

# Thermal Cyclodehydration of Polyamic Acid Initiated by UV-Irradiation

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## ABSTRACT

The use of mass-spectrometry, IR-spectrometry, electron-paramagnetic resonance, mechanical and theoretical methods and the influence of preliminary UV-irradiation on solid phase thermal cyclodehydration of polyamic acid based on pyromellitic dianhydride and 4,4'-diaminodiphenyl ether are studied. Optimum condition of thermal cyclodehydration of polyamic acid using UV-Irradiation has been found to give the high degree of turn. The mechanism of solid phase photoinitiated thermal cyclodehydration of polyamic acid is proposed.

The theoretical calculation of the duration rate of imidization of polyamic acid photothermal cyclodehydration is also carried out.

**Key Words:** polyamic acid, polyimide, UV-irradiation, photothermal treatment, optimization

## INTRODUCTION

The complex physicochemical properties of polyimides (PI) allow their wide application in a number of diverse fields including the aviation, cosmetic and electronic industries. However, the development of new techniques places higher requirements on the polymers used in these fields.

In spite of the extensive possibilities of PI as a thermostable class of polymers, they do not completely satisfy the growing demand of modern technique. The point is that the present methods of preparation of PI do not allow the realization of all the intrinsic potentials contained in their molecular structure. This is connected with the well-known hindering problem of reaction at higher temperature *limitation* [1] leading to a reduction of molecular weight of polyamic acid (PAA). At the earlier stages of thermal cyclo-

dehydration reaction of PAA, this phenomenon is practically finished by the complete kinetic stop of reaction at incomplete conversion of PAA to PI. The authors [2] connect the kinetic stop of the cyclodehydration process of PAA with the presence of unequivalent amount of conformers caused by the repeating isomerization of the carboxyl group or amide bonds. This is explained by the presence of intramolecular and intermolecular hydrogen bonds and also by hydrogen bonds between the polymer and solvent [3].

The main feature of kinetic conversion of PAA to PI is that the reaction mechanism is in competition conditions of such processes as cyclization-disintegration-resynthesis. One of the causes of PAA destruction is the hydrolysis of amide bonds and the disintegration of carboxyamide group in intramolecular mechanism [4]. Therefore, for the reduction of the negative effect

of such undesirable processes and the preparation of PI with improved properties it is necessary to search for more rational ways to manage the PAA cyclodehydration reaction. The management methods for the chemical reaction using different kinds of electromagnetic irradiation (UV, IR, laser and X-ray) are known. Because of the concrete necessary conditions, different wavelengths of irradiation are used. Here it is necessary to note that the use of high energetic irradiation (laser and X-ray) often leads to very poor physical and mechanical properties of the polymer.

UV-irradiation was proved to be more convenient and practical owing to the high selectivity action on the different functional groups of polymer. Therefore, the detailed study of interaction features of UV-irradiation and PAA on different stages of the cyclodehydration process gives rise to interest in both the development of fundamental investigation of the interaction of ray energy with polymers, and solving a practical task connected with the optimization process of preparation of polyimide materials with predicted properties.

## EXPERIMENTAL

The polyamic acid based on pyromellitic dianhydride and 4,4'-diaminodiphenyl ether in dimethylformamide (DMF) as a well known representative of prepolyaryleneimides was chosen for investigation (Scheme 1).

Samples as 8–10  $\mu\text{m}$  thick films were prepared from the PAA solution in DMF by way of drift on the glass surface and drying in a vacuum thermobarochamber ( $T=323\text{ K}$ ,  $P\sim 5\times 10^{-2}\text{ Pa}$ ).

Before execution of the experiments, the samples were exposed to UV-irradiation in air using a quartz mercury lamp PRK-7M(Rus.). The quartz vessel cooled with distilled water was used to cut off the IR-region of irradiation of the light source. The constant temperature and water circulation were provided by a U-10 (Germ.) ultrathermostat.

