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Chemical and Physical Properties of Polyimides: Biomedical and Engineering Applications

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Peter Dineff and Gencho Danev

Additional information is available at the end of the chapter

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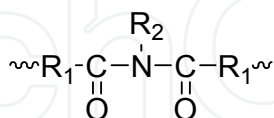
1. Introduction

The development of chemistry and solid matter physics lead to improved technologies in producing polymers and nanosized films such as vacuum deposition and solid state reactions. Over the past 20 years because of intensive research in chemistry and physics of organic materials, place the development of the new area in materials chemistry - organic electronics and photonics (polytronics). Polymer materials are becoming more widely used to improve the quality of human life: from social to high-tech - household appliances, textiles, insulation materials in industry and construction, medical implants, materials for optoelectronics, the formation of nanosized films and more over. Important classes of polymeric materials responded to certain technical requirements are polyimides (PI). They contain in molecules functional group CO-NR_2 called imide. The presence of $n-\pi$ conjugation between non-pair electron of nitrogen atom and π electrons of the carbonyl group makes them resistant to chemical agents and moisture. Mainly the type of hydrocarbon residues (arenes, aliphatic) and the presence of other functional groups (Cl, F, NO_2 , OCH_3 , etc) determine their physical properties and their application in practice. In this chapter will be discussed preparation of PI, the mechanisms of reactions, possible competitive reactions, physical properties, their application as biomedical materials (implants, functionalized nucleic acids) and their application as optical materials for the producing of nanocomposite layers matrix including metallic or dielectric clusters as "guest". One of the achievements in obtaining PI layer is the application of microwave (MW) irradiation combined with low temperature treatment compared to the application of pure thermal imidization. This approach is particularly effective imidization for inclusion of PI layers in multilayer lithography or optical systems in which the formed nanocomposite films are not stable in thermal imidization condition.

1.1. Classification of polyimides

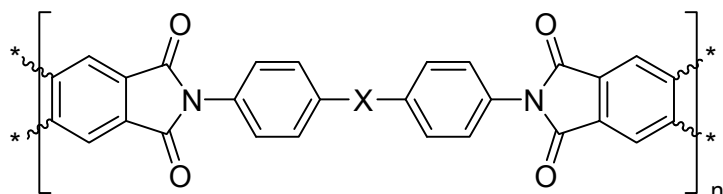
Depending on the polymer chain, the type of hydrocarbon residues and the presence of other functional groups, polyimides can be classified as follows:

1.1.1. Linear



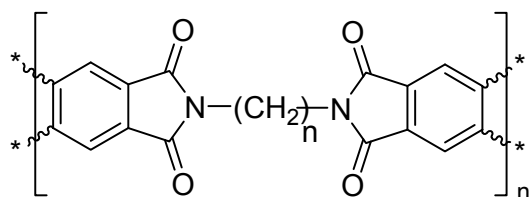
1.1.2. Cyclic

a. Aromatic (main-chain)

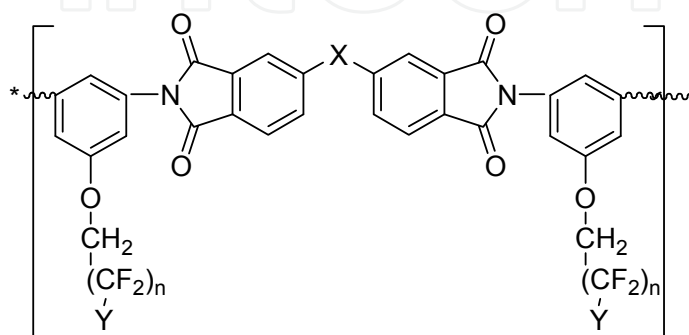


X = -O-, >C=O, >CH₂-, -N=N-, -SO₂- и др.

b. Aliphatic – aromatic (main-chain)

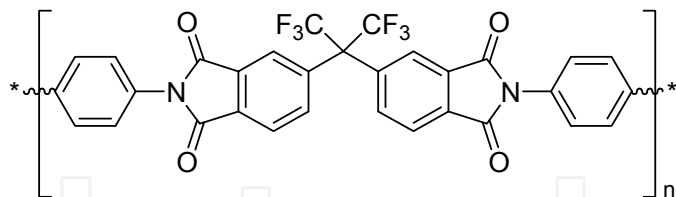


1.1.3. Side-chain



n = 1,2,3,4,5; Y = F, H

1.1.4. Functionalizing



Many polyimide investigations have mainly been concentrated on aromatic polyimides, and little information is available about aliphatic polyimides that are also potential candidates for engineering and biomedical applications.

2. Chemical properties of polyimides

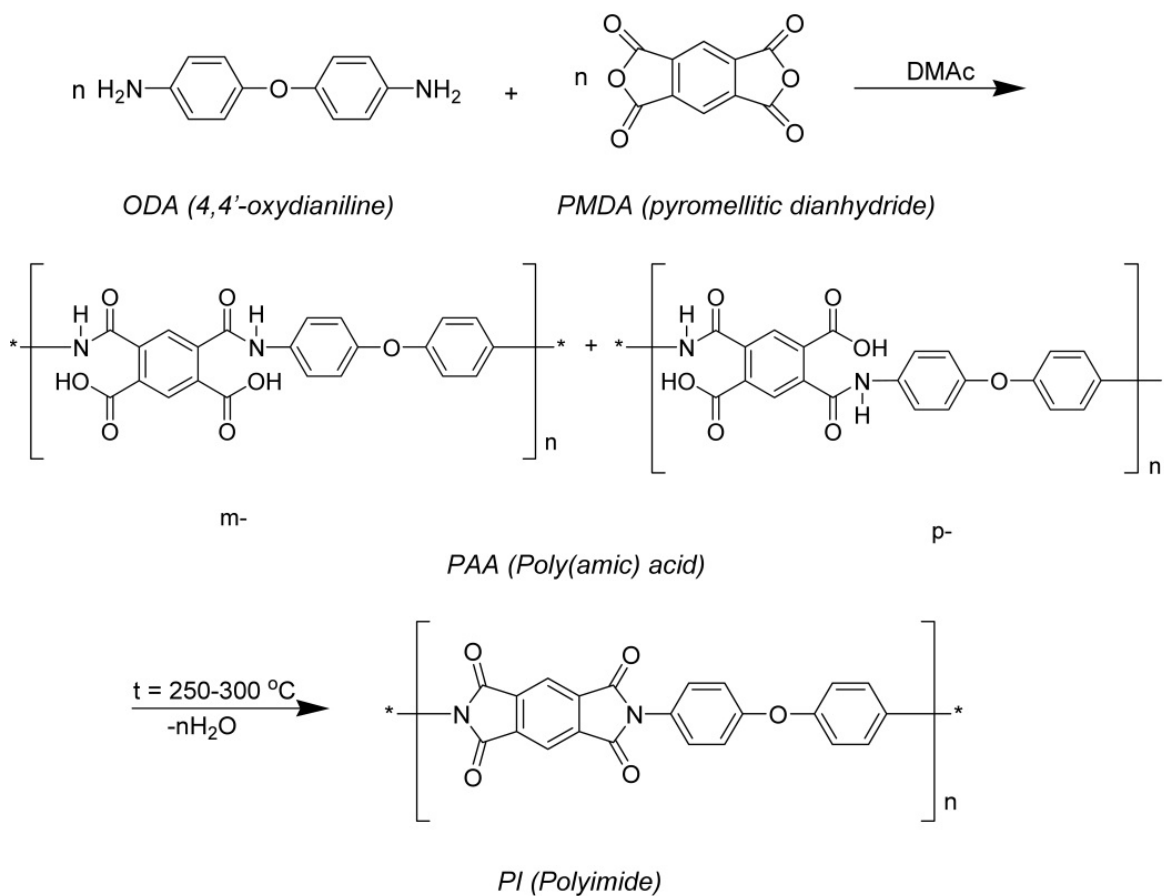
2.1. Preparation and structure of polyimides

Aromatic polyimides generally prepared by a two-step procedure from aromatic diamines and aromatic tetracarboxylic dianhydrides. The chemistry of polyimides is a specific area with large variety of monomers available and several methodologies for synthesis [1,2,3]. The subtle variations in the structure dianhydride and diamine components have tremendous effect on the properties of the final polyimide. The most widely practiced procedure in polyimide synthesis is two-step process via poly(amic acid). The reaction between dianhydride (*pyromellitic dianhydride* PMDA) and diamine (*4,4'-oxydianiline* ODA) is required ambident conditions in dipolar aprotic solvents, such as N-methylpyrrolidone (NMP) or N,N-dimethylacetamide (DMAc). The next polycyclodehydration reaction of poly(amic acid) depending on ratio of precursors lead to final polyimide with different molar mass (Scheme 1) [4,5].

