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Preparation of Polyimide Thin Films by Vapour Deposition and Solid State Reactions

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Abstract

In this chapter we describe the preparation of polyimide thin films by physical vapour deposition and comment on their potential application as a pure material or a thin layer matrix for producing nanocomposite layers. Their superb properties, such as a low dielectric constant, high thermal- and photo-stability, high chemical resistance and high optical transmittance predetermine their wide- spread applications as a casts and layers used as insulators, protective or capsulation layers, mechanical or diffusion barriers, in opto- and microelectronics. The bulk properties of the polyimide allowed the preparation of nanocomposite materials with organic chromophores as a "guest" (the embedded in the matrix nanosized particles). Moreover, some of the "guest" could bind to the polyimide chain. There are numbers of aromatic polyimides which are broadly used as thin layers in nanotechnology.

Vapour deposition of the precursors and solid state reactions of imidization are of a greater priority than the spin coating and dipping methods. These as-deposited films by the vacuum deposition process consist of a dianhydride and diamine mixture, which by solid state reactions is converted to polyimide by thermal treatments or by combined microwave and thermal treatments. The physical vapour deposition as a "dry" method provides high purity for producing thin polymer films of controlled thickness, ratio of precursors and composition control of the so prepared layers. In this chapter we suggest possibilities for the practical application of vapour deposition of precursors and the following solid state reactions.

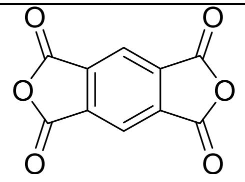
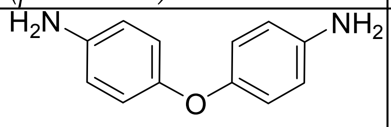
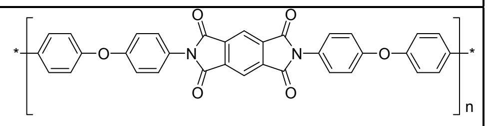
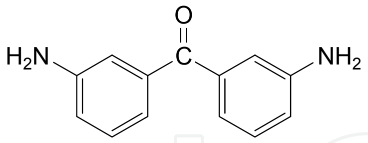
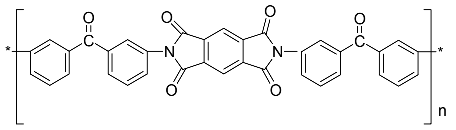
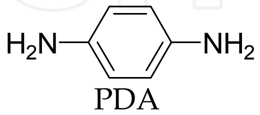
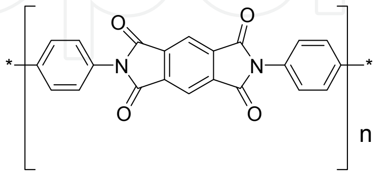
By the used spectral method- Fourier Transform Infrared Spectroscopy for analysis of the investigated kinetics of imidization reactions and microstructure of the layers are studied. The relationship between vapour deposition conditions and the presence of regular chains leading to the appearance of infrared bands is discussed. Polymers are also capable of forming a range of conformations depending on the backbone structure. The conditions for preparation by physical vapour deposition and solid state reaction of polyimide or nanocomposite polyimide layers are discussed.

Key words: Polyimides, thin polymer layers, solid state reactions, vapour deposition, FTIR spectroscopy

1. Application of polyimides in nanotechnology as thin layer matrix for nanocomposites

Polyimides (PI) are a class of organic compounds containing imide bond in their molecule. Aromatic polyimides are well-known polymers and due to the attractiveness of their properties such as a low dielectric constant, high thermal stability, high chemical resistance, high optical transmittance as well as very good mechanical properties. They are used in opto- and microelectronics, as well as in nanotechnology as a matrix in the production of nanocomposite layers (Francisko Raymo, 2007; Strunskus,Y and Grunze,M, 1994; Osvaldo N. Oliveira et al, 2005; Mitchell Anthamatten et al., 2004; C.P. Wong, 1993). Nanocomposite materials represent combinations of substances – polymers, chromophores, metals, etc. in which one component is the matrix and the other one – the "guest", embedded in the matrix as nanosized particles. There is no chemical interaction occurring between the matrix and the "guest". The space volume between the individual molecules allows for the "guest" molecules to be embedded in the matrix pores and a thickening of the layer achieved during the following thermal process.

In Table 1 the initial precursors and the respective PI, which find wide–ranging applications in opto- and microelectronics as modulators, barrier layers, etc. are presented (E. Mazoniene et al., 2006; Steve Lien-Chung Hsua et al., 2003).

Dianhydride *(precursor 1)*	Diamine *(precursor 2)*	Polyimide
 PMDA *pyromellitic dianhydride*	 ODA *4,4′-oxydianiline*	
	 m, m′-DABP *m,m'-diaminobenzophenone*	
	 PDA *phenilendiamine*	

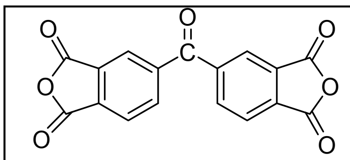
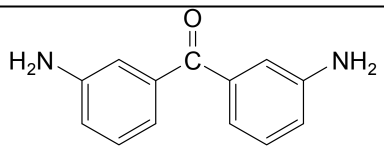
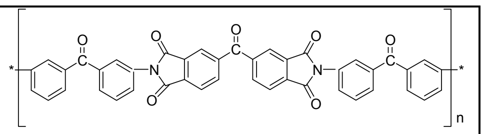
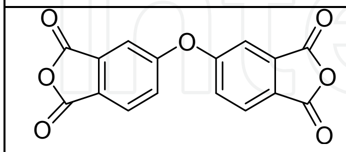
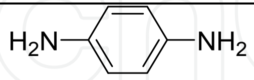
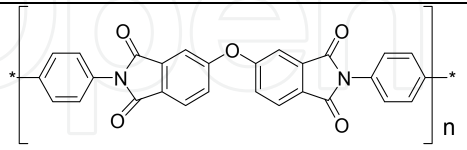
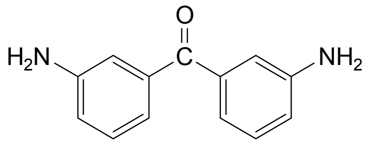
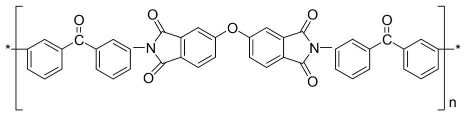
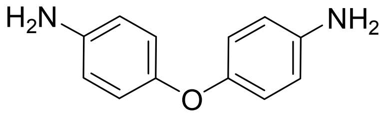
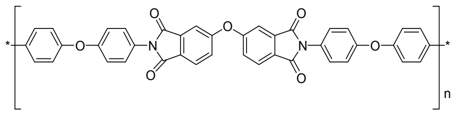
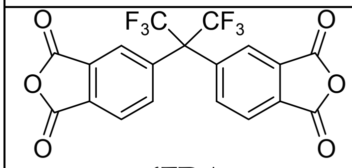
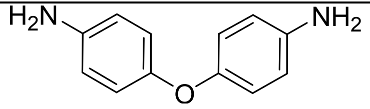
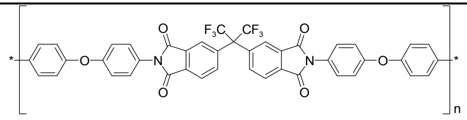
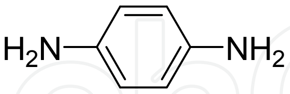
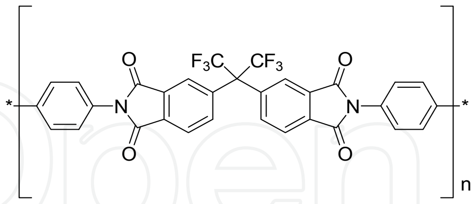
 BTDA *3,3',4,4'-benzophenone tetracarboxylic dianhydride*	 m, m′-DABP	
 ODPA *4,4'-oxydiphthalic anhydride*	 PDA	
	 m, m′-DABP	
	 ODA	
 6FDA *2,2'-Bis-(3,4-Dicarboxyphenyl) hexafluoropropane dianhydride*	 ODA	
	 PDA	

