# 2. Kinetics of PPI thin film growth via polycondensation

Polycondensation or condensation polymerization is one of many polymerization mechanisms [23], which has appeared to be very suitable and convenient to be used for preparing polymer thin films [11-22]. In this way of polymerization the elongation of a polymer chain is connected with chemical reaction between end groups of two bi-functional monomers associated with releasing low weight molecule as by-product [23]. As bi-functional monomers in the polycondensation process aromatic diamines and aromatic dialdehydes are used and the released by-product is water molecule H_2O [9-22]. This way of polymerizing monomers is of great importance especially for preparing polymer thin films by VTE and CVD methods, and what is worth emphasizing, these methods are suitable not only to preparing thin films of polymers that are insoluble in organic solvents, but above all these are the methods of preparing high purity polymer thin films without unintended impurities [22]. For the sake of this publication we are going to analyze kinetics of thin film growth of PPI, the simplest aromatic polyazomethine, with taking advantage of polycondensation process. Problem of preparation high purity polymer thin films is of particular interest for their applications in optoelectronics or photonics, and eventual impurities, if necessary, should be introduced to polymer thin films in a controllable way, as it is the case for inorganic semiconductors [5,6]. PPI thin films are prepared by CVD method via polycondensation of paraphenylene diamine (PPDA) and terephthal aldehyde (TPA) following the reaction as read below (1) [22]

$$\tag{1}$$
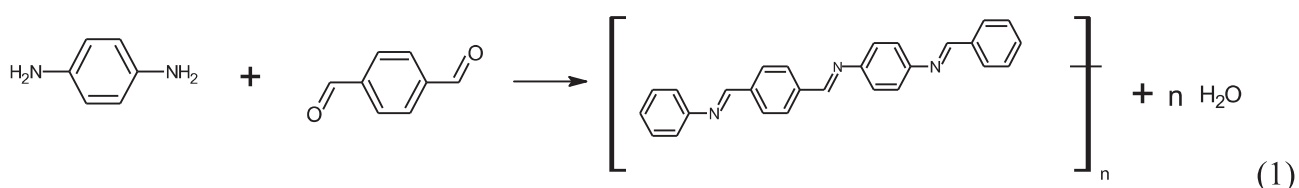
One can see that this polymerization route is associated with elongation of polymer chain and simultaneous releasing one water molecule (H_2O) at each step of the reaction and removing H_2O molecules from the reaction ambiance during the deposition process is of special interest. In fact, it is the case for each chemical reaction that the equilibrium conditions impose that relation of substrates and products involved in the chemical reaction are kept in quantities adequate to the equilibrium constant K [22], so that removing products molecules

from reaction volume drives the forward reaction going from the left to the right, otherwise the reaction is postponed. It is worth mentioning that chemical vapor deposition is running under conditions close to the equilibrium, because not great changes in temperature can switch reaction equilibrium between reaction postponing or going on forward. This is expressed by equation that the change in Gibbs free energy of chemical reaction is equal to the difference between the changes of Gibbs free energies of products (ΔG_{prod}) and substrates (ΔG_{subs}) (2).

$$\Delta G = \Delta G_{prod} - \Delta G_{subs} \qquad (2)$$

The change in Gibbs free energy depends on the change in enthalpy (ΔH) and entropy (ΔS) (3). It is worth mentioning that entropy component is multiplied by temperature, which may have great influence on the Gibbs free energy.

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

On the other hand, the change in Gibbs free energy that is the force driving chemical reactions and structural transformations is closely connected with the chemical reaction constant K (4).

$$K = e^{-\Delta G / kT} \qquad (4)$$

It is clearly seen from equ.4 that $\Delta G < 0$ is equivalent to K > 1 and $\Delta G < 0$, means K < 1. Thus, processes of polycondensation realized within vapor phase must take into account these conditions driving any chemical reaction. Mean degree of polycondensation is given by expression read below (5).

