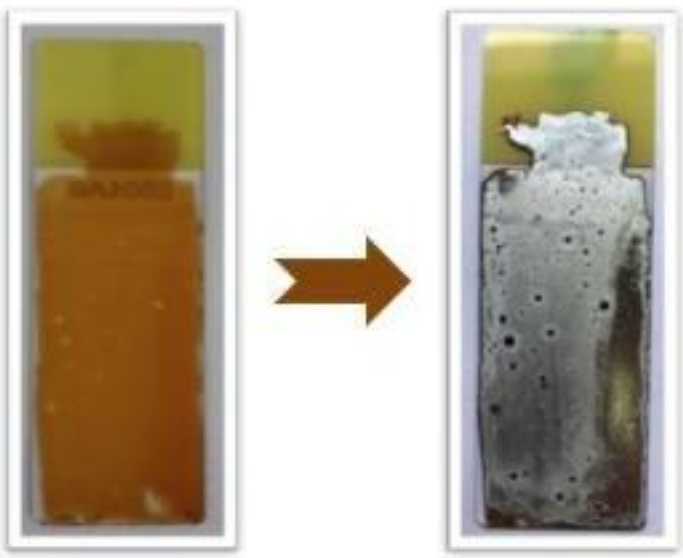


Figure 4.16 The changin of color of AgNps containing PEGMEA/PEGDA nanocompsite films depending on the irradiation time

SEM images of UV-Cured films were in given Figure 4.16 quietly tiny sizes of AgNpswere occured and the view of film was nearly lotus view.