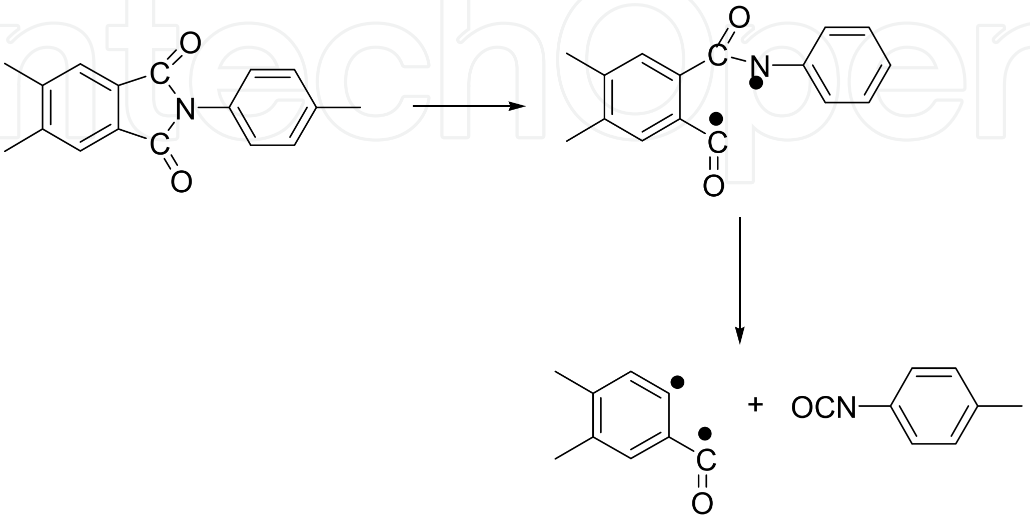
Table 1. Initial precursors and the respective polyimides finding wide–ranging applications in nanotechnology.

The high thermal and chemical stability of PI is interpreted by two factors:

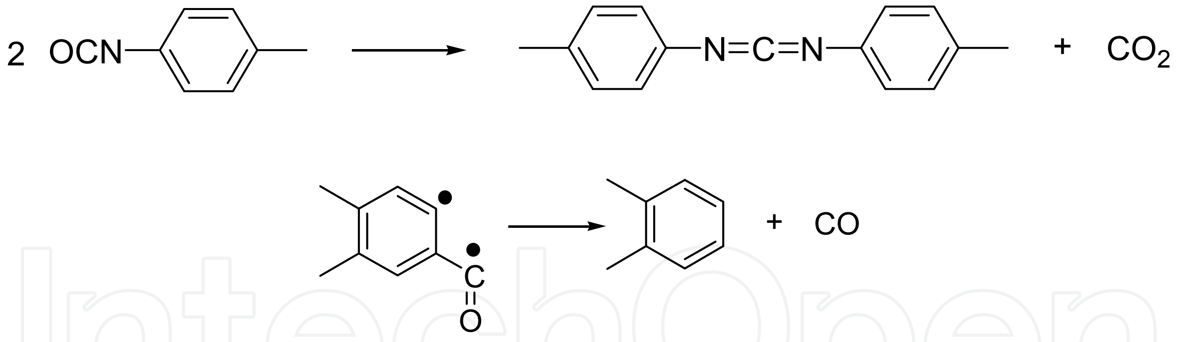
(i) the high resonance energy of the benzene rings due to delocalization of the π-electrons and the great number of resonance structures;

(ii) strength of the imide bonds, resulting from the competitive *n*-π conjugation between the carbonyl group and the non pair electron couple from the nitrogen atom as well as from the conformation state of the 5- member imide ring. The lack of Baer's angular torsion is due to the fact that all C- and N- atoms are in a *sp*^{2} hybrid state with valency angle of 120° and planar conformation of the ring.

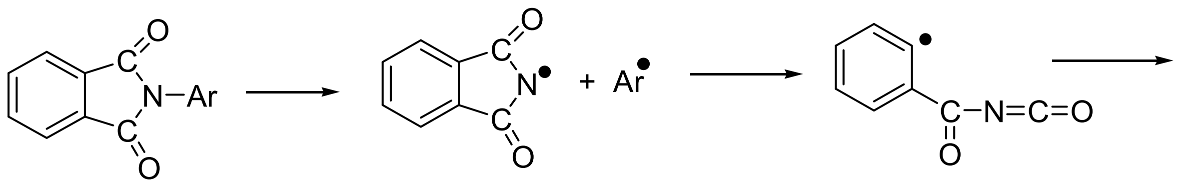
Thermal destruction of the PI obtained from the precursors PMDA (pyromellitic dianhydride) and ODA (4,4′-oxydianiline) is only observed at temperature above 420-450 °C the mechanism studied by R. Ginsburg and J.R. Susko and proven with mass spectrometry (Fig. 1) (R. Ginsburg and J.R. Susko, 1984).

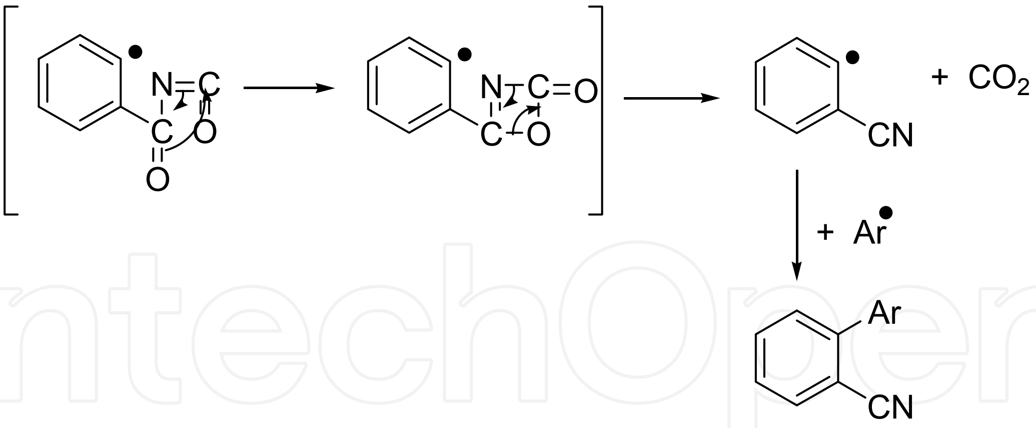


a) *homolytical cleavage of the C-N bond of the imide ring and formation of isocyanate and acylic radical.*



b) *recombination and release of CO_2 and CO.*





c) *decomposition via a rearrangement of the imide ring and CO_2 releasing.*

Fig. 1. Mechanism and principal stages of the thermal destruction of PI: **a)** homolytical cleavage of the C-N bond of the imide ring; **b)** release of CO_2 and CO; **c)** decomposition via a rearrangement of the imide ring.

Aromatic polyimides display attractive properties such as chemical resistance, thermal stability and stability to photo-ageing. They have the capacity to perform the matrix role in the formation of nanocomposite layers with an embedded chromophore as "guest" and are materials of good prospects for applying in contemporary and future nanotechnology.

2. Vapour deposition of thin polymer films

Obtaining of nanostructured polymer layers (from 2-4 nm to 4-5 µm thick) by deposition of their components from the gas phase renders opportunities for the production of novel materials in the field of nanotechnology. The thin layer composite materials obtained by using the vacuum technologies ensure one basic advantage – the absence of solutions and elimination of the necessity of complicated technical solutions for their removal (C.-C. Lee et al., 1993). The deposition in vacuum and the polycondensation between the precursors of the PI matrix a reaction taking place in a solid state represents an attractive method for the formation of thin polymer layers. Polyimides have the capacity of implementing nanocomposite matrix both due to the possibility to be deposited in vacuum and their chemical inactivity, high thermal stability and appropriate optical and dielectric properties (Strunskus,Y and Grunze,M, 1994; E. Spassova, 2003; Iijima M and Takahashi Y, 1986).

Most often conventional polyimides are produced from a solution of polyimide acid (PAA), obtained by polycondensation of dianhydride and diamine. The solution of PAA is deposited on a substrate and the solvent being removed by an ensuing thermal treatment and the PAA imidized to PI. This is the so called "wet" method for obtaining thin layers. The advantages of the wet methods are as follows:

(i) simplicity, fast, performance and the use of a comparatively cheap equipment;
(ii) thin films can be produced from substances hard to melt and sublimate as well as from such thermally unstable and easily decomposed which in vacuum deposition is impossible;
(iii) this is also valid for the compounds of a high molecular mass and low pressure of the saturated vapours in this way "wet methods" being the only alternative for the thin layer formation.