Further thermal treatment of the PAA film

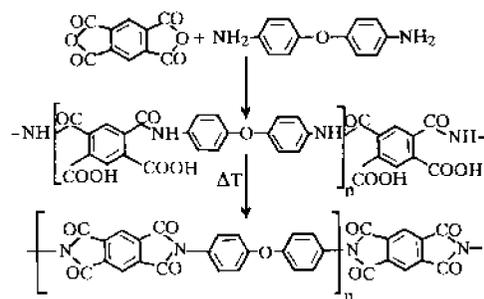
was carried out in a quartz photopyrolytic cell connected to the ionization chamber of an MI-1201(Ukr.) mass-spectrometer[5]. The kinetics of thermal or photothermal cyclodehydration of PAA was studied by volatile yields of processes, correspondingly. The volatile yields were monitored by a KSP-4(Rus.) electronic recorder and by visual display.

IR-spectroscopic investigation was carried out on a SPECORD-75 IR(Germ.) spectrometer. The electron paramagnetic resonance (EPR) spectra were received by an RE-1306(Rus.) radio spectrometer. The mechanical test on films was carried out by routine method.

## RESULTS AND DISCUSSION

The two stage method in which the prepolymer is prepared through soluble PAA and then exposed to a solid phase thermal cyclodehydration, still is the principal method for preparation of polyimides. Taking this into account the thermal and photo-thermal imidization of PAA in the air was investigated.

By means of comparative analysis, some specific features of photothermal cyclodehydration process on previously irradiated prepolymer at the initial stage of imidization and thermal treatment with simultaneous UV-irradiation to complete the imidization process were obtained. In particular, the observed increase of water molecules extraction at thermal destruction of PI, obtained by previous UV-irradiation in the air, means the



increase of polymer defect due to the increasing number of uncyclized groups formed as a result of a possible photooxidation processes (this point can be seen by the noticeable increase of peak intensity of the corresponding oxygen containing groups with  $m/e = 16, 17$  mass-spectra). Here, there is special interest in the behaviour of DMF ( $m/e = 73$ ), used as solvent in relation to UV-irradiation (Figure 1). Figure 1 shows the noticeable displacement of initial DMF extraction temperature for the irradiated films in air and in vacuum in comparison to control samples.

As a result of UV-irradiation, joining of the fundamental structure of free molecules with solvent in the first stage of imidization takes place. Furthermore the intensity of solvent extraction starts to exceed the value for control samples (unirradiated films) almost by two-fold. Here it is necessary to take into account the fact that a free solvent can render a plastifying effect on the cyclization process, promoting achievement of the limited rate of turn. But after the prolonged UV-irradiation of PAA, one can observe the

drastic increase of free solvent extraction velocity in mass-spectra, that can noticeably decrease its role as a plastificator.

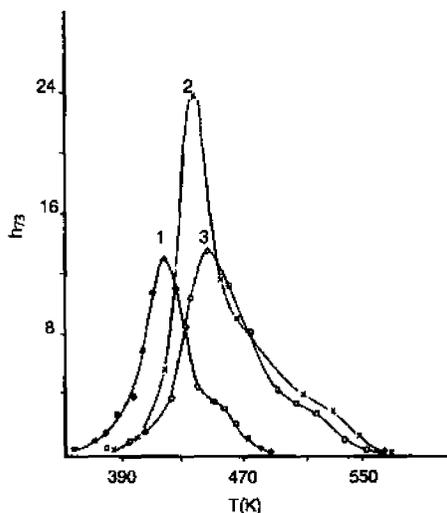
With the ion extraction intensity ( $m/e = 18$ ) ( $H_2O$ ) the kinetics of cyclodehydration process of PAA is observed. Comparison of temperature curves dependent on ion current for control and photothermo-treated samples, shows the advantage of extraction of  $H_2O$  from previously UV-irradiated imidization, that indicates the positive effect of UV-irradiation on the cyclization process of PAA.

The detailed study of molecular processes taking place at interaction between UV-irradiation and PAA indicate the presence of some optimum method of cyclodehydration reaction conduct for preparation of PI with improved properties.

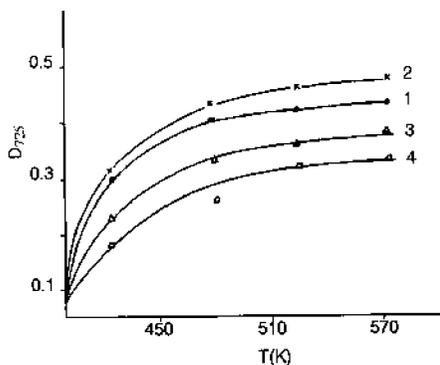
By means of correct selection of time-temperature treatment regimes, it is possible to achieve limited values of amic acid fragment taking part in the formation process of the imide cycles. Use of UV-irradiation requires taking into account that the absorption process of the light quantum has rather individual character and requires special caution when selecting the concrete photothermal treatment regime. This problem for polyimides has not been studied in practice.