$$\overline{P_n} = \sqrt{\frac{Kc_0}{c_a}} \qquad (5)$$

One can see from this equation that the mean polycondensation degree is proportional to the equilibrium constant of polycondensation reaction and starting concentration of monomers and inversely proportional to the concentration of byproducts. Thus, one may expect that the higher the concentration of the starting monomers and the lower concentration of by-product the highest degree of polycondensation process is. Then, removing by-product one pushes the equilibrium constant of the polycondensation reaction in forward direction, thus towards polymer production. To gain any insight into polycondensation process leading to formation of polyazomethine thin films our interest was connected with understanding relation among thermodynamic conditions of CVD deposition of PPI thin films and their structure, morphology and optical properties. This choice resulted from its being the simplest aromatic

polyazomethine, similitude of its optical spectra to those of poly (paraphenylene vinylene) (PPV), the most investigated polymer which was used for optoelectronic and photovoltaic applications [6,7]. This polyazomethine has been prepared by polycondensation of paraphenylene diamine (PPDA) with therephthal aldehyde (TPA). Then, studying has been undertaken on preparation of more complex polyazomethines thin films prepared also via polycondensation of diamines based on such molecules as fluorene, naphthalene, benzidine, diminebenzidine and fat Brown 15R, TPA being used as aromatic dialdehyde [27,32], all of them being illustrating in bg 1. It should be emphasized that polycondensation has appeared the most convenient way of preparing polymer thin films by CVD and TVE methods on glass or quartz substrates [33]. Beyond the diamines shown in   1, one used also complex dialdehydes to combine via polycondensation with PPDA. Polymer thin films deposition by various methods via polycondensation process included polyazomethines having prepared from several aromatic diamines with terephthale aldehyde (TPA) or more complex aldehyde like 1,4-dioksybenzaldehyde (ODBA) with PPDA [34,35]. All those monomers are illustrated in Figure 1, while polyazomethines as-produced are shown in Figure 2. Technological conditions of deposition of thin films of polyazomethines shown in Figure 2 are given in Table1.

4-aminophenylamine

7-amino-9H-fluoren-2-ylanine

Terephthalaldehyde

5-amino-2-naphthylamine

3-amino-4-(1-naphthyldiazenyl)phenylamine

1-1'biphenyl-4.4'-diamine

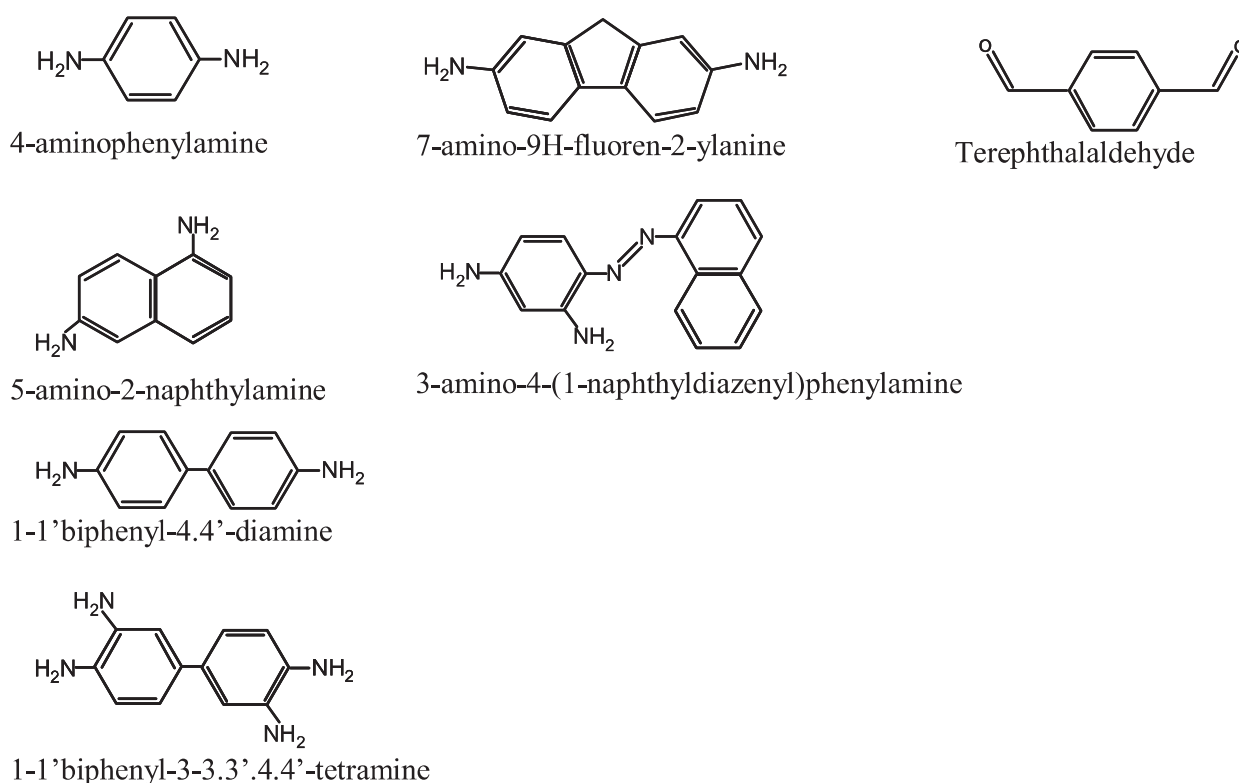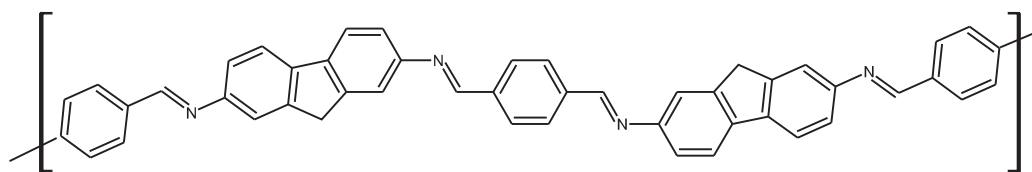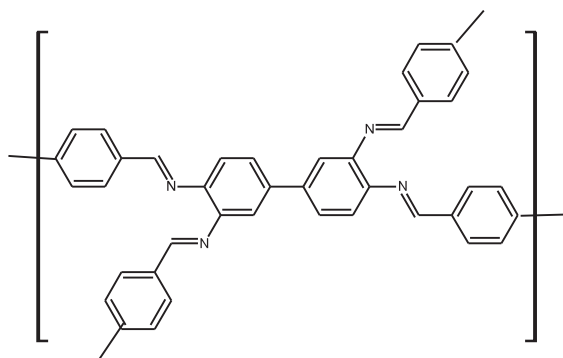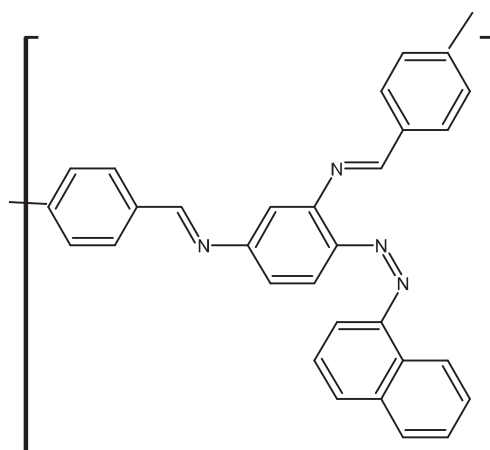1-1'biphenyl-3-3.3'.4.4'-tetramine

