Journal of Thermal Analysis, Vol. 24 (1982) 199—205

EFFECT OF ULTRAVIOLET IRRADIATION ON THE CYCLODEHYDRATION OF POLYAMIC ACIDS

A. TOIROV, YU. N. SAZANOV, L. A. SHIBAEV, Z. A. KABILOV, T. M. MUINOV and T. I. ZHUKOVA

Physico-Technical Institute of the Academy of Sciences of the Tajic SSR, Dushanbe, USSR; Institute of Macromolecular Compounds, the Academy of Sciences of the USSR, Leningrad, USSR

(Received September 25, 1981)

The general features of the effect of UV irradiation on the imidization of polyamic acids have been elucidated by using the analysis of thermal and mechanical properties of the polyimide obtained.

An optimum method of photothermal imidization was found, in which a product with improved thermomechanical properties was obtained.

The main feature of cyclodehydration of polyamic acids (PAA) in the two-stage method of preparation of polyimides (PI) is that this process is carried out in the solid phase with a relatively rigid arrangement of macromolecules. At present the mechanism of reactions occurring in this process is still a point of controversy. In particular, the following features have not been completely elucidated: the reason for the hindered cyclodehydration of PAA at a constant temperature, the nature of processes leading to a drastic decrease in the molecular weight of PAA in the temperature range from 373 to 523 K, and the relationship between degradation processes and the mechanical and other properties of PI.

As a result of the heating of the polymer above 523 K, the processes of resynthesis of macromolecules occur. They compensate only to a small extent the decrease in molecular weight due to degradation. The polymer strength attains only 6% of the theoretical value calculated on the basis of the initial molecular weight of the PAA. This fact indicates that the mechanical characteristics of the existing polymers can be greatly improved [1]. The part played by the solvent precipitated in the product after drying of the PAA during cyclodehydration has not yet been elucidated. On the one hand, it is known that such a solvent as DMF can react with the PAA and thus increases the amount of defects in the polymer [2]. On the other hand, the solvent can form solvates with the PAA, preventing the formation of strong intermolecular hydrogen-bonds in its structure and thus acting as a plastifier. This may lead to more favourable conditions for the closing of the five-membered imide ring [3]. The effect of a decrease in the molecular weight of the PAA can be reduced by choosing optimum technological conditions of cyclodehydration and using various basic or acidic catalytic additives [4].

In this work an attempt has been made to study by mass-spectrometric thermal analysis [5] the effect of UV irradiation on both the process of thermal cyclodehydration of the PAA itself and the thermal and mechanical characteristics of the PI formed as a result of this process.

Experimental

A well-known polyimide (PM) based on pyromellitic dianhydride and diaminodiphenyl ether was chosen for investigations. For the performance of thermal and photothermal imidization, 12–14 μm thick films of its prepolymer (PAA-PM) were placed in a pyrolytic quartz cell directly connected to the ionization chamber of the MI-1201 mass-spectrometer (USSR). Samples were maintained under high vacuum ($\sim 10^{-5}$ Pa) at room temperature for a fixed time required for the elimination of extraneous gases and volatile impurities, and thermal or photothermal imidization was carried out. The PI-PM samples could subsequently undergo thermal degradation without exposure of the films to the atmosphere. The construction of the pyrolytic cell made it possible to irradiate the samples continuously with filtered or unfiltered light of PRK-2M or PRK-7 mercury lamps (USSR). During each experiment the mass-spectra (the energy of the ionizing electrons was 50 eV) of residual and resultant gaseous products were continuously recorded. The quantitative estimation of volatile products [6] was carried out without taking into account the differences in ionization cross-sections. The intensity of the incident light was measured with an actinometer. PAA samples intended for mechanical test were imidized under a vacuum of 1.33 Pa in an instrument described elsewhere [7].

Results and discussion

Fig. 1 shows the mass spectra of products isolated after (a) thermal and (b) photothermal imidization, with irradiation of the PAA by unfiltered light of the PRK-2M lamp, and also (c) the difference mass-spectrum, illustrating the fact that the rates of the elimination of H_2O (*m/e* 17) and DMF (*m/e* 73) increase for

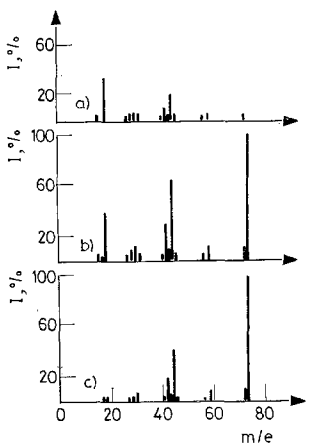

Fig. 1. Mass-spectra of volatile products eliminated from PAA-PM at 420 K. a — thermal imidization, n — photothermal imidization, c — difference-mass spectra