The shortcomings of the „wet" methods are as follows:

(i) the exigency of a solvent or a combination of solvents;
(ii) in the case of using a solvent the latter should be inert chemically to the substance and form a solution with it as well as to be easily removable;
(iii) in the elimination of the solvent the film is deformed and the surface morphology is uneven and with a number of defects;
(iv) „wet methods" cannot be used for obtaining of very thin films of even thickness as well as in the cases of substrates with a complex form;
(v) a shorter "shelf life". The solutions of the initial compounds are especially sensitive to an increased moisture;
(vi) in using strongly volatile and toxic solvents there is an augmentation of the risk to the environment and people's health.

The overcoming of the „wet methods" shortcomings is achieved by the introduction of the method of physical vacuum deposition. Vacuum deposition displays number of opportunities for broadening the spectrum of novel materials of suitable electrical, optical and mechanical properties. In it, the different precursors are evaporated in a high vacuum and are deposited at comparatively low temperature on appropriate substrate followed by a thermal treatment. In the case of PI the purpose of the thermal treatment is the run of polycondensation reactions in solid state till completion of the PI formation. As a consequence of these reactions leading to a release of water and imidization also a certain pack of the layer is achieved. Some more substantial advantages of the vacuum deposition are as follows:

(i) as compared with the „wet methods" the possibility for side reactions to take place is minimum (Strunskus,Y and Grunze,M, 1994; E. Spassova, 2003; Salem J et al., 1986);
(ii) an even surface morphology and thickness in the interval between nanometers and microns are much easier to achieve without the presence of any rough defects;
(iii) a possibility for a precise control of the multitude of the process parameters: degree of evacuation, mode of evaporation (thermal, electron beam, magnetron, etc.) and a computerized control of the source temperatures with feedback, guarantee for a manageability of the deposition rates and the ratios of the precursors in the flux, etc. These constitute substantial prerequisites for the production films of reproducible composition, structure and thickness, but also demands considerable resources and highly qualified specialists;
(iv) the risk to environment and people's health is reduced to minimum.

The method of physical vapour deposition for thin-layer production also displays certain disadvantages that go as follows:

(i) not all substances are susceptible to evaporation since some of the decompose prior to reaching an equilibrium pressure over their saturated vapours or in cases when it is too low. In such a case an evaporation of even rate is very hard to be achieved in practice;
(ii) the precursors have to close evaporation temperatures so that a vapour flow of an even temperature could be formed;
(iii) a costly technical equipment is necessary and as mentioned above a highly trained technical staff is exigent.

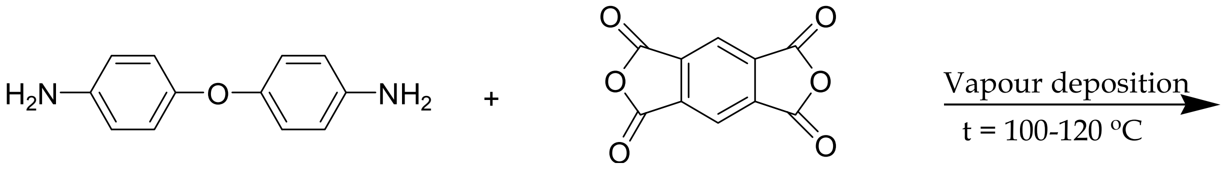
The quality and structure of the obtained films to great extent depend on method used for their production. The deposition of the precursors in high vacuum with following thermal processing and the reactions of polycondensation and imidization taking place is a „dry" method since solvents are not implemented. Besides, the method is compatible with the technologies demanding a high degree of purity, low moisture and allows for the formation of uniform layers on substrates of complex configuration which is hard to achieve if not impossible with the „wet methods" (Salem J et al., 1986; K.S. Sree Harsha, 2006). The vacuum deposited layer of dianhydride and diamine is treated in two steps at defined temperature (from 180 to 350°C) to obtaining PI.

In the usage of the „wet methods" the nanocomposite layers are produced by a complex combination of processes leading to obtaining of the initial solution containing matrix components and „guest" particles. Also, the latter would not yield quality nanostructured layers not only due to the shrinkage of the film after the evaporation of the solvent and the impossibility for its thorough removal but because of the uneven distribution of the „guest" in the matrix as well. In the case of the vacuum evaporation an automatic, computerized regulation of the "guest" deposition rate and the precursors of the polymer matrix are attained as well as the movement of the substrate against the evaporation flux. In that way conditions for obtaining quality thin layer nanostructured materials of even distribution and precise concentration control of the „guest" in the polymer matrix are ensured (Salem J et al., 1986; K.S. Sree Harsha, 2006).

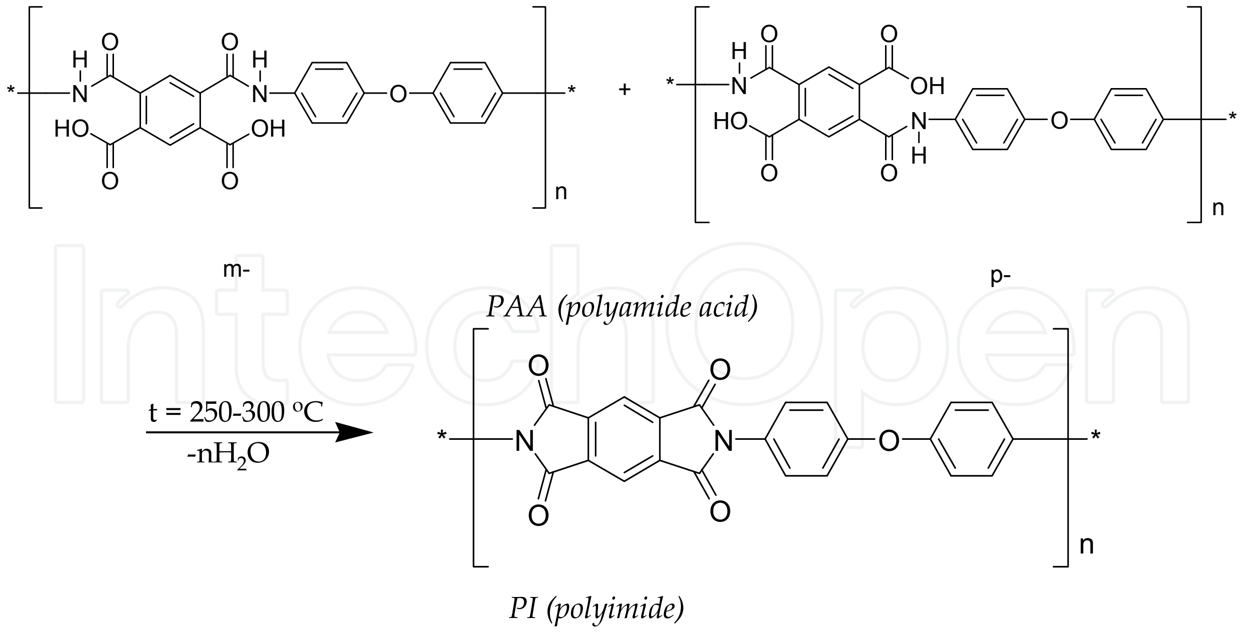
The considered methods for deposition of thin polymer layers constitute a part of the technological process of formation of layers with good parameters– optical transmittance, reflexive capacity, conductivity, etc. The comparison of the two methods with their advantages and disadvantages bring about to the further development of the process of quality film formation. Our view is 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, imidazion and layer formation designed for obtaining standard PI or nanocomposite products of reproducible composition, thickness, structure and properties.

3. Solid state reactions in polyimide films formation

In the vacuum deposition of the precursors PMDA (pyromellitic dianhydride) and ODA (4,4′-oxydianiline) at temperature of 120-145°C reaction of polycondensation to PAA (polyamide acid) with opening of the anhydride ring of PMDA takes place (Ac-S_N2 - 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 polycyclodehydration in solid state to linear PI. The reaction is presented in scheme 1. In Fig. 2 the FTIR spectra of the thin films of PMDA, ODA and PAA in the range of 1900-650 cm^{-1} are presented.