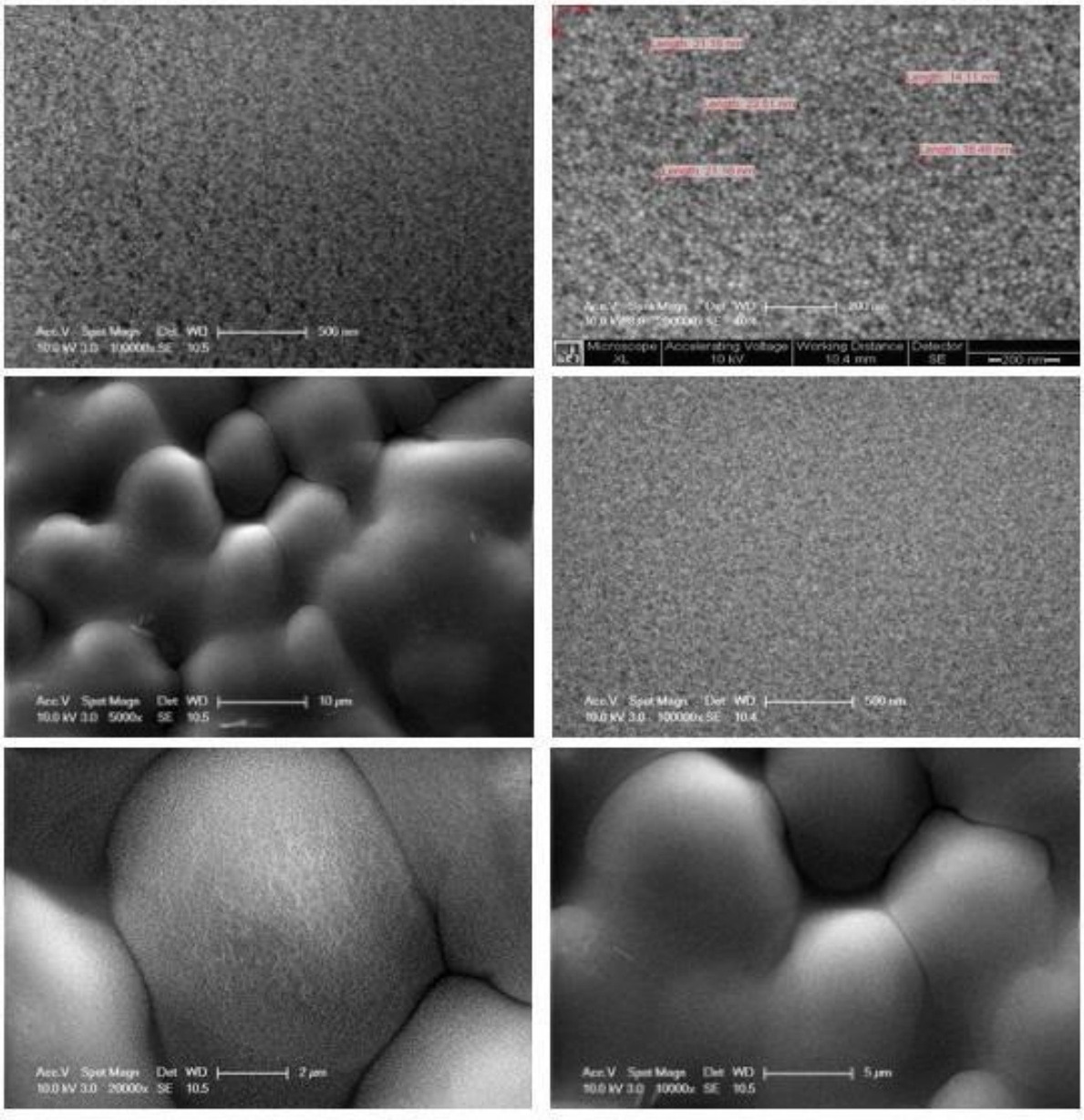


Figure 4.17 SEM images of AgNps prepared in PEGMEA/PEGDA polymer matrix

REFERENCES

[1] Hofer, M.; Moszner, N.; Liska, R. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 6916

[2] Yang K., Fn H., Malloy, KJ., Brinker, C.J., Sigmon, T.W., (2005) "Thin Solid Films",491,38

[3] Cook, D., (1991). "Kinetics and Properties of Photopolymerized Dimethacrylate Oligomer", Journal of Applied Polymer Science, 42: 2209-2222.

[4] Wang, D.Y, Lin, H.C., Yen, C.C., (2006)," Thin Solid Films", 515, 1047

[5] Kork, S.; Yilmaz, G.; Yagci, Y., (2015)," Poly(vinly-alcohol)-Thioxanthone as One-Component Type II Photoinitiator for Free Radical Polymerization in Organic and Aqueous Media", Macromol. Rapid Comm., 36, 2015, 923-928

[6] Wayne, C.E. and Wayne, R.P. (1996) Photochemistry, Oxford University Press, Oxford.

[7] Turro, N.J. (1965) Molecular Photochemistry, Benjamin, New York.

[8] Jon H. Hardesty and Bassam Attili, "Spectrophotometry and the Beer-Lambert Law: An Important Analytical Technique in Chemistry", Collin College, Department of Chemistry.

[9] Xu, F., Yang, J.L., Gong, Y.S., Ma, G.P., ve Nie, J., (2012). "A Fluorinated Photoinitiator for Surface Oxygen Inhibition Resistance", Macromolecules, 45: 1158−1164.

[10] Guillet, J. (1985)., "POLYMER PHOTOPHYSICS AND PHOTOCHEMISTRY", CAMBRIDGE UNIVERSITY PRESS, CAMBRIDGE

[11] OpenStax, Chemistry. OpenStax CNX. Jun 20, 2016

[12] Aydin, M., Arsu, N., Yagci, Y., (2003), "Thioxanthone Acetic Acid Derivatives as Photoinitiators for Free Radical Polymerization", Macromol. Rapid Commun., 24, 718– 723

[13] Cowan, D. O., & Drisko, R. L. (1976). "Elements of organic photochemistry", Plenium Press. New York and London.

[14] Aydin, M., Arsu, N., Yagci, Y., Jockusch, S., Turro, N., (2005), "Mechanistic Study of Photoinitiated Free Radical Polymerization Using Thioxanthone Thioacetic Acid

as One- Component TypeII Photoinitiator", Macromolecules,38,4133-4138

[15] Arsu, N., Reetz, I., Yağcı. Y., and Mishra, M.K., (2007). Handbook of Vinyl Polymers: Radical polymerization and Technology, "Photoinitiated Radical Vinyl Polimerization", 8:142-171.