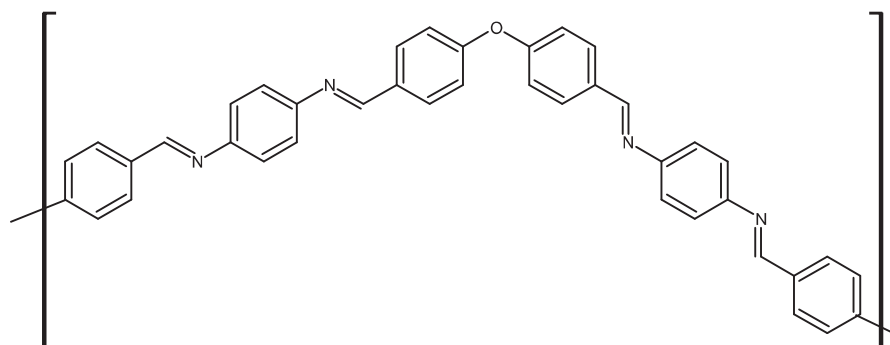*Figure 1. Aromatic diamines and terephthal aldehyde monomers for polyazomethines*

poly(2,5-fluorene-1,4-phenylene-azomethine) (FPI)

poly(tetramineboiphenylene-phenyleneazomethine) (BPI)

poly(1,3-phenylene(4-phenyleneazonaphtyl)-1,4-phenyleneazomethine) (PNAPI)

poly(p-phenyleneazomethine-oxygene) (PPI2)

Figure 2. *Polymer chains of various polyazomethines*

Table 1. Technological conditions of polyazomethines thin films deposition [19]

Film	Deposition time (s)	Temperature Diamine (°C)	Temperature Aldehyde (°C)	Vacuum (10^{-6} Tr)	Thickness (nm)
FPI	300	145	51	20	100
PNAPI	300	160	49	20	90
BPI	300	165	48	20	220

It seems important to indicate that TVE deposition process even though realized by means of condensation polymerization might be named also as physical vapor deposition (PVD) method to emphasis that monomers were transported from the crucible towards the substrate where within adsorption layer deposition process associated with reactions of polycondensation between end groups of the relevant monomers takes the place. The backbones of the as-prepared polyazomethines as it is seen from Figure 2, are rather complex, and their repeating units are composed of phenylene rings or biphenylene rings or fluorene or naphtyl rings and azomethine linkages connecting them with aldehyde phenylene ring, respectively.