Reactions between cyclic anhydrides and primary diamines run as S_N2Ac mechanism (bimolecular nucleophilic acyl substitution). The reaction running in two steps, the first is attaching of nucleophilic reagent to electrophilic carbonyl C-atom. The intermediate poly(amic acid) is formed by the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. Thus reaction is irreversible, because the amino group is strong nucleophilic agent, consequence is not good leaving group than the hydroxyl group from the carboxylic acid [1,2,5,6]. In addition, anhydride cycle have not good resonance stability and charge delocalization, because oxygen atoms have equal electronegativity and electron structure. The second step is nucleophilic ring closure due to dehydration and imide ring formation. One of the disadvantages of this method is unavoidable presence of solvents and need for their removal [7]. During the polycyclodehydration side reaction is run that defy stereoregular control [1]. In figure 1 shows the structural formulas of the side products of the reaction for obtaining PI.

These side compounds caused defects in the synthesized PI film. They are unwanted impurity in production of nanostructured films with chromophores as a "guest" in the matrix, since they lead to low quality of dielectric and optical properties of layers. At

temperatures above 200 °C by intramolecular rearrangement isoimide convert to imide (Scheme 2) [9,10].



Scheme 1. Scheme 1. Reaction between ODA and PMDA to PAA with following cyclodehydration to PI.

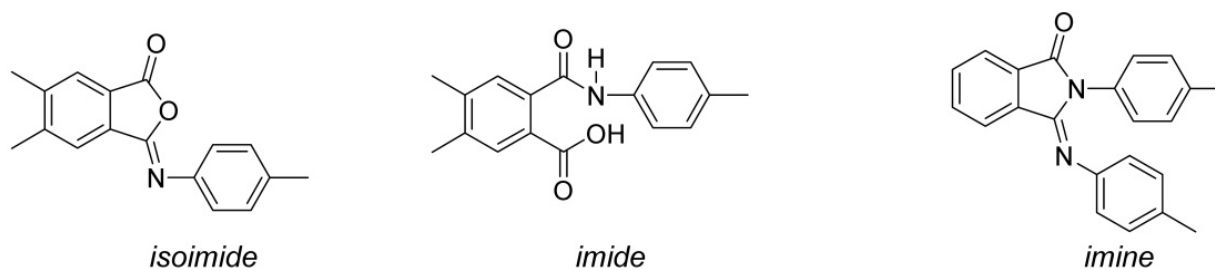
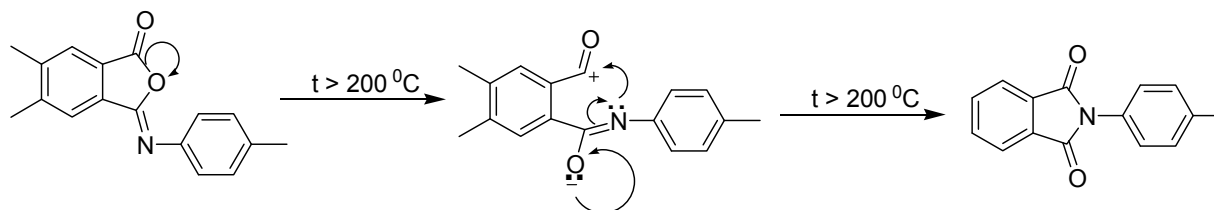
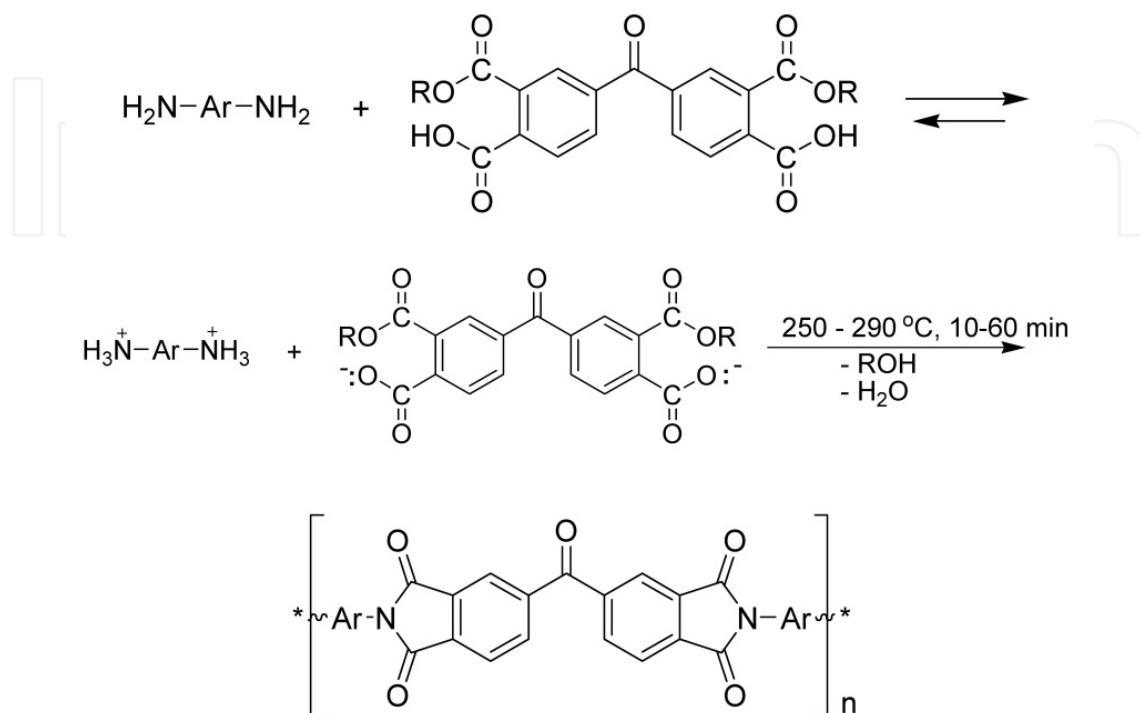


Figure 1. Structural formulas of side compounds of the reaction for preparation of PI.



Scheme 2. Intramolecular rearrangement of isoimide to polyimide.

Another way for synthesis of polyimides from Nylon-Salt-Type Monomers has been reported from Imai [4]. The method based on the melt polycondensation of diamine and pyromellitic acid half diester (pyromellitic acid diethyl ester) (Scheme 3).



Scheme 3. Synthesis of PI from pyromellitic acid half diester and diamine.

These salt monomers have been prepared as white crystalline solids by dissolving an equimolar amount of each individual diamine and tetracarboxylic acid half diester in hot ethanol (or methanol), and subsequently cooling the resultant solution. The author has been found that imidization (polycondensation) of salt run to polyimide for 10 min at $250\text{ }^\circ\text{C}$. The high-pressure polycondensation of the salt monomer has been applied. The pressure affect on the temperature and reaction time that directly afforded high molecular-weight polyimide. This method is useful for the synthesis of the polyimides having well defined structures, compared with the other synthetic methods [4].