ODA (4,4′-oxydianiline) *PMDA (pyromellitic dianhydride)*



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

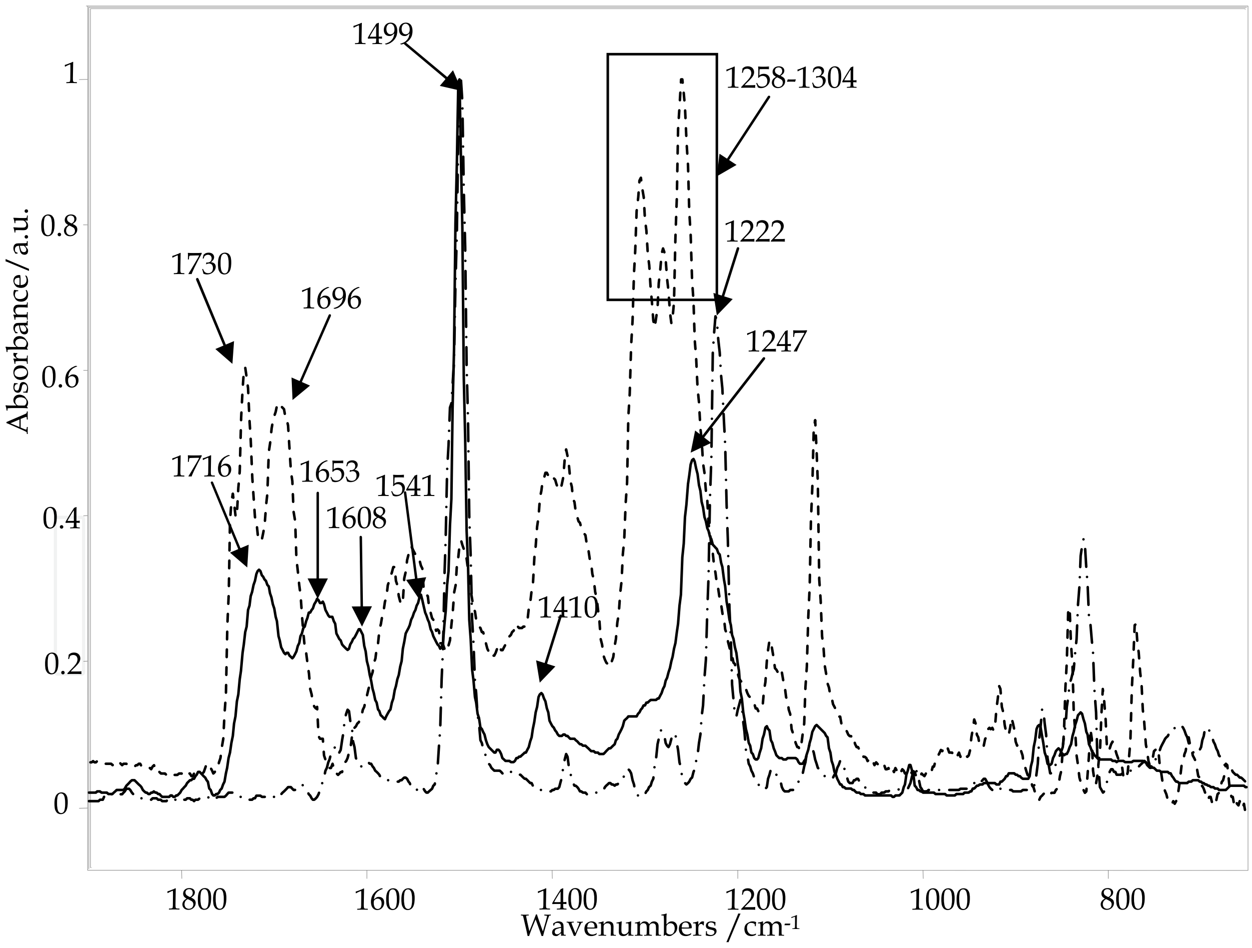


Fig. 2. FTIR spectra of the vacuum deposited films of: - - - - - -PMDA; —·—·— ODA; ——— simultaneously deposited both precursors in a mole ratio of PMDA : ODA= 1:1(PAA).

The band v 1716 cm^{-1} for the >C=O group in the PAA spectrum is 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 v 1653 cm^{-1} (>C=O amide I band) and δ 1608 cm^{-1} (N-H amide II band). The bands characterizing PMDA and ODA are presented in Table 2 (Gerd Kaupp, 2002; M.B. Saeed and Mao-Sheng Zhan, 2006).

Absorbance bands/cm^{-1}	
PMDA	v_{as} 1746 >C=O (anhydride) v_s 1730 >C=O (anhydride) v 1696 >C=O (acid – hydrolysis of the anhydride) v 1499 C-C (aromatic ring) δ 1258-1304 C-O (anhydride ring and C-OH acid)
ODA	δ 1610 N-H (NH_2) v 1499 C-C (aromatic ring) δ 1222 C-N (C-NH_2)

Table 2. Assigning of the main bands for PMDA and ODA.

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 in the vacuum deposition method this process is performed in only one step. According to the kinetic theory of the collisions the rate of the reaction mainly depends on the energy factor i.e. the number of the collisions between the particles of the reagents. These collisions are called effective and chemical interaction takes place only between the particles taking part in them. The rate of the reaction also depends on the so-called factor of orientation (a possible space volume factor) between the reagents, particles. It expresses the probability for their appropriate spatial orientation needed for the accomplishment of effective collisions between them. The reactions between vacuum deposited precursors of PMDA and ODA take place with less by products since the molecules have sufficient spatial accessibility for effective compound as compared to the reactions in a solution. In the course of the compound of PMDA and ODA in the process of vacuum deposition a gradual and even deposition of PAA takes place which ensures the production of high quality thin layers. The obtained PAA layer is subjected to a thermal treatment for imidization to PI with a reaction of polycyclodehydration taking place (the closure of the ring after the Ac-S_N2 – mechanism). It has been established that the imidization commences at temperature of over 170 °C and the reaction takes place under kinetic control. Save for the chemical reaction process of thickening the layer also occurs which leads to obtaining a quality thin layer matrix devoid of defects on the surface (M.B. Saeed and Mao-Sheng Zhan, 2007). The FTIR spectra of the layers of PAA and PI are presented in Fig.3.

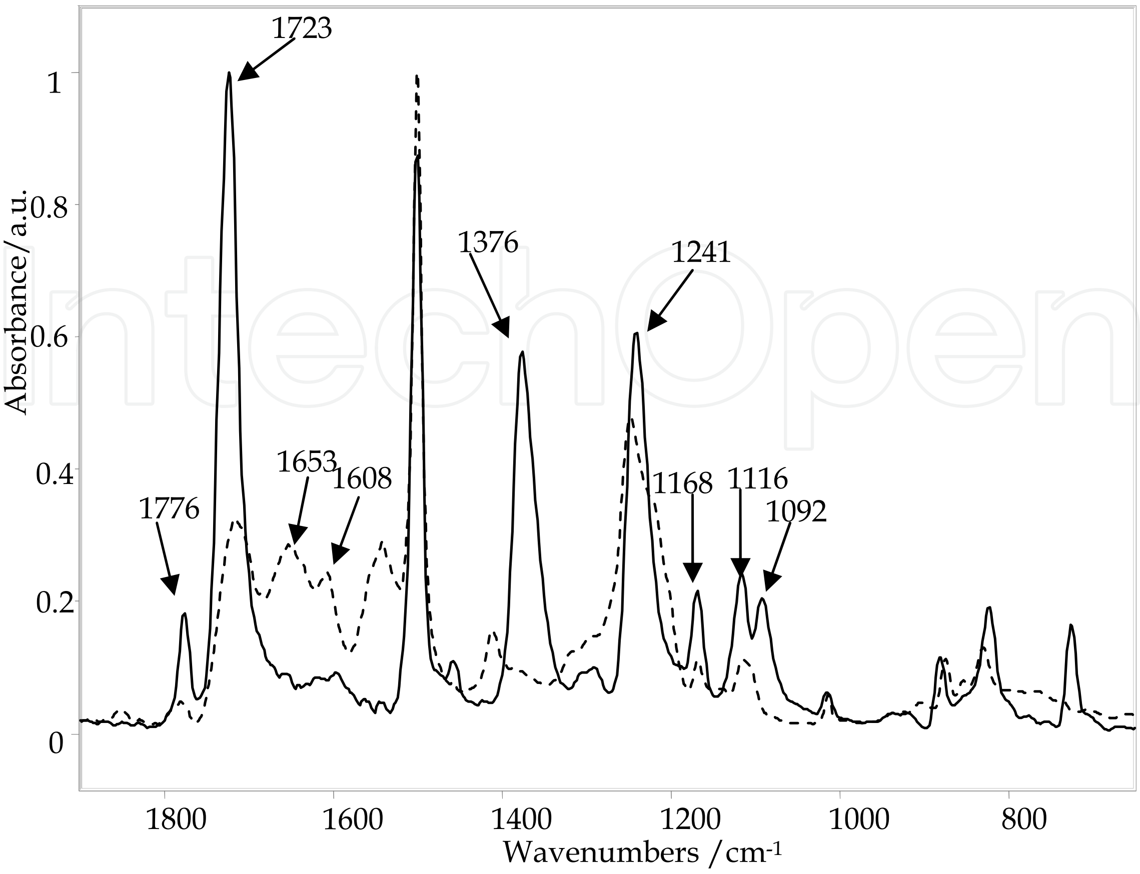


Fig. 3. FTIR spectra of vacuum deposited films with thickness 200 nm and PMDA:ODA(PAA)=1:1 - - - - - thermally untreated; ——— thermally treated 1 h at 300 ºC.