Then, the size of the unit cell can be quite large because monomers are diamines and dialdehydes, so that like it is the case for PPI, alternate azomethine groups in the backbone of each polymer take –CH=N- or –N=CH- orientations. Thus, they are doubled while compared with similar conjugated polymer with vinylene linkages.

2.1. CVD PPI film deposition

Kinetics of CVD method of preparation of polyazomethine thin films has been discussed in details in our earlier paper on deposition of PPI thin films [22] and it will be outlined here, moreover the kinetics of preparation of the above mentioned polyazomethines by both CVD and VTE methods are not very different from the case of PPI thin films. In chemical vapor deposition technique with transport agent chemical reactions run under conditions close to the reaction equilibrium, so that changing temperature of the transported species can switch the chemical reaction progression between the forward and backward directions. The experimental setup for the CVD deposition of PPI thin films via polycondensation of aromatic diamines and terephthale aldehyde is outlined in Figure 3. The idea that was behind design of both horizontal and vertical arrangements was to divide the stream of gaseous argon which was the

transport agent into three equivalent streams, two of them flowing each over a boat with the relevant monomer kept at adequate temperature, and the third substream might be used to transport doping agent, so that it flows over the boat containing doping agent otherwise it was argon only stream, which effectively diluted the stream transporting monomers molecules. These streams of equal intensities transporting monomers merged into one stream in order for the monomers molecules to be mixed up before the stream as one entity was flowing into the reaction chamber where the substrate was mounted. As it was described elsewhere [22] the pipes through which stream of reagents was flowing were verified whether or not polymer film grew upon the pipe wall, but no traces of polyazomethine film on the pipe wall were found. While growing polymer films in the horizontal setup, the argon stream transporting mixed up monomers molecules entered the reaction chamber whose diameter was large compared to the inlet pipe diameter. In consequence, when entering the reaction chamber the intensity of the stream flow has undergone some drastic slow down that was accompanied with temperature decrease, because both the chamber and substrate were kept at room temperature, so that thermodynamic conditions became relevant for the polymerization process to be running forward. The CVD technique applied the polymerization is expected to run at the interface of the gaseous and solid phases within the adsorption layer formed upon the substrate by impinging molecules of reagent species. During the whole CVD processes made in both
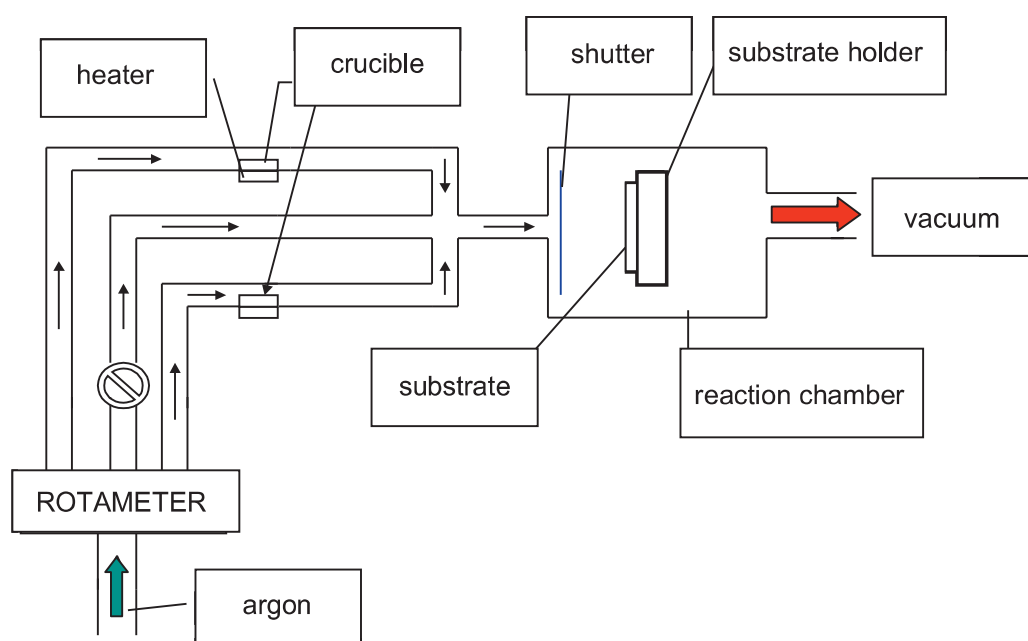