2.2. Vapour deposition and solid state reaction

The development of the chemistry of polymers and their application in nanotechnology many researchers have been seen alternative forms for obtaining nanosized films. Our studies have focused primarily on vapour deposition of precursors and solid state imidization reaction [7,10,11,12]. Vapour deposition processes of organic layers play an important role in polytronics. They allow the construction of systems without solvents, based on principle of bottom-up and have significant role in the formation of intermediate and protective layers. Important advantages of vapour processes are follows: (i) vacuum deposition is basically a cleaning process from impurities and resulting deposited layers

have a much higher purity. This reduces problems with local anisotropy properties, polymorphism, etc.; (ii) vapour process allows the run of additional activated or modified processes as resulting deposited films are changed and improved properties: higher physical density, polymerization, high chemical purity and others. This is related take plasma processes, electronic flow, microwave irradiation or photon interaction. All these additional processes generate enough number of active particles as free radicals and ions in the gas phase. The disadvantage of these so-called vapour assistance deposition processes is the need for very precise control [7,13].

In the vacuum deposition of the precursors PMDA and ODA at temperature of 120-145 °C reaction of polycondensation to PAA with opening of the anhydride ring of PMDA takes place (Ac-Sn₂-reaction). These processes are to great extent accelerated and controlled in the thermal treatment of the condensed solid phase which represents PAA, with regard to their transformation to PI by means of reaction of polyclodehydration in solid state to linear PI [7,10,11]. The FTIR spectra of individual films of PMDA, ODA and PAA are shown in figure 2.

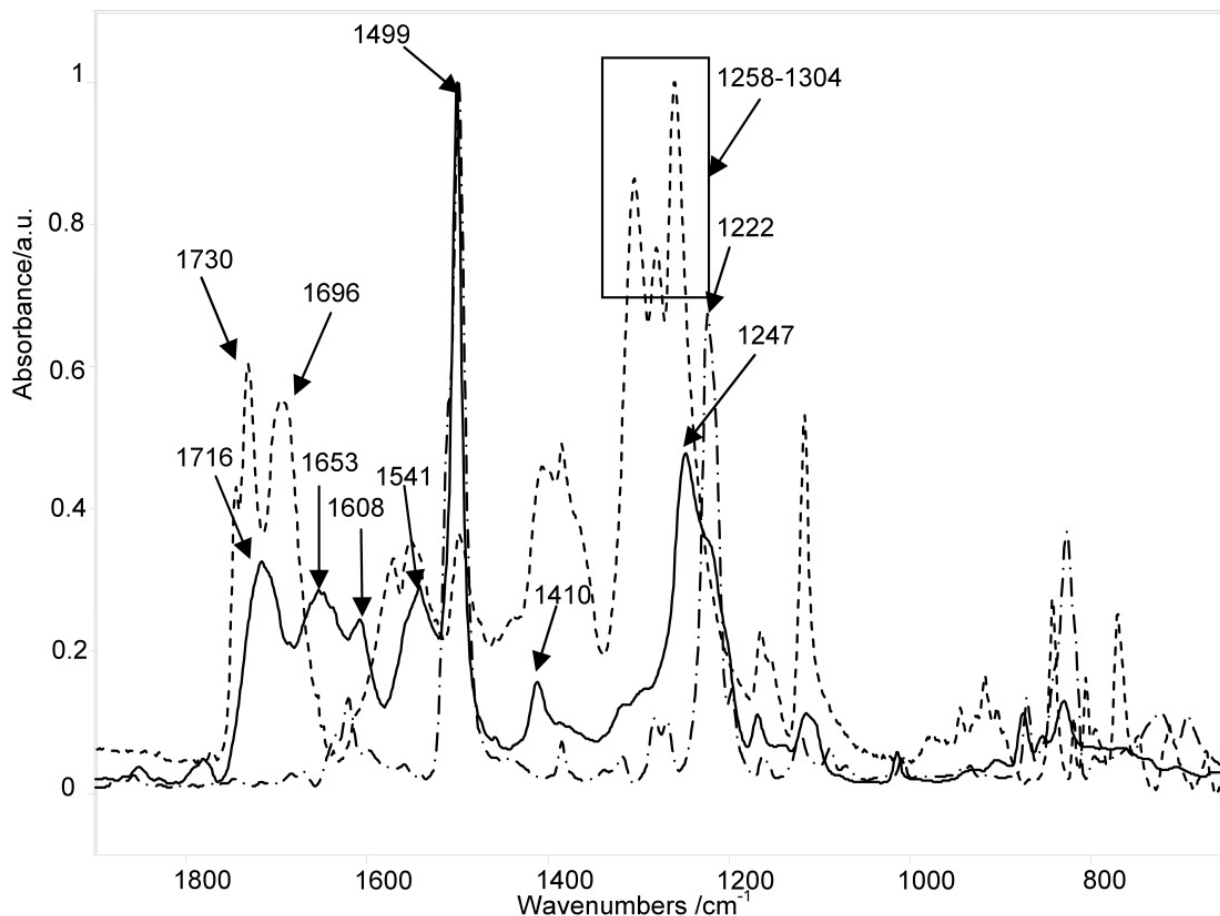


Figure 2. FTIR spectra of the vacuum deposited films of: - - - - - PMDA; - · - · - ODA; ———— simultaneously deposited both precursors in a mole ratio of PMDA : ODA= 1:1(PAA).

The band ν 1716 cm^{-1} for the $>\text{C}=\text{O}$ group in the PAA spectrum related to acid. The presence of hydroxyl group of the acid (C-OH) is corresponded at δ 1247 cm^{-1} . The amide bond is

identified by the bands at ν 1653 cm^{-1} ($>\text{C}=\text{O}$ amide I band) and δ 1608 cm^{-1} (N-H amide II band).

Compared to the classical methods for producing films from PAA, in which the acid is preliminarily obtained in a solution and after that deposited as a thin film usually by spin coating, in the vacuum deposition method this process is performed in only one step. More and more researcher accept that the method of vacuum deposition provides for a greater degree of purity in the thin film production, opportunity for controlling and computerizing the processes of heating, imidization and layer formation designed for obtaining standard PI or nanocomposite products of reproducible composition, thickness, structure and properties [12,14]. In figure 3 are compared the spectra of PAA and solid imidization film of PAA to PI obtained after thermal treatment.