[16] Fouassier, J.P., (1995). Photoinitiation, Photopolymerization and Photocuring, Münih: Hanser Publishers.

[17] Balta, D.K., Cetiner, N., Temel, G., Turgut, Z., Arsu, N, (2008). "An annelated thioxanthone as a new Type II initiator", J. Photochem. Photobiol. A: Chem., 199(2-3): 316-32.

[18] Cokbaglan, L., Arsu, N., Yagcı, Y., Jockusch, S., Turro, N., (2003), "2-Mercaptothioxanthone as a Novel Photoinitiator for Free Radical Polymerization", Macromolecules, *36* (8), pp 2649–2653

[19] S. Oliver, H. Wagh, Y. Liang, S. Yang, C. Boyer, Enhancing the antimicrobial and antibiofilm effectiveness of silver nanoparticles prepared by green synthesis, J. Mater. Chem. B (2018), [21] Braun D., K. U. (1991). J. Phys. D: Appl. Phys. 24:564–72

[20] Yağcı, Y., Jockush, S., Turro, Nicholes J., (2010). "Photoinitiated Polymerization: Advences, Challenges, and Opportunities", Macromolecules, 43,6245-6260

[21] Davidson, R.S., (1999), "Exploring the Science, Technology and Applications of UV and E.B. Curing", SITA Technology Ltd., London.

[22] Keskin, S., & Arsu, N. (2006). Polym. Bull. 57. 643-650

[23] Dietliker, K., (1991). "CHEMISTRY AND TECHNOLOGY OF UV AND EB FORMULATION FOR COATING"

[24] M. Jayandran, M. Muhamed Haneefa , V. Balasubramanian, (2015). "Green synthesis and characterization of Manganese nanoparticles using natural plant extracts and its evaluation of antimicrobial activity", Journal of Applied Pharmaceutical Science Vol. 5 (12), pp. 105-110

[25] Dogruyol, S. K., Dogruyol, Z., & Arsu, N. (2003). J. "Polym. Sci. Part A: Polym. Chem." "49:4037-4043

[26] Minakshi Das, Kyu Hwan Shim, Seong Soo A. An1 & Dong Kee Yi, (2011) “Review on Gold Nanoparticles and Their Applications” The Korean Society of Environmental Risk Assessment and Health Science and Springer

[27] Turro, N.J., Ramamurthy, V., and Scaiano, J.C. (2010) Modern Molecular Photochemistry of Organic Molecules, University Science Books, Sausalito.

[28] T. Çeper, N. Arsu, Photochemically prepared gold/polymer nanocoatings: formation of gold mirror, Macromol. Chem. Phys. 218 (2017) 1700030.

[29] S. Mutlu, et al., Thioxanthone-anthracene-9-carboxylic acid as radical photoinitiator in the presence of atmospheric air, J. Polym. Sci. A-Polym. Chem. 56 (2018) 1878–1883.

[30] E. ¨Ozçelik Kazancıo˘glu, et al., Photochemical synthesis of nanocomposite thin films containing silver and gold nanoparticles with 2-thioxanthone thioacetic acid-dioxide and their role in photocatalytic degradation of methylene blue, Surfaces Interfaces 22 (2021) 1–14,

[31] G.S. Batibay, O.T. Gunkara, N. Ocal, N. Arsu, Thioxanthone attached polyhedral oligomeric silsesquioxane (POSS) nano-photoinitiator for preparation of PMMA hybrid networks in air atmosphere, Prog. Org. Coatings 149 (2020),

[32] H. Tar, T.I. Kashar, N. Kouki, R. Aldawas, B. Graff, J. Lalev´ee, Novel copper photoredox catalysts for polymerization: an in situ synthesis of metal nanoparticles, Polymers, 12 (2020) 2293,

[33] K.C Smith, 1977, The Science of Photobiology, Springer, Boston, MA

[34] M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, WileyVCH, 1994, New York.