Figure 3. *Set-up for CVD deposition of polyazomethines thin films, according to [22]*

horizontal and vertical setups, the deposition process and the polycondensation reaction were supported with the use of the pump exhausting transport agent and byproducts from the reaction chamber. Clean pipe walls indicated that the species transported by argon essentially have not polymerized, though while sticking with one another small molecules with two distinct functional groups could eventually be formed, but this decreased number of molecules being carried on and so decreased probability for them to knock and clash to combine into oligomer with more than two repeating units. The conditions of PPI thin film deposition by CVD method and related morphology of the as-prepared films are collected in Tables 2 and 3, respectively. The reaction equilibrium constant according to (2-5) depends exponentially on Gibbs free enthalpy $\Delta G = \Delta H - T\Delta S$, where changes of free enthalpy (G), enthalpy (H) and entropy (S) concerns relevant changes of products and substrates, changing the sign of ΔG means switching the reaction between the state of reaction stoppage or reversing and the state of product formation. Thus, it is expected that $\Delta H/T$ and ΔS were not too high at room temperature, as otherwise spontaneous reaction rather than reaction reversibility conditions ($\Delta G \approx 0$) would be reached [22].

Table 2. CVD technological parameters of PPI thin film preparation

Film	T_{PPDA} (K)	T_{TPA} (K)	Flow rate l/min	Time (s)	Distance (cm)	Streams number	Thickness (nm)
A	335	326	80	120	5	2	200
B	334	326	80	180	4	2	200
C	340	326	150	60	5	2	200
D	334	326	80	420	4	3	170
E	343	327	80	90	5	3	180
F	315	313	60	1500	5	3	50

Table 3. Morphology of PPI thin films

Thin film	RMS roughness (nm)	Thickness (nm)	Growth rate (nm/s)	Grain size (μm)
a	5.0	200	2.5	0.4
b	10.3	200	2.2	0.2-0.3
c	7.5	200	3.1	~0.1, >1.0
d	9.9	170	0.4	0.2-0.3
e	6.3	180	1.8	~0.1
f	32.3	50	0.1	~0.4, ~ 1.0

On the other hand, it has been noticed that film formation process runs easily and rapidly which seems to manifest rather low energy barriers for the intermediate states and the reaction speed is attributed to rather high probability of relevant molecules sticking with one another suggesting high enough concentrations of reagents molecules in the stream. Thus, one may think that the stream impingement onto the substrate provide not only monomers molecules but also two or three molecular units which while adsorbed on the surface can combine with one another building up polymer film. It is clearly seen that reaction of polyazomethine formation run within the adlayer at the vapor phase/substrate interface between arriving jumping and knocking and clashing one against another molecules of terephthal aldehyde and paraphenylene diamine. The higher frequency of clashing events between monomers with different end groups, the higher probability their reaction, resulting in polymer chain becoming longer and longer with releasing H_2O by-products. During the process the contributing monomers are kept at relevant temperatures of about 323-350K, while the glass substrate is at temperature 300K.

Such temperatures of monomers were chosen in order for polycondensation process was running at nearly 1:1 stoichiometry of PPDA and TPA molecules being monomers, as evaporation temperature of PPDA is higher than that TPA. Then, applied temperature regime of the argon stream transporting two mixed monomers made the reaction running forward towards the film formation to be displaced towards substrate area where decreased temperature enforced reaction to be shifted towards polymer chain formation. It is thought that kinetics of polymer thin film deposition is bringing some confirmation of Flory' rule stating that the activities of end groups involved in polycondensation process are independent of the length of chain to which they are attached [23]. This seems to be in accordance with X-ray diffraction patterns nearly coinciding with those reported by Luzny et al. [13,14] for bulk PPI prepared by solution techniques. While the vertical setup was used, the transporting argon substreams flew through three pipes and in each of them the streams were flowing around the crucible filled with monomers, so that vapors of the relevant monomers molecules were undertaken mainly due to diminished static pressure in the vicinity of the crucible, as it bis indicated in Figure 4. Then, the substreams flowing out of the three channels merge inside so-called collimator from which through top pupil the stream of mixed up monomers molecules is flowing towards the substrate mounted in the holder just above the collimator opening. During the deposition process the reactor volume behind the substrate is evacuated with the use of rotary pump, which seems to be element supporting reactants streams flowing throughout

the reactor [33,34]. Thin films of polyazomethines were deposited by physical vapor deposition (PVD) method in the experimental setup outlined in Figure 5.