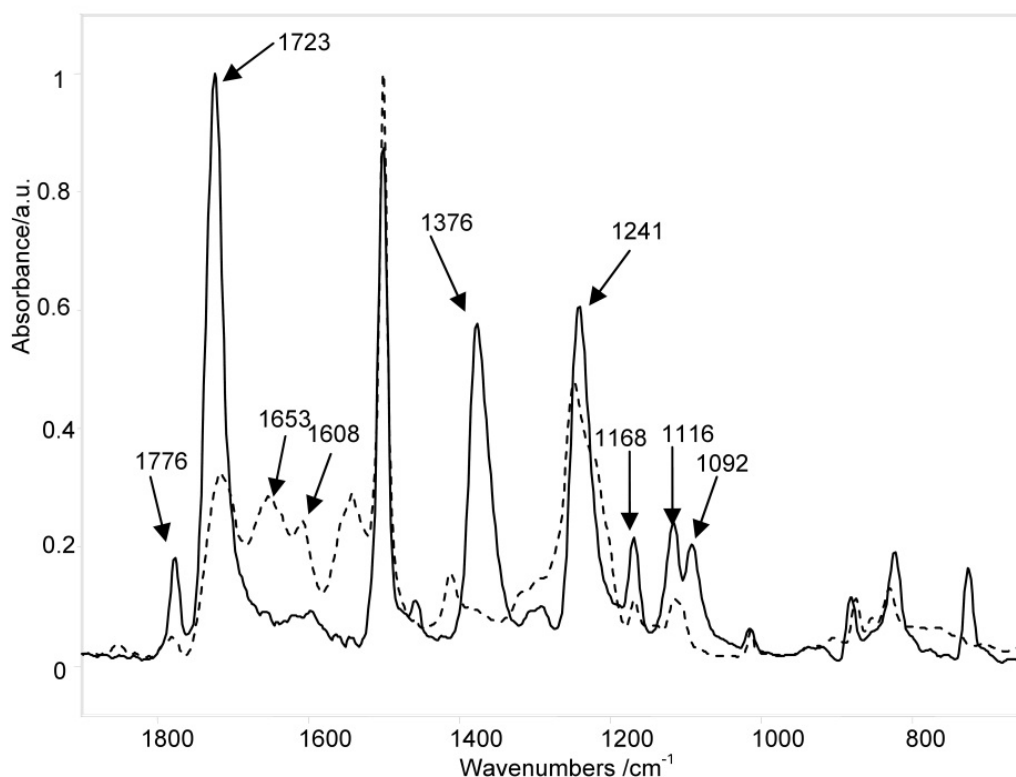
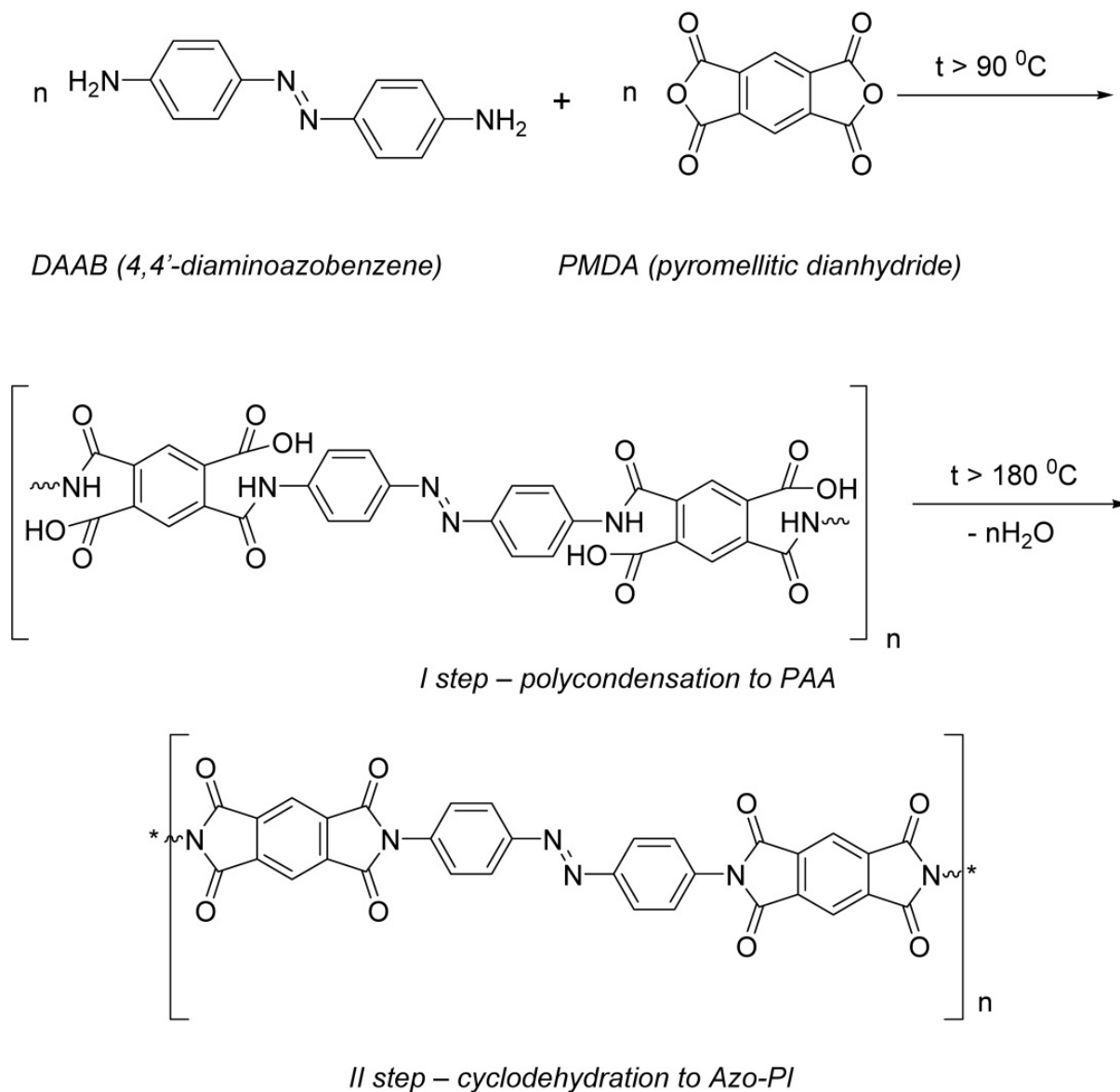


Figure 3. FTIR spectra of vacuum deposited films with thickness 200 nm and PMDA:ODA(PAA)=1:1 ----- thermally untreated; -----thermally treated 1 h at 300 °C.

The bands at ν_s 1776 and ν_{as} 1723 cm^{-1} characterize the $>\text{C}=\text{O}$ groups of the imide ring. The imidization confirmed by the $\nu_{\text{C-N}}$ 1376 cm^{-1} imide III band where a minimum is observed in the spectrum of the untreated layer in this frequency. The exits of new bands in the area deformation vibrations for C-O and C-N bonds respectively at 1241, 1168, 1116 and 1092 cm^{-1} is observed [7,9,10].

Similarly, the vacuum deposition gives the opportunity to syntheses of azo-polyimide, type "main-chain". In this case, as starting precursors were used PMDA and DAAB (4,4'-diaminoazobenzene), which are then vacuum deposition in a thin layer subjected to thermal

and microwave treatment for imidization reaction to polyimide (Scheme 4) [7,15]. As is seen the azo-chromophore is covalently bonded in the polymer matrix. So a preparation of colored polymer is realized without to incorporate in the matrix an additional chromophore.



Scheme 4. Reaction between PMDA and DAAB to Azo-PI

The resulting films were characterized by FTIR and UV-VIS spectroscopies before and after imidization. It was studied kinetics imidization at different temperatures. The results show that optimal conditions for imidization are temperature 300 °C for 1 h. It is known that azobenzene derivatives possess optical properties associated with optical anisotropy due to photoisomerisation photoorientation of azochromophore, perpendicular to the direction of the polarized beam. These properties of azobenzene derivatives are important for their application in nonlinear optics and nanotechnology, optical modulators, optical recording media and other devices [16,17,18,19].

2.3. Microwave synthesis

One of the achievements of polymer chemistry is development of microwave synthesis. It is new and promising methods in organic synthesis, that time of the reaction manifold shorten. The literature describes that reaction occurs within hours or days, by microwave synthesis reaction time is greatly reduced - from 5 to 30 min [19,20,21]. Microwaves are distributed evenly in the reaction mixture, which makes the temperature field uniform (homogeneous) and radio frequency radiation provides the energy required for the reaction, and molecules get more energy (E_a) and the reaction speed increases manifold [20,21,22,23].

Our investigation showed that after combined treatment - MW and thermal, the imidization reaction take place for 5 to 15 min that is confirmed by FTIR spectroscopy. The quality of the film is identical with the one of PI obtained only after a thermal treatment for 1h at 300 °C. The method carried out allowed for PI production to be optimized by the involving of MW treatment of vacuum deposited films [10, 24].

It was found that the prerequisite for obtaining films of PI without mechanical defects is the establishment impact energy. It was investigated and established optimum conditions of MW and thermal treatment. Our suggestion that the type of energetic treatment power and time can be reduced to the substitution of different parameters: time, power and intensity of impact is not confirmed, i.e. it was not prepared the PI films with the same imidization degree in terms variation of treatment. Experimentally proved that 5 hours additional heat treatment at 170 °C is not offset one hour treatment at 250 °C. By applying the DTA (Differential Thermal Analysis) and FTIR spectroscopy was found to be necessary to achieve clearly defined temperatures for better imidization to PI. These results are also valid in MW treatment. Only the combination of both MW and heat, leading up to the high imidization. It was found that higher imidization degree achieved for 15 min. after application of MW and thermal treatment at 250 °C compared with only thermal treatment [24,25,10]. Therefore, the mechanism of the reaction according Scheme 1 and 6 requirements not only affect energy and same temperature achievement in the layer, but also requires strict established parameters: the type of treatment, power and time of action to achieve a high imidization degree.