The results show that following the thermal treatment the imidization has been completed to the production of PI since compared with the thermally untreated layers the bands for amide I and amide II in the PI spectrum are missing. The bands at v_s 1776 cm^{-1} and v_{as} 1723 cm^{-1} characterize the >C=O groups of the imide ring. The imidization is confirmed by the v_{C-N} 1376 cm^{-1} imide III band where a minimum is observed in the spectrum of the untreated layer at this frequency. The emergence of new bands in the area of the deformation vibrations for the C-O and C-N bonds respectively at 1241, 1168, 1116 and 1092 cm^{-1} is observed. The band at 1376 cm^{-1} is used for the qualitative and quantitative determination of the imidization degree. The imidization degree is determined by the absorbance FTIR spectra according to the Lambert- Beer's Law and represents the ratio of the number of imidized groups to the number of all imidizable groups (Equation 1) (Gerd Kaupp, 2002; M.B. Saeed and Mao-Sheng Zhan, 2006):

$$\textbf{Imidization Dergee} = \frac{\textbf{Number of imidzed groups} - \text{ni}}{\textbf{Total number of imidizable groups -} \text{ na}}$$

Equation 1. Determining imidization degree.

Where, n_i is the number of imide groups and n_a is the number of amide groups.
The FTIR (Fourier-Transform InfraRed) spectroscopy is one of the methods for qualitative and quantitative analysis of organic polymers and nanocomposites. FTIR spectroscopy in the range 4400-650 cm^{-1} is used both for identification of functional groups and for the

determining the microstructure of polymer and nanocomposite films. It is a non-destructive qualitative and quantitative method for analyzing thin organic nanocomposite layers. The reliability, quickness and accessibility of the method are advantages as compared with the other spectral methods for analysis (A. Georgiev et al., 2008; Barbara Stuart, 2004). The date from the FTIR spectral analysis of organic polymers and composites depend on the mode of their obtaining and the physical properties of the used materials. Mainly the experiment is related to the technique of taking the spectra and the whole range of spectroscopic techniques which serve for the mathematical processing of the primary results. The selection of the technique not only depends on the physical nature of the material but on the reproducibility of the measurements as well. The specific peculiarities in the polymer spectrum are also related to the method for the sample preparation. Thus, for example due to the uneven thickness of the film the direct quantitative measurements are quite difficult especially in the cases of the "wet" methods for the formation of the films under study (Liliane Bokobza, 2002; V.P. Tolstoy et al., 2003; John M. Chalmers and Neil J. Everall, 2002). The quantitative FTIR spectroscopy is based on the Lambert- Beer's Law (Equation 2).

$$A = \lg\left(\frac{Io}{I}\right) = a_{\upsilon}bc$$

where:

c - concentration of the substance [mol/l];
b - thickness of the layer [cm];
a_υ *– molar absorptivity [l/mol.cm];*
I_0 *– intensity of the incident light [J/s.m^2];*
I - intensity of the transmitted light [J/s.m^2];

Equation 2. The Lambert- Beer's Law

Quantitative measurements can also be taken of polymer films as well by using the method of the internal standard and normalization of the spectrum in the suitable range. In the polycyclodehydration of PAA the imide band at 1376 cm^{-1} grows intensively. The FTIR absorbance bands used for qualitative and quantitative analysis of PI and PAA are presented in Table 3 (Gerd Kaupp, 2002; M.B. Saeed and Mao-Sheng Zhan, 2006).

Absorbance band/ cm^{-1}	
Polyimide	v_s 1776 >C=O v_{as} 1723 >C=O v 1376 C-N
Polyamide acid	v 1716 >C=O (COOH) v 1653 >C=O (CONH) δ 1608 C-NH
Standard	v 1501 *p*-substituted benzene rings

Table 3. FTIR absorbance bands used for the qualitative and quantitative defining of PI and PAA

The peak at v 1501 cm^{-1} [C-C (Ar)] characterizes *p*-substituted benzene rings. It is used as an internal standard and does not change at the imidization time. That is why the degree of imidization can be indirectly defined by the ratio of the absorptions (the corrected areas of the bands) at 1723 or 1376 cm^{-1} to 1501 cm^{-1} (Gerd Kaupp, 2002; M.B. Saeed and Mao-Sheng Zhan, 2006; Vasilis G. Gregoriou and Sheila E. Rodman, 2002).

Nanotechnologies due to the fact that they present the greatest modern technical challenge have been the subject of intensive studies and development. The solution of the problems accompanying the different trends in this technology of the future imposes the creation and implementation of novel specific sources of energy impact. As mentioned above, the additional heating has been commented on as aimed at acceleration and raising the degree of the imidization process as a pre-condition for the formation of PI. Logically enough a question is posed: as the thermal treatment or most generally speaking the energy impact on the precursors leads to PI formation would it be not appropriate for another type of energy treatment to be implemented for the same purpose? Another specific source of energy action is the microwave (MW) interaction (from 300 MHz to 30 GHz) with matter (Komarneni S and Katsuk H, 2002; Michael D and Mingos P, 2005). The task of applying a MW action in the thin layer systems on the basis of which the entire structure of microelectronics and micromechanics is built appears to be exceedingly attractive. The opportunities for activation and control of the chemical processes in the solid and liquid phases also implies the need of creating new conditions in the preparation of novel materials and the development of waste-free technologies. These opportunities encompass the macro-, micro- and nano- levels of action.

Such are the expectations based on these results:

(i) a considerable reduction of the time for the additional processes taking part in the technologies and their accomplishment in situ without the release of harmful and toxic substances;
(ii) development of the methods for obtaining nanocomposite thin layers;
(iii) a high selectivity in the production of an impact applying the MW irradiation in complex thin layer systems.

The microwave technology displays potential advantages in the polymer material production both in the bulk production and as thin films (Michael D and Mingos P, 2005; D. Lewis et al., 1995). MW synthesis is a method of good prospects for synthesizing of polymers in a thin film making it possible for the temperature and time for imidization to be significantly reduced. At the same time the application of this method in nanotechnologies for thin layer production for the needs of opto- and microelectronics render an opportunity for optimization until quality nanocomposite films are obtained.

Studies of ours (D. Dimov et al., 2007; D. Dimov et al., 2006) and others (Michael D and Mingos P, 2005; D. Lewis et al., 1995) on the imidization reactions in the solid state of thin PI films are also focused on establishing the opportunities for the application of the MW synthesis. The main target of these purposed studies is to find conditions for lowering the temperature and reducing the time for imidization which is of utmost importance in the production of nanostructured layers with an embedded chromophore as a “guest”. Most chromophores at high temperatures and a prolonged thermal influence lose part of their optical properties or destructed (F. Kajzar and J. D. Swalen, 1996; V. Degiorgio and C. Flytzanis, 1993). In the case of MW synthesis the molecules receive additional energy and the rate of the reaction grows (Michael D and Mingos P, 2005). In the case of the combined treatment (MW and thermal) the imidization reaction takes place for 5 to15 min which is confirmed by the spectra in Fig. 4. The quality of the obtained films is identical with the one of PI obtained only after a thermal treatment for 1h at 300 °C. In the spectrum of the PI layer treated with MW for 5 min and thermally treated for 15 min at 300 °C the intensity and the area of band at 1382 cm^{-1} are smaller than that at 15 min MW and 15 min thermal treatment at 300 °C. It is clearly seen that same value of the temperature and time of the thermal treatment the time of MW treatment considerable influence on the imidization. Consequently, duration of the MW treatment and the temperature values are importance for the imidization degree and the quality of the obtained films.