The dynamics of molecular movement responsible for the PAA cyclization process was studied by characteristic absorption peaks alteration according to the IR spectra. The alteration of absorption peaks exhibits an intensity of  $725\text{ cm}^{-1}$  and  $1780\text{ cm}^{-1}$  describing the deformation vibration of  $C=O$  groups and vibration of imide cycle, respectively. Optical density values of samples exposed to previously phototreatment at the different time-temperature conditions have been determined that a maximum value can be achieved after UV-irradiation of PAA-films for 1 minute at  $373\text{ K}$  with further completion of reaction by thermal imidization (Figure 2).

In accordance with a finding that the optical density is directly proportional to the imidization rate, one can guess, that the found regime of polymer treatment allows achievement of the highest range of PAA to PI. This is explained by



**Figure 1.** Mass-thermogram of dimethylformamide yield followed by the previous UV-irradiation of the PAA at room temperature: 1- the initial film, 2- UV-irradiation in the air, 3- UV-irradiation in vacuum.



**Figure 2.** The relationship between optical density absorption peak  $725\text{ cm}^{-1}$  versus previous phototreatment conditions of the PAA in the air: 1- the initial film, 2-4- during 1 min(2), 5 min(3), and 20 min(4) UV-irradiated films at 373 K.

the UV-irradiation quantum selectivity action, when selectively excites the functional groups responsible for the cyclization and thereby not only creates the useful energetic condition for the cyclization, but considerably decreases the temperature value of imidization. This permits decrease of the effect of unfavourable processes such as hydrolytic disintegration and reaction slow rate and stoppage developing at high temperatures.

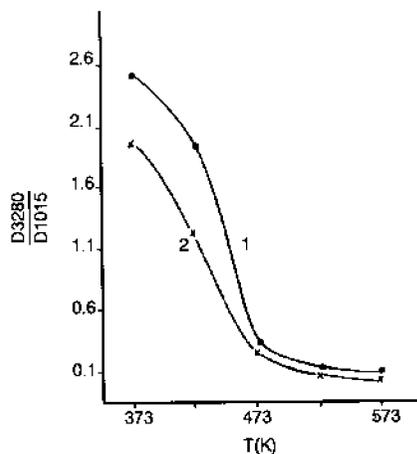
One can easily see from a comparison of temperature dependence of optical density absorption the characteristic peak of  $3280\text{ cm}^{-1}$ , corresponding to the valent vibration of  $\text{NH}$ -groups to standard absorption of peak  $1015\text{ cm}^{-1}$  (Figure 3). The increase of the optical density value of peak  $3280\text{ cm}^{-1}$  for the phototreated samples is a result of previously chosen action regime effect on the prepolymer.

It is known that with the cyclic imide formation at the imidization the isoimide links formation can take place as well [7]. The less the content of isoimide cyclics, the higher the level of elastic modulus, tensile strength and thermo-stability of PI films. In this connection, the consideration of the problem of how to obtain the optimum method of PAA photothermal imidi-

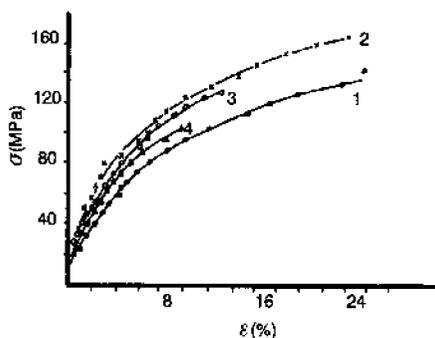
zation influence on the mechanical properties of prepared PI may be of a scientific and a practical interest. The results of mechanical tests for phototreatment and control samples are given in Figure 4. It can be seen that the increase of irradiation time leads to drastic decrease of the samples elongation caused by formation of interchain bonds whereas the maximum value has been achieved as a result of previous UV-irradiation of PAA for 1 minute at 373 K in the imidization stage.