Table 1

Amount of main volatile products eliminated during PAA imidization (in % to the initial mass)

m/e	Imidization conditions					
	dynamic heating up to 500 K		static heating (5 hr)			
			T = 373 K		T = 423 K	
	without irrad.	irrad. λ = 240—400 nm	without irrad.	irrad. λ = 240—400 nm	without irrad.	irrad. λ = 240—400 nm
17	0.045	0.181	0.002	0.012	0.080	0.232
18	0.221	1.381	0.007	0.063	0.370	1.300
28	0.750	1.140	0.064	0.735	0.863	1.031
44	6.430	7.230	0.517	0.453	6.257	6.480
73	16.000	14.280	1.349	0.872	17.878	10.150

the irradiated sample. Evidently, photoexcitation of functional groups favours the acceleration of cyclodehydration and, even to a greater extent the dissociation of the complex of the amido acid with DMF.

The table gives the results of evaluation of the amounts of some ions formed in the mass spectrometric analysis of products of thermal and photothermal imidization. These results were obtained by graphical integration of the yield curves of ions having the corresponding mass. It is clear that in the cases of both dynamic and static heating, photoirradiation leads to an increase in the relative amount of fragmentary ions and to a decrease in the amount of the DMF molecular ions. The analysis of these changes is difficult, because the mechanism for dissociative ionization of irradiated molecules of DMF, H_2O, CO and CO_2 is unknown.

Evidently, it is advisable to evaluate the total effect of irradiation on PAA cyclodehydration on the basis of parameters which are not related to ionic processes occurring in the mass spectrometer. The thermal stability (T_0) of PI may be used as such a parameter. It is determined by using theoretical curves of mass loss during dynamic heating. The data on its determination for samples irradiated with light of different wavelengths are given in Table 2. In these experiments the total intensity of the incident light was maintained approximately constant and was $\sim$3.34 Wt/cm^2. The data reported here show that the maximum value of T_0 was attained when the sample was irradiated with UV light (λ = 240—400 nm). The effect of irradiation with visible light (λ = 350—600 nm) is less pronounced. Probably, apart from some positive stabilizing action, light in this spectral range also has a negative effect, partially destroying the PAA structure, in particular carboxylic groups [8]. It should be noted that formally these values of T_0 are not in accordance with the definition of thermal stability, because in this series of experiments the samples were irradiated both in the stage of cyclodehydration of the PAA and in that of PI degradation. A series of experiments was carried out

Table 2

Amount of main volatile products recorded during PAA imidization and the thermal degradation of resultant PI (in % to the initial mass)

m/e	Imidization conditions			
	dynamic heating up to 1000 K	dynamic heating with irradiation		
		complete spectrum of PRK-2M	λ = 240—400 nm	λ = 350—600 nm
12	0.028	0.043	0.030	0.029
16	0.042	0.091	0.043	0.041
17	0.063	0.282	0.066	0.080
18	0.258	1.442	0.257	0.305
28	3.952	6.902	3.963	3.590
42	3.555	4.165	2.588	3.290
44	10.612	16.189	13.420	14.680
66	1.280	0.797	1.061	1.302
73	16.720	15.965	19.600	14.700
94	6.253	2.77	4.643	7.466
Thermal stability, K	715	750	790	775

to establish an optimum temperature at which the PAA should be irradiated to attain maximum thermal stability and to obtain mass-spectra the interpretation of which would not be complicated by additional ionization of gaseous products due to UV irradiation. In these experiments PAA did not undergo pretreatment. As already mentioned, simultaneous photo- and thermal treatment at 373 K yields PI exhibiting maximum thermal stability. One can probably assume that the degree of imidization of the PI obtained by photothermal treatment is higher. Moreover, the results listed in Table 3 show that the amount of isolated DMF

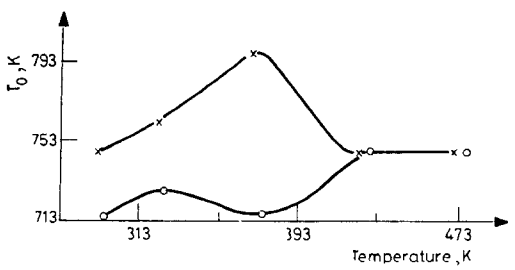

Fig. 2. Thermal stability of PI-PM *vs* conditions of PAA-PM imidization: 1) Thermal treatment under vacuum at ~ 1.33 Pa for 5 hr, (○) 2) Thermal treatment and irradiation (λ = 240 - 400 nm) for 5 h (×)