2.4. Kinetic of the imidization

The kinetics of imidization is measured by the degree of transformation of PAA into PI by given output parameters - temperature and time of reaction. Appropriate method for determination of imidization degree is FTIR spectroscopy. The band at 1376 cm^{-1} is called imide III (C-N-C vibrations) band and using for qualitative and quantitative estimations of imidization degree in the present of internal standard at 1500 cm^{-1} (C-C_{Ar} vibrations) [26,27]. The imidization degree of PAA to PI was determined using eq 1.

$$\text{Degree of imidization} = \frac{(\text{peak area at } 1376\text{cm}^{-1})\text{time}/(\text{peak area at } 1500\text{cm}^{-1})\text{time}}{(\text{peak area at } 1379\text{cm}^{-1})_{300\text{ }^{\circ}\text{C}}/(\text{peak area at } 1500\text{cm}^{-1})_{300\text{ }^{\circ}\text{C}}} \quad (1)$$

Yang et al. was used Seo model to correlate of imidization with time [28]. In Seo's approach the rate constant was proposed as $k(t) = b \times \text{sech}(-at)$. Inserting into the first-order rate equation, the relationship between the degree of imidization and curing time is obtained as:

$$-\ln(1 - x) = -\frac{2b}{a} \tan^{-1} e^{-at} + \text{const.} \quad (2)$$

The constant in eq. (2) was obtained by fitting with the experimental data to the original Seo model. However the constant in eq. (2) was found to be 0.785 by fitting the experimental data at the initial condition ($t = 0, x = 0$). Hence, the kinetic equation was expressed as eq (3)

$$-\ln(1 - x) = -\frac{2b}{a} \tan^{-1} e^{-at} - 0.785. \quad (3)$$

The parameters a and b were expressed in the form of Arrhenius expressions in this study, which are shown as eqs (4) and (5)

$$a = A_a \exp(-E_a/RT) \quad (4)$$

$$b = A_b \exp(-E_b/RT) \quad (5)$$

The constants A_a , A_b and E_a were calculated from Arrhenius plots of the parameters a and b . The assumption that the parameter b in the original Seo model is independent of temperature conflict obviously with the fact that the rate constant of first-order reaction $k(t)$ is a function of temperature since $k(t)$ approaches b at the initial time, $t \rightarrow 0$. The corresponding activation energy obtained from parameter a should be the energy barrier for the transition state and parameter b represents the rate constant for the imidization reaction.

3. Physical properties of polyimides

3.1. Intramolecular interaction

The formation of charge transfer complex (CTC) has been studied from many researches [29,30]. They reported that CTC formed between dianhydride and diamine groups in polyimides being an important reason for high glass transition temperature (T_g) of polyimides [29,30]. The increased interchain attractive forces due to such interactions were proposed as effectively increasing the chain rigidity and hence the T_g . It was also proposed that the presence of any bridging group in the dianhydride had a strong influence on the glass transition as it changed its electron affinity and hence promoted the possibility of CTC formation. Figure 4 shows the idealized form of such an interaction between the dianhydride and diamine groups.

In terms of electronic structure of PI is a prerequisite for strong intermolecular interactions and charge transfer. The nitrogen atom is electron donor to carbonyl group which is electron acceptor, this leads to electron move and charge interactions. On the other hand they are interactions between aromatic rings with their π electronic sextet, which lead to parallel and planar orientation of individual chains to each other. Many of the properties of the PI's dependent on intramolecular interactions due to the use of vapour processes and

solid state reactions to obtain essential to create packing of the polymer chain and effective CTC.

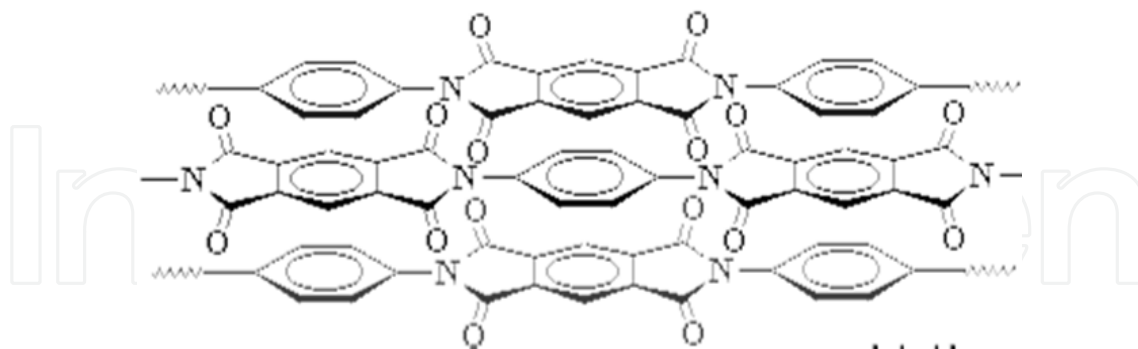


Figure 4. Idealized charge transfer complex formation between dianhydrides and diamines

3.2. Thermal stability

Thermo-Gravimetric Analysis (TGA) is an appropriate method for estimation of thermal stability of polymers. In figure 5 TGA curves presented our experiments after thermal treatment of ODA and PMDA mixture [11].

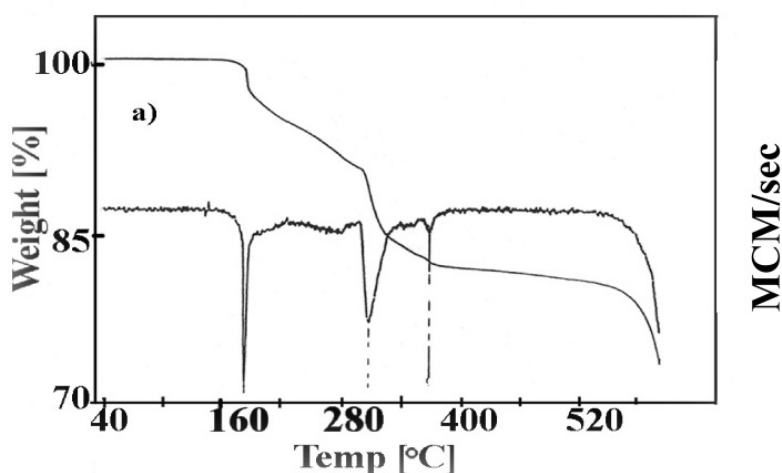


Figure 5. TGA curves of ODA and PMDA powder mixture (1:1 ratio)

Two drastically changes of the TGA curves are observed at about 180°C and about 280°C, which indicate relatively weight loss of 3% and 9%. These values correspond to one or three mols of water. It is well known that the polycondensation reaction of ODA and PMDA (Scheme 1), takes place by separate of water. Therefore is quite logical to accept that the weight loss is a consequence of the process starting at lower (180°C) temperature till the moment the PAA is obtained. With increasing the temperature the interaction process continues and at higher (280°C) temperature the dehydration leads to imidization and PI formation. It is also clearly seen (Fig. 5), that the rest of the sample remains stable up to 520°C. As the rest most probably is consisting of PI, it can be underline that the PI considering the destruction or weight loss is stable at temperatures higher than 500°C.

3.3. Optical transmittance

High light transmittance for a wide spectral range in combination with dielectric and chemical resistance properties is an attractive feature for potential applications as encapsulating layers, protective films and intermediate for micro- and optoelectronics. In figure 6 presents a series of spectra of PI obtained under different conditions. It is seen that the conditions for the PI films do not significantly affect the values of transmittance in the range 80 to 92 % in a relatively wide spectral range λ 420-900 nm.