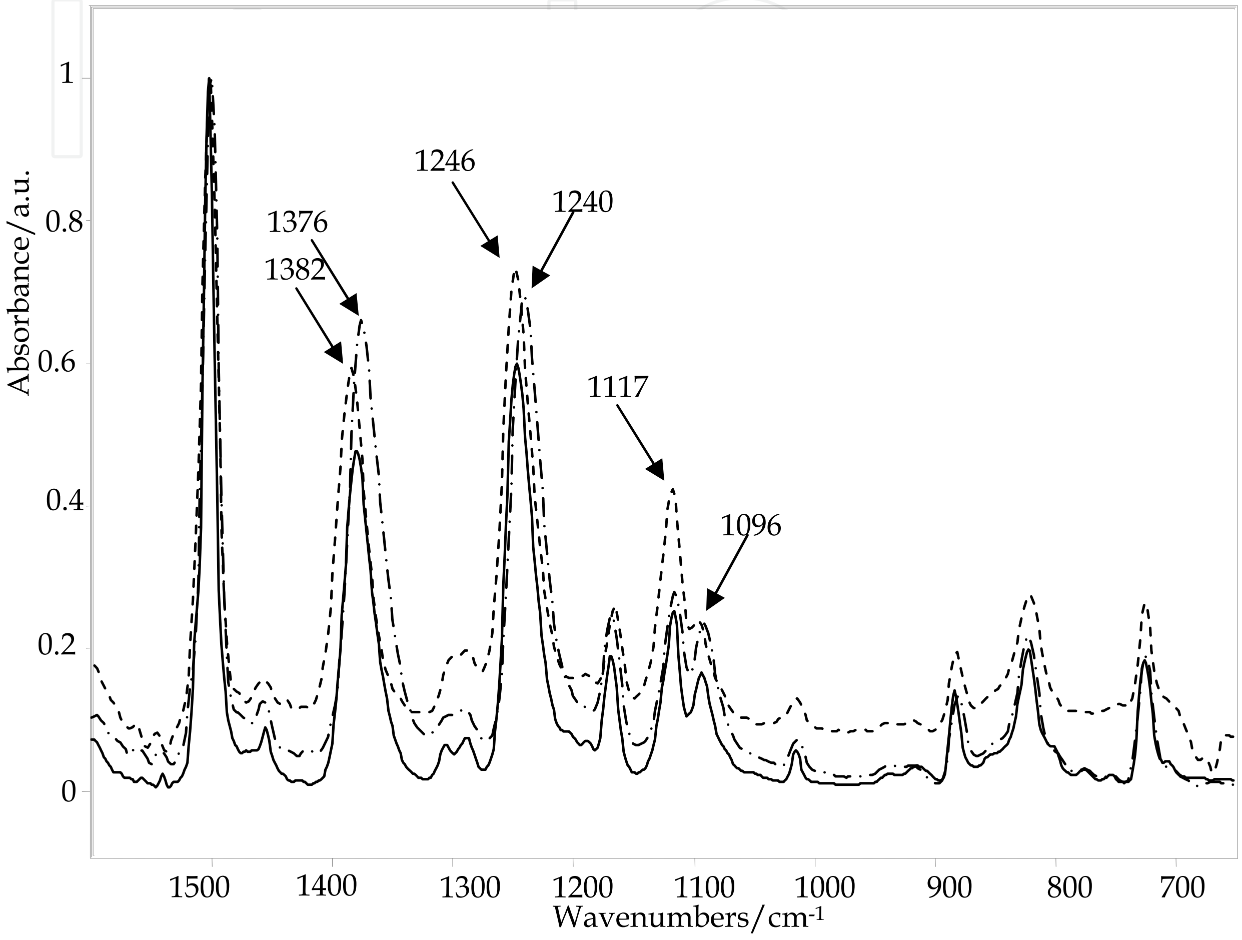


Fig. 4. FTIR spectra of vacuum deposited films with thickness 200 nm of: ——— PI, MW treated for 5 min and thermally treated for 15 min at 300 °C; - - - - - - PI, MW treated for15 min and thermally treated for 15 min at 300 °C; —·—·— PI, thermally treated for 1 h at 300 °C.

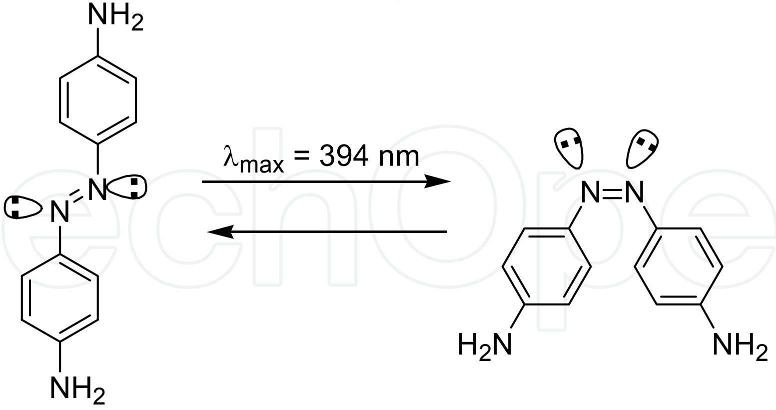
Polyimides	Band area at 1501 cm^{-1}/a.u.	Band area at 1382 cm^{-1}/a.u.	Imidization degree
PI treated for 5 min MW and thermally treated for 15 min at 300 °C	14.05	13.16	0.96
PI treated for 15 min MW and thermally treated for 15 min at 300 °C	16.30	17.24	1.05
PI thermally treated for 1 h at 300 °C	15.93	19.34	1.21

Table 4. Bands area at 1501 and 1382 cm^{-1} and imidization degree of the PI obtained after MW and thermal treatment.

The results from the calculations of the imidization degree are presented in Table 4. The PI treated for 15 min MW and thermally treated for 15 min at 300 °C displays a higher degree of imidization than that treated for 5 min MW and thermally treated for 15 min at 300 °C. These results are compared with the results about the PI obtained after thermal treatment for 1h at 300 °C. The experiments carried out allowed for the method for PI production to be optimized by the introduction of a MW treatment of the vacuum deposited layers from ODA and PMDA.

A part of our efforts are made with regard to the creation of azo-polymer of the "main chain" type as well in which the azo- chromophore is covalently bound to the polymer matrix. We have used the precursors DAAB (4,4′-diaminoazobenzene) and PMDA (pyromellitic dianhydride) as initial monomers (Petrova TS et al., 2003; A.Georgiev et al., 2008). The covalent bonding of the chromophore by a "side-chain" or a "main-chain" is of considerably greater perspective for the production of organic nanostructured layers due to their greater stability and uniform density as compared with the "host-guest" system. The azo-benzene derivatives have been the subject of extensive investigations for a long time (Osvaldo N. Oliveira et al, 2005; Cristina Cojocariu and Paul Rochon, 2004). In the aromatic azo-compounds the azo-group is formed by σ- and π- bonds between two nitrogen atoms. Such structure determined planar configuration of the σ- skeleton at the functional group and the angular localization of substitutes to it. The existence of the π-bond between the nitrogen atoms in the DAAB molecule explains the availability of the π- diastereoisomery. E- diastereoisomers are thermodynamically more stable than Z- diastereoisomers (Fig. 5). When the polymer nanocomposite is irradiated by linearly polarized light optical anisotropy is observed as a result from the photo-isomerization and photo-orientation of the azo-chromophore perpendicular to the direction of the polarized beam. Later this effect has been recorded also in other azo-polymer films that have found application in the development of devices for preservation of reversible optical information. Photoisomerization is observed when the chromophores pass from the low-energy trans-form to the cis-form after absorption of light (Fig. 5). The reverse process is accompanied by emitting of thermal energy but it could be also induced light. Trans-cis-trans isomerization cycle leads to shifted of the $\lambda_{max\ in}$ the absorption UV-VIS spectrum and the isomers posses different properties – dipole moments, refraction indexes and space volume (Osvaldo N. Oliveira et al, 2005;