Polyazomethine deposition process carried out by PVD method is performed by sublimating monomers placed in two separate crucibles mounted in the vacuum chamber [26]. Before deposition process started the reaction chamber with crucibles filled with the monomers is exhausted to produce high vacuum. The substrate was cut off with the shutter until the temperature of monomers in crucibles attained required temperatures and the vacuum attained the required level. Then, the shutter was opened and the deposition process started.
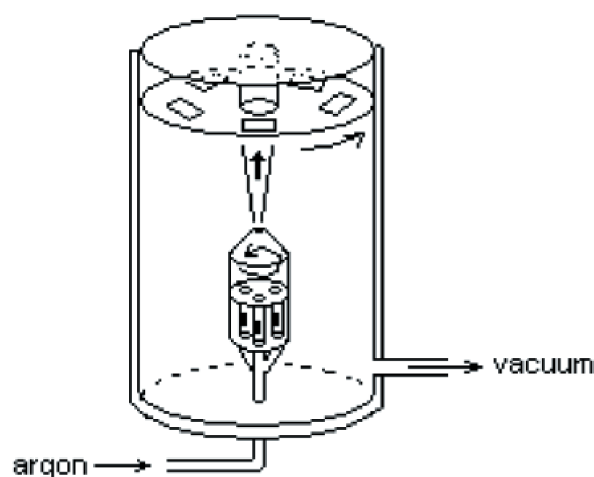

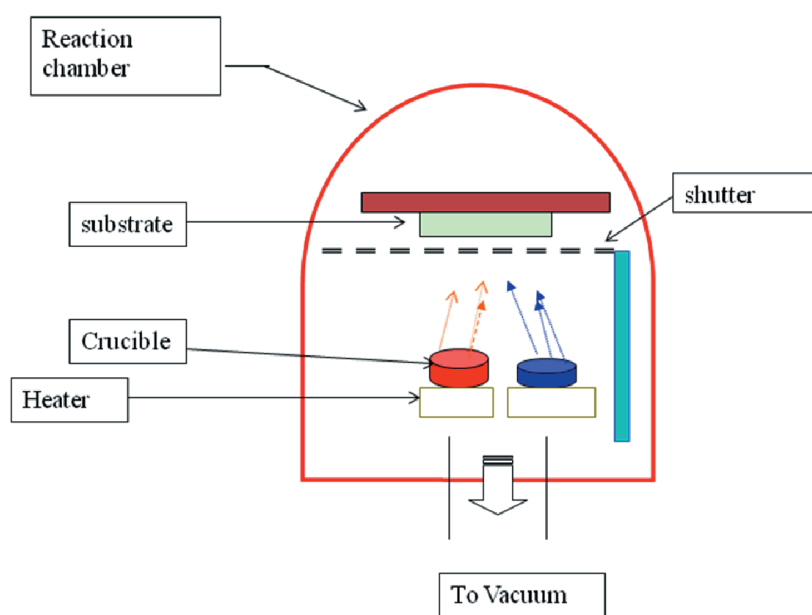**Figure 4.** *Set-up for double-source vacuum thermal evaporation [33]*

Figure 5. *The technological set-up for PVD deposition form two sources*

The streams of monomers transporting molecules of reactants towards the substrate, though sublimation temperatures depended on monomers used, but in case of the simplest polyazomethine they were not very different from their values applied during CVD processes. However, essentially for the same reasons, temperatures of monomers were different and their difference was of about 10-15°C in order for the film growth conditions approached polycondensation conditions with nearly 1:1 ratio of the monomers molecules impinging onto the surface of the substrate. Thin films of polyazomethines were also prepared under conditions of rather low vacuum with exhausting rotary pumping kept running during the whole deposition process. While preparing thin films of polyazomethines by condensation polymerization using much complex monomers, such as fluorene diamine, benzidine diamine or fat Brown R15 the temperatures used for subliming aromatic diamines were much higher and were within the range 145-165°C, while terephthal aldehyde temperature being at the level of 50-60°C.