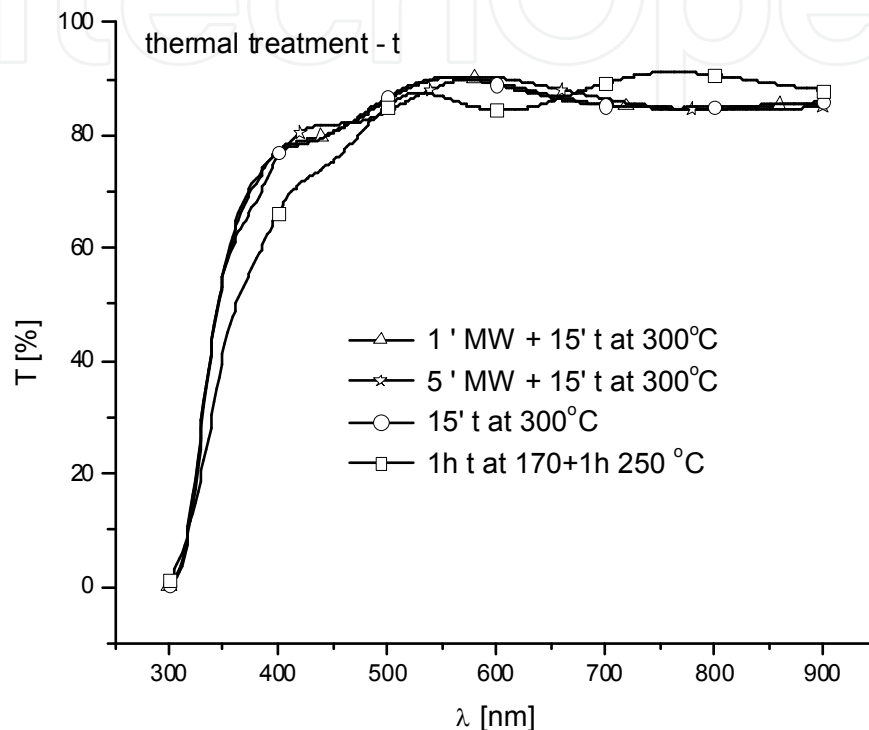


Figure 6. Spectral dependence of transmittance (T) for PI (PMDA-ODA) films 0,22 μm prepared under different conditions.

3.4. Electrical properties

The possibility of treatment condensation of the precursors in Ar atmosphere during vapour deposition can be interpreted as incorporation of pores, i.e. change the density or porosity of the condensed films of ODA and PMDA respectively, and the influence of pores on the permittivity PI layers. There was also depending on the reduction of dielectric constant with increasing imidization degree which is higher for higher temperatures of treatment in view of running imidization reaction [31,32,33]. Tables 1 to 3 are summarized data for conductivity, dielectric constant and capacity of the PI films with different composition, thickness, condition of the substrate or energy treatment and influence the conditions for obtaining PI or composite layers with embedded nanosized carbon particles.

Impressive ability to drastically change the conductivity by incorporation of carbon particles. The measured differences in conductivity depending on the concentration of "guests" - carbon 0,55% and 1,4% vol, respectively filling factor can be interpreted as a

condition of embedded clusters. Therefore, there is the possibility of one side by vacuum deposition of the precursors and conditions of thermal treatment to influence the parameters examined. On the other, through the incorporation one type particles created opportunities to change individual parameters in a wide range in identical composition, for example different conduction with or without embedded carbon [30,31].

Thickness d [μm]	Thermal treatment [$^{\circ}\text{C}$]	Permittivity [ϵ]
0.1	1 h 170 $^{\circ}$ C + 1 h 250 $^{\circ}$ C	3.0 - 3.2
0.1	1 h 170 $^{\circ}$ C + 1 h 350 $^{\circ}$ C	2.8
0.22	1 h 170 $^{\circ}$ C + 1 h 250 $^{\circ}$ C	3.1 - 3.3
0.22	1 h 170 $^{\circ}$ C + 1 h 350 $^{\circ}$ C	2.9

Table 1. Thermal dependence of polyimide permittivity.

Vacuum deposited layer 500 nm	Capacity [pF]	Permittivity [ϵ]
Planetary rotating substrates	9	3.2
Linearly moving substrates	11	3.4

Table 2. Polyimide capacity (C) and permittivity (ϵ) depending on the dynamic state of the substrates during the vapour depositions of precursors.

Type of layer formation	Conductivity (σ), [$\text{ohm}^{-1}\text{m}^{-1}$]
Without Ar (residual pressure 10 $^{-4}$ Pa)	1.9 $\times 10^{-8}$
With Ar (residual pressure 10 $^{-2}$ Pa)	0.7 $\times 10^{-14}$
With 0.55 vol.% Carbon	2.0 $\times 10^{-5}$
With 1.4 vol.% Carbon	4.0 $\times 10^{-1}$

Table 3. Polyimide conductivity (σ) depending on the type of layer formation

4. Biomedical and engineering application

4.1. Biomedical

Polymer materials have been established as excellent materials in chemistry, automotives and electronics to interconnect different components, to electrically insulate conductors and to survive harsh corrosive environments. Polyimides are the most common material class for substrate and insulation materials in combination with metals for interconnection wires and electrode sites. Therefore, it is quite natural that the medical device industry has focused its attention to polyimides for medical devices in general and especially for encapsulation and insulation of active implants. Neural implants are technical systems that are mainly used to stimulate parts and structures of the nervous system with the aid of implanted electrical circuitry or record the electrical activity of nerve cells. Their application

in clinical practice has given rise to the fields known as “neuromodulation” and “neuroprosthetics” or neural prostheses. Neuromodulation, namely the stimulation of central nervous system structures to modulate nerve excitability and the release of neurotransmitters, alleviates the effects of many neurological diseases. Deep brain stimulation helps patients suffering from Parkinson’s disease to suppress tremor and movement disorders. It is also a treatment option for severe psychiatric diseases like depression and obsessive-compulsive disorder. Neural prostheses aim to restore lost functions of the body, either sensory, motor or vegetative. All neural implants have to fulfill general requirements to become approved as a medical device - they must not harm the body and should stay stable and functional over a certain life-time which is in most cases in the range of decades. Generally polyimides are used as an insulation or passivation layer, polyimides provide protection for underlying circuitry and metals from effects such as moisture absorption, corrosion, ion transport, and physical damage. Furthermore, it acts as an effective absorber for alpha particles that can be emitted by ceramics, and as a mechanical stress buffer. Key properties are thermoxidative stability, high mechanical strength, high modulus, excellent insulating properties, and superior chemical resistance. Devices made of polyimide have elicited only mild foreign body reactions in several applications in the peripheral and central nervous system showing good surface and structural biocompatibility. They have proven to be biostable and functional for months in chronic *in vitro* and *in vivo* studies. Most often used polyimide is BPDA-PPD as biomaterial and commercially available under the trademark of DuPont’s PI2611 or UBE’s U-Varnish-S (figure 7) [34]

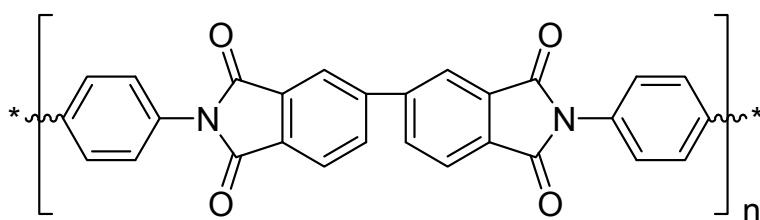


Figure 7. Structure of BPDA-PPD polyimide.