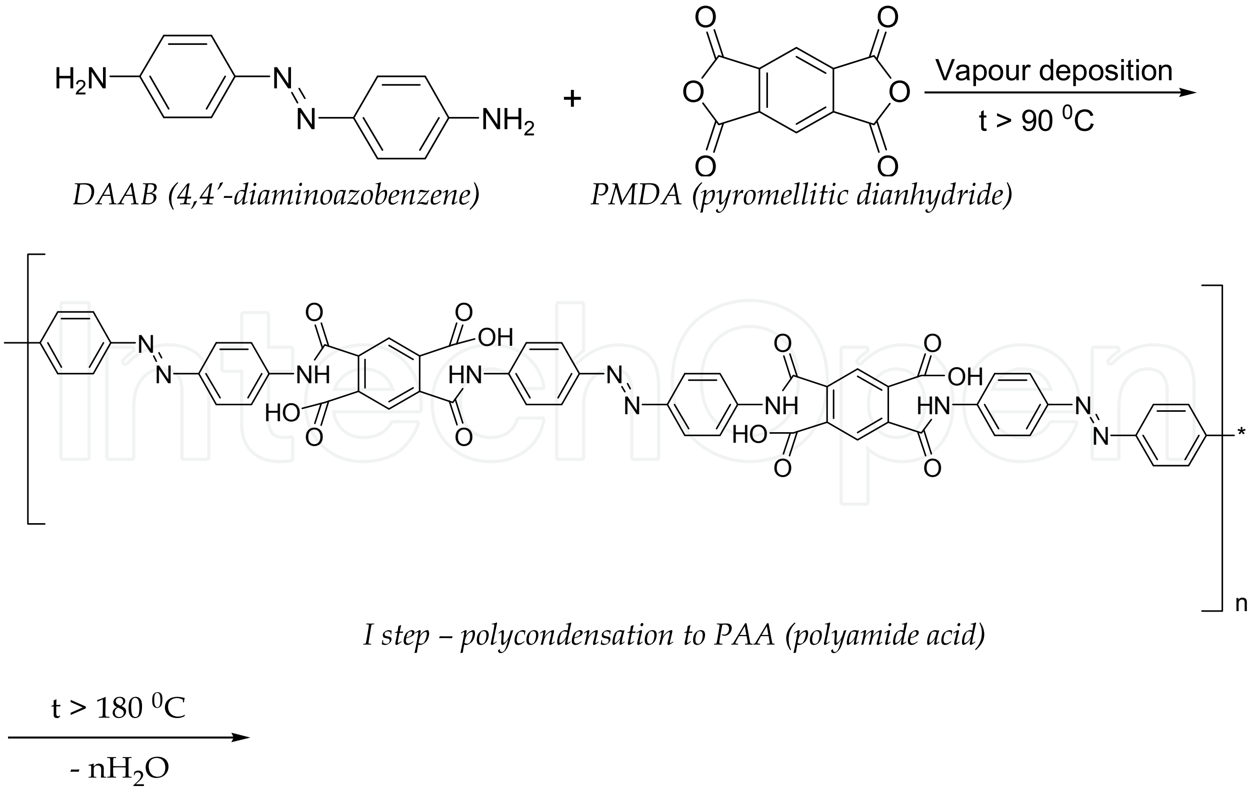
Cristina Cojocariu and Paul Rochon, 2004). These properties of the aromatic azo-compounds give possibility for detail investigation with the aim of optimization of their properties and the creation of new nanostructure films of better physico-chemical properties.



Trans (E)- Cis (Z)- isomers (diastereoisomers)

Fig. 5. Photo-isomerization of 4,4′-diaminoazobenzene (DAAB).

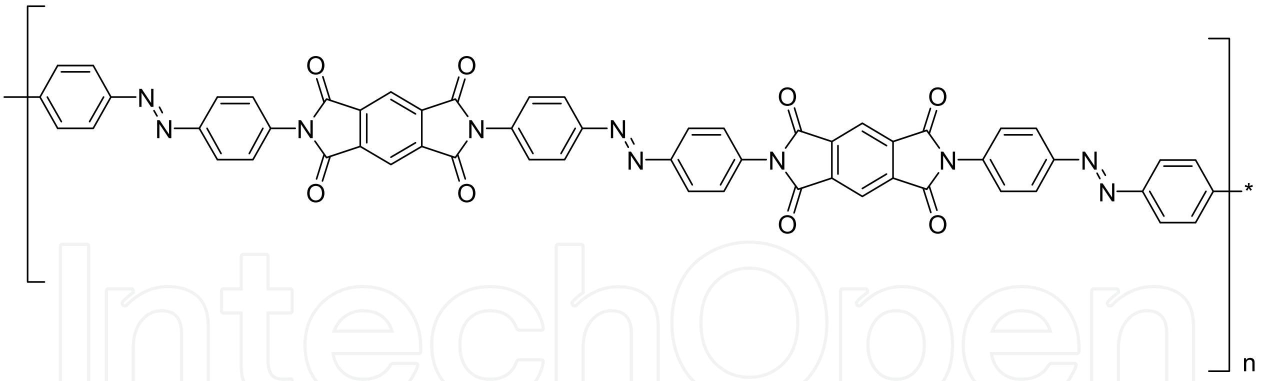
Scheme 2 illustrates the polycondensation between PMDA and DAAB and the following cyclodehydration to linear azo-polyimide (Azo-PI). The covalently bound to the polymer chain chromophores are preferable to the „guest-host" system, because the covalent bonding ensure a uniform and dense layer without defects in the polymorph structure and the physico- chemical properties of the layer are significantly improved.



DAAB (4,4′-diaminoazobenzene)

PMDA (pyromellitic dianhydride)

I step – polycondensation to PAA (polyamide acid)



II step-cyclodehydration to Azo-PI (Azo-polyimide)

Scheme 2. Reaction between PMDA and DAAB to Azo-PI.

Having in mind the structure and the spectral properties of the Azo-PI there is perspective to be successfully employed as a polymer matrix in the formation of nanostructure layers with potential application as optical modulators, optical recording media and other optical devices (Petrova TS et al., 2003, Valtencir Zucolotto et al., 2004).

We suppose that PAA (polyamide acid) is formed since the simultaneous vacuum deposition of the two precursors DAAB and PMDA as thin deposited film. Our assumption is confirmed by the FTIR spectrum presented in Fig. 6. Reaction of polycyclodehydration to Azo-PI takes place following the MW treatment of the film for 5 min ensued by the thermal at 30 min at 300 °C.