[35] F. A. Carey, R. J. Sundberg, Advanced Organic Chemistry, Plenum Publishing Corporation, 2000.

[36] J. Mattay, A. G. Griesbeck: Photochemical Key Steps in Organic Synthesis, Wiley-VCH, 1994.

[37] A. Gillbert, J. Baggott, Essentials of Molecular Photochemistry 1991, Blackwell Scientific Publications, London

[38] Khan, I., Saeed, K., Khan, I., (2017). “Nanoparticles: Properties, Applications and Toxicities”, Arabian Journal of Chemistry,

[39] Zaarour, M., Roz, M.E., Dong, B., Retoux, R., Aad, R., Cardin, J., Dufour, C., Gourbilleau, F., Gilson J.P. ve Mintova, S., (2014). "Photochemical Preparation of Silver Nanoparticles Supported on Zeolite Crystals", 30:6250-6256.

[40] Anderson, M., (2012). Light, Introduction to Physics, Britannica Educational Publishing, 1, Ebook.

[41] Bishop, C.A., (2011). Vacuum Deposition onto Webs, Films, and Soils, 2nd Edition, Elsevier, UK.

[42] Valeur, B., Berberan-Santos, M.N., (2012). Molecular Fluorescence: Principles and Applications, 2, John Wiley & Sons.

[43] Lago, M.A., Quirós, A.R.B., Sendón, R., Bustos, J., Nieto, M.T. & Paseiro, P., (2015). "Photoinitiators: a food safety review", Food Additives & Contaminants: Part A, 32:779-798.

[44] Tehfe, M.A., Louradour, F., Lalevée, J., Fouassier, J.P., (2013). "Photopolymerization Reactions: On the Way to a Green and Sustainable Chemistry", Appl. Sci., 3:490-514.

[45] Allen, N.S., Segurola, J., Edge, M., Santamari, E., McMahon, A., (1999). "A Comparative Kinetic Study of Commercial Photoinitiators for UV/Visible Curable Acrylate Clear Coatings", Surface Coating International, 82:67–76.

[46] Crivello, J.V., Jang, M., (2003). "Anthracene Electron-Transfer Photosensitizers for Onium Salt Induced Cationic Photopolymerizations", J. Photochem. Photobiol. A:Chem., 159:173–188.

[47] Breton, G.W., Vang, X., (1998). "Photodimerization of Anthracene: A Photochemical Cycloaddition", Journal of Chemical Education, 75(1)

[48] Sakamoto, M., Majima, T., (2010). "Photochemistry for the Synthesis of Noble Metal Nanoparticles", Bull. Chem. Soc. Jpn., 83:1133-1154.

[49] Bruce, P.G., Scrosati, B., Tarascon, J-M., (2008). "Nanomaterials for Rechargeable Lithium Batteries", Angew. Chem. Int. Ed., 47:2930-2946.

[50] Hu, C.C. ve Tsou, T.W., (2002). "Ideal Capacitive Behavior of Hydrous Manganese Oxide Prepared by Anodic Deposition", Electrochem. Commun., 4:105-109.

[51] Balta, D.K., Arsu, N., Yagci, Y., Jockusch, S., and Turro, N.J., (2007). "Thioxanthone-Anthracene: A New Photoinitatior for Free Radical Polymerization in the Presence of Oxygen", Macromolecules, 40(12): 4138-4141

PUBLICATIONS FROM THE THESIS

Papers

1. Mutlu, S., Metin, E., Aydin Yuksel, S., Bayrak, U., Nuhoglu, C., & Arsu, N. (2021). In-situ photochemical synthesis and dielectric properties of nanocomposite thin films containing Au, Ag and MnO nanoparticles. European Polymer Journal, 144, 110238.

Conference Papers

1. Bayrak, U., Mutlu, S., Batıbay, G. ve Arsu, N., (2017). "Fotokimyasal Olarak In-Sitü Mn Nanoparçacık Sentezi ve Nanokompozit Filmlerin Hazırlanması", 8.Ulusal Kimya Öğrenci Kongresi, İstanbul.