The UV-irradiation on polymers, as a rule is accompanied by the radical reaction activation leading to the irreversible structure alteration, which at the same time, leads to the alteration of mechanical, thermal and other properties of polymer. For velocity study of this radical the EPR method [8] can give useful information. By considering the possibility of this method, we have studied the detailed feature of the radical formation process at thermal imidization of PAA with previous UV-irradiation.

The comparison of EPR-spectra of investigated PI-films shows the existence of experimental fact connected with a decrease of signal size for previous UV-irradiated films (Figure 5). In our

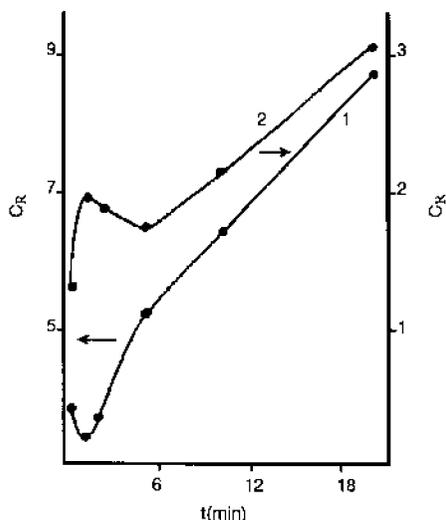


**Figure 3.** The relationship between  $D_{3280}/D_{1015}$  versus previous phototreatment conditions of the PAA in the air: 1- initial film, 2- UV-irradiated PAA ( $t=1\text{ min}$ ,  $T=373\text{ K}$ ).



**Figure 4.** The results of mechanical tests of PI films obtained by previous photothermal treatment of the PAA followed by the thermal imidization: 1- initial film, 2-4- during 1 min(2), 5 min(3) and 20 min(4) UV-irradiated films at 373 K.

opinion this is connected with direct activation of radical reaction at the transformation moment of PAA conversion to PI. As for the linear part of dependence  $C_R = C_R(t)$ ,  $C_R$  being the free radical concentrations, probably a new radical formation



**Figure 5.** The relationship between the free concentration radicals formed in the PAA (1) and PI (2) versus previous UV-irradiation time.

takes place having a chain mechanism due to prolonging of UV-irradiation. At least this leads to the imbalance of energy that is necessary for cyclization.

For the PAA there is a reverse reaction taking place. In the *anomalous* point  $t=1$  minute,  $C_R$  has a maximum value. This seems to be an evidence of the increase of free radical concentration at the given time and temperature interval which can lead to sufficiently increase of functional groups activity taking part in the cyclization reaction. At the vicinity of point  $T=373$  K, PAA prepolymer shows a maximum sensitivity to UV-irradiation.

The formation of new active radicals promotes the process of energy transfer to the corresponding free degree and as a result creates the maximally favourable conditions for imide cycles formation. Furthermore the energetic balance of that system are violated with increase of UV-irradiation prolongation.

Thus, use of EPR spectroscopic method essentially completes the information on the mechanism of molecular processes happening with the photothermal treatment of PAA and allows us to discern the mechanism of the process. Hence, the elucidation of features making up the form and properties of macroradicals is necessary not only for the utilization of polymer materials, but also for directional modification by choosing an optimum condition of synthesis.

At present there is not an exact theoretical explanation for imidization degree interrelations with the main kinetic parameters of the process. This is connected with an extraordinary complicated PAA cyclodehydration process, stipulated by many factorial phenomena. Based on the statement that the macroscopic variation of PAA cyclodehydration reaction parameters can be expressed by macroscopic quantities obtained from experiment, there is a possibility to evaluate the UV-irradiation effect at the imidization process.

One of informative parameters is an effective activation energy. By the determination of activation energy interrelation process with the PAA imidization degree, one can receive informa-

tion about the macroscopic mechanism of processes taking place at the conversion moment of PAA to PI.

A model calculation of PAA imidization degree by the variation of effective activation energy value and heat velocity was carried out.