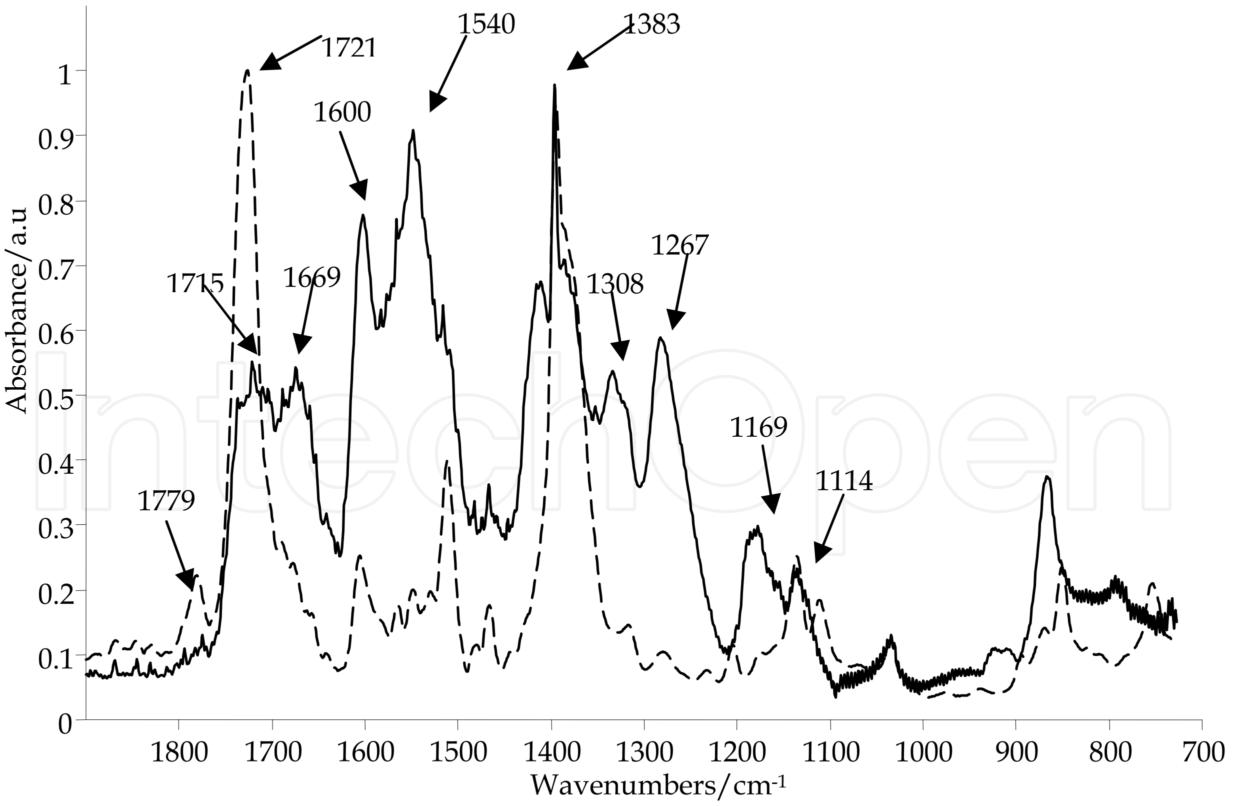


Fig. 6. FTIR spectra of vacuum deposited films with thickness 250 nm: —— DAAB:PMDA ratio 1:1(PAA); - - - - - - Azo-PI, obtained after 5 min MW treatment and 30 min thermal treatment at 300 °C.

In the spectrum of deposited films (Fig. 6) the typical bands characterizing PAA for amide I 1669 cm^{-1} ($\nu_{C=O}$) and amide II (δ_{N-H}) are identified at the broad and complex band at 1540 cm^{-1}, which overlaps with the second band of stretching vibration of C-C from the benzene ring. The broad band in the carbonyl area at 1715 cm^{-1} related to the >C=O group of acid. The bands at 1308 and 1267 cm^{-1} related to the deformation vibrations of C-OH (an acid). After the MW and thermal treatments process of imidization to Azo-PI takes place. The band at 1383 cm^{-1} is typical for imidization process. The typical bands for >C=O from the imide ring are identified at ν_s 1779 cm^{-1} and ν_{as} 1721 cm^{-1} (narrow and intense band). In the Azo-PI spectrum a minimum at 1669, 1540, 1308 и 1267 cm^{-1} is observed which confirms the imidization process. The stretching vibration for C-N at 1114 cm^{-1} are shifted towards the lower frequencies due to the lowering of the force constant for the stretching vibration in the imide ring as compared with the spectrum of the untreated layer (1169 cm^{-1}). The presence of azo-group is confirmed by the optical spectra of the corresponding films. Transmission at λ_{min} = 394 nm characterizing the azo-group is observed in the UV-VIS spectra of vacuum deposited films from DAAB and DAAB and PMDA (Fig. 7).

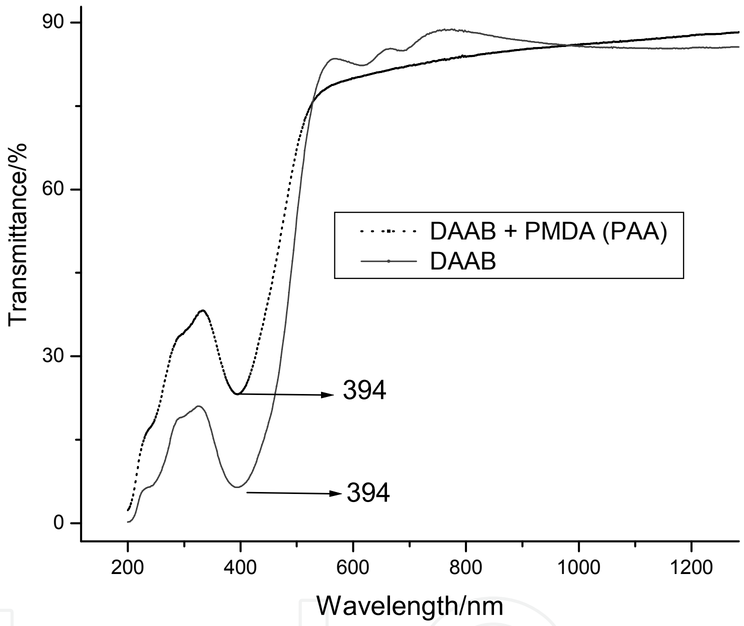


Fig. 7. UV-VIS spectra of vacuum deposited, untreated films from DAAB and DAAB: PMDA=1:1

The UV-VIS spectrum of Azo-PI (Fig. 8) is typical in which hyperchromic and hypsochromic effects are observed following the imidization and transmission minimum being weak at λ_{min} = 300 nm. The energy of the electron transitions grows significantly due to the decrease of π-conjugation after the imidization.

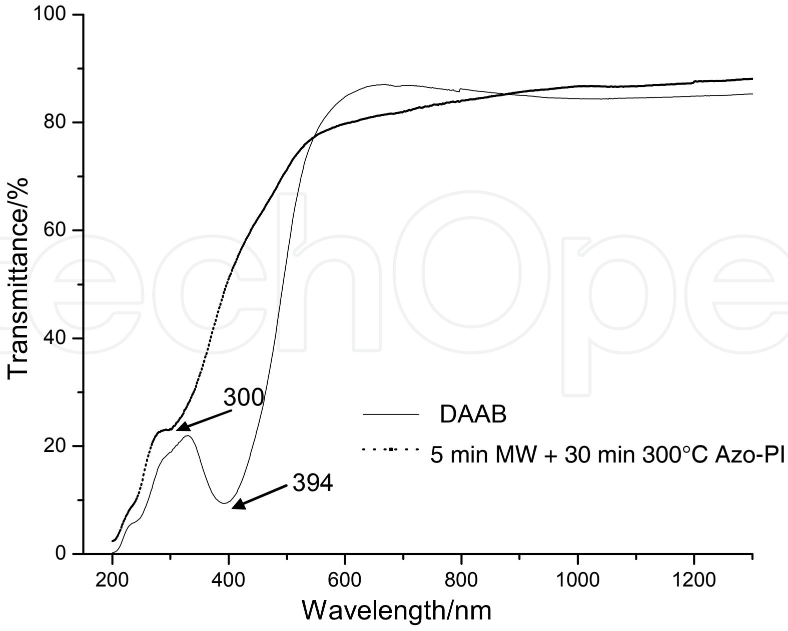


Fig. 8. UV-VIS spectra of vacuum deposited films from DAAB and Azo-PI.

The azo-polymer of the "main-chain" type, where the azo-chromophore is covalently bound to the polymer matrix represents material of good prospects in the formation of nanostructured layers for the purposes of micro- and optoelectronics, media for optical recording and other devices.

4. Conclusion

Systemized results from a study carried out with the aim for production of PI (polyimide) films by vacuum deposition and solid state reactions of diamine (ODA– 4,4′-oxydianiline) and dianhydride (PMDA- pyromellitic dianhydride), following transformation to PI by thermal treatment are presented in this chapter. It has been applied combined (thermal and MW) treatment with the purpose of obtaining layers of a smooth, defectless surface and reproducible composition and thickness. The established technical conditions allow for the production of PI layers of a proven composition and high imidization degree as prerequisites for acquiring a number of attractive properties of theirs– high transmission, high chemical resistivity and well pronounced dielectric properties at high thermal stability. FTIR spectroscopy was used in these investigations of the films. It has been shown that the determination of optimal parameters is importance for the production of PI layers with high quality.

A new approach in the preparation of "main-chain" polyimide films containing an azo-group is developed. After MW and thermal treatment the deposited layers from the precursors DAAB (4,4′-diaminoazobenzene) and PMDA (pyromellitic dianhydride) are transformed to Azo-PI by solid state reaction. The imidization reactions has been confirmed by FTIR spectroscopy. The approach provides the opportunity by the reaction of both precursors to obtain Azo-PI and to overcome the necessity of evaporation of compounds by the classical fabrication of dye containing composites with PI matrix.

As a result from the research carried out and the solutions forwarded defectless films of a reproducible composition, smooth surface, high chemical stability, desired levels of dielectric properties with the preservation of high thermal resistance have been obtained. These properties of theirs as well as the possibility for them to be used as an appropriate thin layer matrix for embedding of metals, salts and dyes they could contribute to the creation of novel nanocomposite materials i.e. the development of material science also in the nanomaterial reality.

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Polymer Thin Films

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This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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