Advanced microtechnologies offer new opportunities for the development of these active implants. Biocompatible materials such as titanium and polyimide are potential candidates in encapsulating implant devices. A. Main et al. have been tested laser joined titanium-polyimide samples for bond strength, and was observed that the laser bonding parameters such as laser power and feed speed affect the bond strength of all material systems [35]. The applicability of laser joining for a specific material combination and the selection of the appropriate approach depends on the optical properties of the materials. The need to join dissimilar materials occurs as the encapsulation includes functional elements such as electrodes used for neural stimulation or modules with defined micropores for the effusion of drugs. Currently, the implants such as pacemakers and cochlea implants are being used to treat cardiac and hearing disorders, respectively. Examples of other implants include neural and muscular stimulators for the treatment of seizures caused by epilepsy, and implantable drug delivery systems to locally effuse chemicals and drugs such as pain medication, hormones and other pharmaceutical compounds. Research is underway to develop subretinal

implant devices that will replace damaged photoreceptor cells. These damaged cells fail to send electrical signals to the rest of the eye and eventual the brain, that results in blindness [36]. The study of Humayun et al. has showed successful results to restore vision by permanently implanting a retinal prosthesis in the blind eye. These active implants utilize microelectronic devices that are developed on biologically toxic materials such as silicon. Jong-Mo Seo et al. have been development biocompatibilities of polyimide microelectrode array for retinal stimulation [37]. They development a platinum electrode- embedded polyimide film and tested in feline eye. The authors used flexible polyimide selected as the substrate material of gold microelectrode array to minimize the damage during ophthalmic surgery and to get better contact to retina. To evaluate the feasibility of polyimide microelectrode array as a retinal prosthesis, in vitro and in vivo biocompatibility have been shown that retinal pigment epithelial on gold electrode-embedded polyimide film in a monolayer after 10 days of culture, and showed good affinity to it. Electroretinography revealed no difference between the transplanted eye and the healthy eye. Gold electrode-embedded polyimide film showed good biocompatibility in vitro and in vivo test and was suitable as a candidate biomaterial for the fabrication of retinal stimulator in visual prosthesis system.

Development of nanotechnology and chemistry of polyimide have been applied in biology and medicine as nano-biosensor device, biochips and thin film DNA immobilize. Biochips, particularly those based on DNA, are powerful devices that integrate the specificity and selectivity of biological molecules with electronic control and parallel processing of information. Examples of current applications of DNA chips include genomic analysis to screen and identify single nucleotide polymorphisms or to sequence gene fragments, pathogen identification, and gene expression profiling. Other possible features of a DNA chip surface include the presence of microelectrodes based on PI matrix thin films, that can be used as sensing devices and to generate electric fields that promote the migration of oligonucleotides, hybridization and covalent binding [39]. Forster et.al. have been purposed the Nanochip™ with a layered polyimide structure that supports the controlled electrophoretic transport of oligonucleotides [40]. They shown show that the biased electrodes preserve the integrity of the DNA by performing an electronic reverse-dot blot hybridization assay after electrophoretic transport of the target oligonucleotides [40]. This nanodevice in future can serve as the basis for a low cost specific biomolecular detection tool in clinical diagnostics.

4.2. Engineering

The attractiveness and applicability of the PI's are determined not only from single their characteristics like high chemical and thermal stability, high optical transmission, high electrical resistance, but most important is their saving at combination of the cited properties [41,42]. The combination of the high optical transparency by simultaneously high chemical and thermal stability make the PI very attractive material for applying as capsulating or protective layers, films for laser microstructuring in micro- or optoelectronic, etc. [11,42]. Additionally, it could be noted the influence of the fast unlimited choice of the "guest" to enlarge the number of composites for many different purposes – from conductive or insulating transparency or colored films until insulating substrates, optical, chemical and

thermal stable coatings [15,43]. Recently, much research interest focuses on polyimide films containing azobenzene fragments. These films are interest because of their potential application as photoactive materials for optical recording, biosensors, reversible optical switch, liquid crystal, photosensitive elements, optical information storage, holographic effect etc. An intensive research effort is being undertaken to use holographic techniques for optical information storage and optical information processing. Holographic storage is technologically very promising because information storage capacity, that can be reached with this technique, is much higher compared with other techniques (the storage capacity of CD is 0.7 GB, of DVD is from 4.7 to 17 GB, of PAP DVD is about 40 GB, of HOLO CD could be 1 TB) [19,44]. Development of holographic technology depends on the properties of recording materials. For such practical applications materials besides of specific requirements viz the principal the presence of photochromic moieties, the thermal stability of orientation alignment, the high optical non-linearity, high damage threshold, chemical resistance, mechanical endurance, they should exhibit the high optical quality ability and feasibility of device fabrication which are determined in wide range by their solubility. Significant efforts have been made to improve solubility of polyimides by designing their structure [45].

5. Conclusions

In this chapter, we have discussed methods for obtaining of polyimides, chemical properties and physical parameters that are related with obtaining nanosized films by vapour deposition. It was discussed possibilities for the solid state synthesis of polyimides in thin film and applied microwave synthesis. The studies show that can be obtained homogeneous films without defects on the surface and volume of layers with controlled density, thickness and dielectric properties. The developments of polymer chemistry produce polyimide films with covalent bonded chromophore to the chain. One of these achievements is our development a method for solid state synthesis of azo-polyimide.

Polyimide layers are suitable matrix for incorporation of metal, salts, chromophores as nanoscale particles to obtain of nanocomposite materials. It was discussed the possibility of use polyimides in materials chemistry and nanomaterials, one of these applications is the use for making biomedical implants for neurology, ophthalmology, biosensor device and chips which are a powerful tool in clinical diagnostics. Another important trend is use in electronics and optoelectronics such as dielectric substrates and intermediate barrier layers, creating nanocomposite films with various nanosized particles such as dyes, metal, dielectric and other clusters.

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6. References

- [1] Strunskus Y, Grunze M (1994) Polyimides—fundamentals and applications. In: Crosh M, Mittal K, editors. New York: Marcel Dekker. pp. 187–205.
- [2] Marc J.M. Abadie Alexander L. Rusanov (2007) Practical Guide to Polyimides. Smithers Rapra Technology Limited. pp 45-77.
- [3] Bessonov, M.I., Koton, M.M., Kudryavtsev, V.V. and Laius, L.A (1987) Polyimides: Thermally Stable Polymers. Plenum, New York, 2-nd edition. pp. 56-187.
- [4] Yoshio Imai (1999) Rapid Synthesis of Polyimides from Nylon-Salt-Type Monomers. In: Progress in Polyimide Chemistry I. H.R. Kricheldorf editor, Springer. pp. 3-20.
- [5] Rohit H. Vora, P. Santhana Gopala Krishnan, S. Veeramani and Suat Hong Goh (2003) Poly(amic acid)s and their ionic salt solutions: Synthesis, characterization and stability study. In: Polyimides and Other High Temperature Polymers, Vol. 2. K.L. Mittal editor. VSP. pp. 14-35.
- [6] Harris, F.W. (1990) Polyimides. Wilson D., Stenzenberger, H.D., Hergenrother, P.M., Chapman and Hall editors. New York. pp. 23-96.
- [7] Anton Georgiev, Erinche Spassova, Jacob Assa and Gencho Danev (2010). Preparation of Polyimide Thin Films by Vapour Deposition and Solid State Reactions. Polymer Thin Films. Abbass A Hashim editor. InTech. pp. 71-92.
- [8] D. Sek, A. Wanic (2000) High-temperature polycondensation of six membered dianhydrides with o-substituted aromatic diamines 1. Model compounds investigations. Polymer. 41: 2367-2378.
- [9] D. Yu. Likhachev, S.N. Chavlin, Yu. A. Zubov, R.N. Nurmukhamedov and I. Ye. Kardash (1991) Effect of chemical structural defects on morphology of polyimide films. Polymer Science.33(9):1885-1894.
- [10] Anton Georgiev, Ilyana Karamancheva, Dejan Dimov, Ivailo Zhivkov, Erinche Spassova (2008) FTIR study of the structures of vapor deposited PMDA–ODA film in presence of copper phthalocyanine. Journal of Molecular Structure. 888: 214-233.
- [11] E. Spassova (2003) Vacuum deposited polyimide thin films. Vacuum. 70: 551-561.