As an initial equation, we used the chemical kinetics equation, describing the imidization process of initial materials by heating [9]:

$$\frac{dy}{dt} = K(T)(1-y)^{p(T)} \quad (1)$$

where  $y$ : polyimide concentration (imidization degree),  $K(T)$ : reaction constant,  $p(T) = 2$ : rate. It is known that the reaction velocity constant must be found by the Arrhenius equation:

$$K = K_0 \cdot e^{-U_{\text{eff}}/RT} \quad (2)$$

where  $U_{\text{eff}}$ : effective activation energy. In the case of photothermal cyclodehydration one can assume that:

$$U_{\text{eff}} = U - h \bar{\nu}$$

where  $\bar{\nu} = \nu \int I(\nu) d\nu$ : average value of light frequency of the spectra. Since the heating is realized with constant velocity:

$$C = \frac{dT}{d\tau} \quad (3)$$

where  $C$ : heating rate. Solving equations (1) and (3) and taking into account (2) for the imidization degree, we arrive at the following expression:

$$y = 1 - \left\{ 1 + K_0 \int_0^t \exp\left[-U_{\text{eff}}/R(T_0 + C\tau)\right] d\tau \right\}^{-1} \quad (4)$$

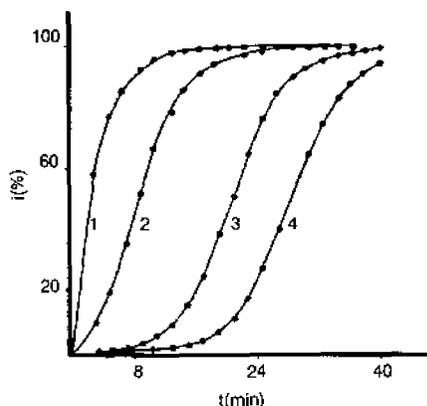
where  $t$ : imidization time,  $T = T_0 + C\tau$ ,  $\tau$ : heating time, and  $T_0 = 373$  K.

Using well known numerical values for  $K_0$ ,  $R$ ,  $T_0$  and determining the value for  $U_{\text{eff}}$  and  $C$  from the experiment, one can calculate the imidization degree for the corresponding process elapse at predicted concrete conditions. The results of such calculations are shown in Figure 6. The comparison shows that a measurable  $U_{\text{eff}}$

alteration stipulates a noticeable time interval alteration, which is necessary to achieve the maximum imidization degree. Of most interest is the shortening of imidization time.

For the value  $U_{\text{eff}} = 18$  kcal/mol (75.24 kJ/mol) the quantity of  $t$  during which the imidization degree achieves a maximum value is about 10–12 minutes. By means of a further decrease of  $U_{\text{eff}}$  value, it is possible to achieve the  $t$  value shortened up to second share at the time of high imidization degree after the prolonged heating at least for a few hours. This will be achieved by virtue of such negative processes as hydrolysis, which stops the reaction by increasing the temperature since the decrease in imidization degree will not have a negative effect on cyclization.

Hence, the model calculation of PAA imidization process allows the selection of optimum conditions for the reaction and, as a result, it will be possible to prepare PI with the improved properties. We have compared the calculated (using expression (4)) and experimental curves for the case of previously UV-irradiated PAA of 1 minute duration at 373 K. For the  $U_{\text{eff}} = 20$  kcal/mol (83.60 kJ/mol) and  $C = 5$  grad/min, the



**Figure 6.** The calculated relationship between the PAA imidization degree versus time at  $C = 5$  grad/min: 1—  $U_{\text{eff}} = 18$  kcal/mol (75.24 kJ/mol), 2—  $U_{\text{eff}} = 20$  kcal/mol (83.60 kJ/mol), 3—  $U_{\text{eff}} = 23$  kcal/mol (96.14 kJ/mol), 4—  $U_{\text{eff}} = 25$  kcal/mol (104.50 kJ/mol).

well coinciding curves were observed.

Consequently, the obtained PAA photo-thermal cyclodehydration conditions are optimal.

## CONCLUSION

Depending on the chosen specific conditions of the experiment simultaneous heating with UV-irradiation can prove to have a positive effect on PAA cyclodehydration reaction both in vacuum and in air.

The long irradiation by UV-light led to oxidative-destruction phenomena in prepolymer structure regardless of the other irradiation conditions.

The optimum imidization process was found, in which PI, with improved physico-mechanical characteristics was obtained.

By direct independent spectroscopic methods, the PAA photoinitiated thermal cyclodehydration mechanism was elucidated.

The theoretical calculation of PAA photothermal imidization was carried out. The expression describing the dependence of PAA cyclization degree with energetic characteristic of

the process was found.

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