- [12] KiRyong Ha and John L. West (2002) Studies on the photodegradation of polarized UV-exposed PMDA–ODA polyimide films. *Journal of Applied Polymer Science*. 86: 3072-3077.
- [13] K.S. Sree Harsha (2006) *Principles of Physical Vapor Deposition of Thin Films* Elsevier, San Jose State University, CA, USA, first edition. pp. 11, 367, 961.
- [14] Mitchell Anthamatten, Stephan A. Letts, Katherine Day, Robert C. Cook, Anthony P. Gies, Tracy P. Hamilton and William K. Nonidez (2004) Solid-state amidization and imidization reactions in vapor-deposited poly(amic acid). *Journal of Polymer Science: Part A: Polymer Chemistry*. 42: 5999-6010.
- [15] A. Georgiev, I. Karamancheva, D. Dimov, E. Spassova, J. Assa, G. Danev (2008) Polyimide coatings containing azo-chromophores as structural units. *Journal of Physics: Conference Science*. 113: 012032.
- [16] Masashi Takahashi, Takashi Okuhara, Tomohiro Yokohari, Koichi Kobayashi (2006) Effect of packing on orientation and cis–trans isomerization of azobenzene chromophore in Langmuir–Blodgett film. *Journal of Colloid and Interface Science*. 296: 212-219.
- [17] Cristina Cojocariu and Paul Rochon (2004) Light-induced motions in azobenzene-containing polymers. *Pure Applied Chemistry*. 76:1479-1497.
- [18] Kiyooki Usami, Kenji Sakamoto, Norio Tamura, Akihiko Sugimura (2009) Improvement in photo-alignment efficiency of azobenzene-containing polyimide films. *Thin Solid Films*. 518: 729-734.
- [19] Ewa Schab-Balcerzak, Lukasz Grobelny, Anna Sobolewska and Andrzej Miniewicz (2006) Cycloaliphatic–aromatic polyimides based on diamines with azobenzene unit. *European Polymer Journal*. 42: 2859–2871.
- [20] Brittany L Hayes (2002) *Microwave Synthesis: Chemistry at the Speed of Light*. CEM Publishing. pp. 11, 77, 95.
- [21] Michael D., Mingos P. (2005) Theoretical aspects of microwave dielectric heating. *Microwave Assisted Organic Synthesis*. Tierney J., P., & Lidstroem P. editors. Blackwell Publishing Ltd. pp. 63-179.
- [22] C. Oliver Kappe, Doris Dallinger and S. Shaun Murphree (2009) *Practical Microwave Synthesis for Organic Chemists*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. pp. 11, 87, 161, 203.
- [23] Yumin Liu, Y. Xiao, X. Sun, D. A. Scola (1999) Microwave irradiation of nadic-end-capped polyimide resin (RP-46) and glass–graphite–RP-46 composites: cure and process studies. *Journal of Applied Polymer Science*. 73(12): 2391-2411.
- [24] D. Dimov, A. Georgiev, E. Spassova, I. Karamancheva, Y. Shopov and G. Danev (2007) Microwave assisted processes for producing thin layer materials in the field of nanotechnologies. *Journal of Optoelectronics and Advanced Materials*. 9(2): 494-499
- [25] Richard Hoogenboom and Ulrich S. Schubert (2007) *Microwave-Assisted Polymer Synthesis: Recent Developments in a Rapidly Expanding Field of Research*. *Macromolecular Rapid Communication*. 28: 368–386.

- [26] M.B. Saeed, Mao-Sheng Zhan (2006) Effects of monomer structure and imidization degree on mechanical properties and viscoelastic behavior of thermoplastic polyimide films. *European Polymer Journal*. 42:1844-1854.
- [27] M.B. Saeed, Mao-Sheng Zhan (2007) Adhesive strength of partially imidized thermoplastic polyimide films in bonded joints. *International Journal of Adhesion & Adhesives*. 27: 9-19.
- [28] Chang-Chung Yang, Kuo Huang Hsieh and Wen-Chang Chen (2003) "A new interpretation of the kinetic model for the imidization reaction of PMDA-ODA and BPDA-PDA poly(amic acid)s". In: *Polyimides and Other High Temperature Polymers*, Vol. 2. K.L. Mittal editor. VSP. pp. 37-45.
- [29] Fryd, M (1984) Structure –T_g relationships in Polyimides: Synthesis, Characterization and Properties, Vol. 1. Mittal K.L. editor. Plenum New York. pp. 377-384.
- [30] St. Clair, T.L. (1990) In *Polyimides*. Wilson D., Stenzenberger, H.D., Hergenrother, P.M., Chapman and Hall editors. New York. pp. 187-208.
- [31] D. Dimov, E. Spassova, J. Assa and G. Danev (2009) Ion beam assisted physical deposition of polyimide. *Journal of Optoelectronics and Advanced Materials*.11(10): 1436 - 1439.
- [32] V. Strijkova, D. Dimov, A. Paskalevaa, I. Zhivkov, E. Spassova, J. Assa, G. Danev (2005) Electrical properties of a thin layer polyimide matrix *Journal of Optoelectronics and Advanced Materials*. 7(3):1319-1322.
- [33] F.-Y. Tsai, Y.-H. Kuo and D. R. Harding (2006) Properties and structure of vapor-deposited polyimide upon electron-beam irradiation. *Journal of Applied Physics* 99: 064910.
- [34] Christina Hassler, Tim Boretius, Thomas Stieglitz (2011) Polymers for Neural Implants. *Journal of Polymer Science: Part B: Polymer Physics*. 49: 18–33.
- [35] A. Mian, G. Newaz, I. Vendra, N. Rahman, D.G. Georgiev, G. Auner, R. Witte, H. Herfurth (2005) Laser bonded microjoints between titanium and polyimide for applications in medical implants. *Journal of Materials Science: Materials in Medicine*. 16: 229– 237.
- [36] Keekeun Lee, Amarjit Singh, Jiping Heb, Stephen Massia, Bruce Kima, Gregory Rauppc (2004) Polyimide based neural implants with stiffness improvement. *Sensors and Actuators B*. 102: 67–72.
- [37] Humayun, M. S.; de Juan Jr, E.; Weiland, J. D.; Dagnelie, G.; Katona, S.; Greenberg, R.; Suzuki, S (1999) Pattern electrical stimulation of the human retina. *Vision Research*. 39: 2569–2576.
- [38] Jong-Mo Seoa, Sung June Kimb, Hum Chunga,b, Eui Tae Kimb, Hyeong Gon Yua, Young Suk Yua (2004) Biocompatibility of polyimide microelectrode array for retinal stimulation. *Materials Science and Engineering C*. 24: 185–189.
- [39] F. Fixe, A. Faber, D. Gongalves, D.M.F. Prazeresl, R. Cabea , V. Chu , G. Ferreira and J.P. Conde (2002) Thin film micro arrays with immobilized DNA for hybridization analysis. *Materials Research Society*. 723: 125-130.

- [40] Anita H. Forster, Michael Krihak, Paul D. Swanson, Trevor C. Young and Donald E. Ackley (2001) A laminated, flex structure for electronic transport and hybridization of DNA. *Biosensors & Bioelectronics* 16: 187–194.
- [41] G.Danev, E. Spassova, J. Assa, J. Ihlemann, D. Schumacher (2000) Excimer laser structuring of bulk polyimide material. *Applied Surface Science*. 168: 162-165.
- [42] G. Danev, E. Spassova, J. Assa (2005) Vacuum deposited Polyimide – A Perfect Matrix for Nanocomposite Materials. *Journal of Optoelectronics and Advanced Maters*. 7(3): 1379-1390.
- [43] M. Hasegawa and K. Horie (2001) Photophysics, Photochemistry, and optical properties of polyimides. *Progress in Polymer Science*. 26: 295-335.
- [44] E. Grabiec, E. Schab-Balcerzak, D. Sek, A. Sobolewska, A. Miniewicz (2004) New polyamides with azo-chromophore groups. *Thin Solid Films*. 453–454: 367–371.
- [45] M. Moniruzzaman, P. Zioupos, G.F. Fernando (2006) Investigation of reversible photo-mechanical properties of azobenzene-based polymer films by nanoindentation. *Scripta Materialia*. 54: 257–261.