Table 3

Amount of main volatile products recorded during thermal degradation of samples obtained by preliminary imidization under different conditions (in % to the initial mass)

m/e	Temperature conditions, K									
	photothermal imidization $\lambda = 240-400$ nm, $t = 5$ hr						Thermal imidization, $t = 5$ hr			
	293	323	373	423	473	dynamic heating	323	373	423	473
12	0.027	0.132	0.024	0.045	0.052	0.028	0.035	0.028	0.048	0.128
16	0.103	0.086	0.044	0.046	0.057	0.042	0.034	0.040	0.055	0.107
17	0.573	0.263	0.155	0.037	0.019	0.063	0.054	0.041	0.034	0.048
18	1.525	1.199	0.838	0.083	0.029	0.258	0.153	0.098	0.076	0.079
28	5.244	7.072	5.410	3.845	1.213	3.952	2.279	2.921	4.586	1.748
42	1.312	2.723	2.500	1.595	0.110	3.555	2.349	3.098	0.546	0.123
44	7.920	16.010	13.200	15.144	7.468	10.612	11.646	15.124	12.243	12.650
66	0.563	0.948	0.800	1.771	2.555	1.280	3.252	1.282	1.910	0.697
73	25.220	10.181	19.034	6.934	0.276	16.720	12.171	16.570	2.412	0.310
94	2.670	3.429	3.435	8.486	17.691	6.253	8.789	6.851	9.810	15.125

(*m/e* 73) was greater in the case of photothermal treatment than for thermal treatment alone. Evidently, in the former case the elimination of DMF from the PAA was facilitated, because the complex of DMF with PAA dissociates more completely under the influence of UV irradiation. As a result, the isolation of DMF occurred at lower temperatures and the extent of side reactions between DMF and PAA at higher temperatures decreased. This led to a decreasing number of defects in the PI, which can appear as a result of these reactions. The lower amount of phenol (*m/e* 94) formed during dynamic heating can also serve as indirect evidence of a higher degree of cyclization in the case of photothermal treatment.

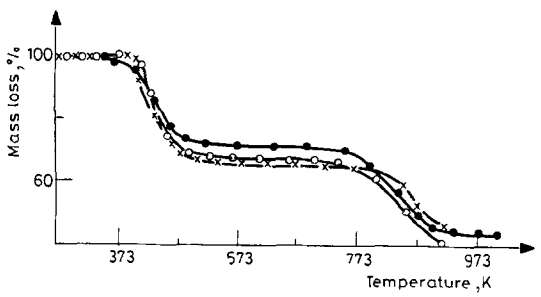

Fig. 3. Mass loss *vs* imidization conditions for PAA-PI films undergoing dynamic heating and pretreatment: 1) initial film (•), 2) irradiated film ($\lambda = 240-400$ nm) at $T = 373$ K for 5 h (×), 3) thermal treatment under the same conditions without irradiation (○)

Hence, the above results suggest that the thermal treatment of PAA film at 373 K, with simultaneous irradiation with UV light (λ = 240–400 nm), leads to an improvement in the thermal characteristics of the PI. Naturally, the materials exhibiting a combination of high thermal and high mechanical properties are of practical interest. It was necessary, therefore, to establish the effect of UV irradiation on the mechanical properties of these PI. It should be noted that the procedure of preparation of films for mechanical tests differed from that of films for thermal investigations. The samples were heated at various rates up to 510 K,

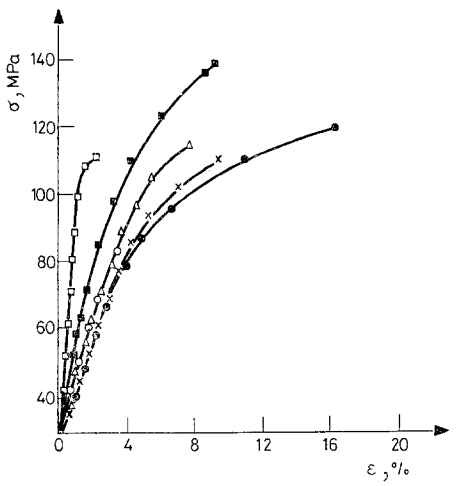

Fig. 4. Diagram of stretching of film of polyimide PM imidized under dynamic conditions of heating at various rates up to 510 K. 1) Initial film(•); 2) t = 30 min with irradiation by the light of a PRK-7 lamp (×); 3) t = 1 h with irradiation by the light of a PRK-7 lamp (△); 4) t = with irradiation by the light of a PRK-7 lamp (□); 5) t = 3 h with irradiation by visible light (λ = 350–600 nm) (○); 6) t = 3 h with irradiation by UV light (λ = 2110–400 nm) nm) (■)

both with irradiation (intensity 3.34 Wt/cm^2) and without it under a vacuum of about 1.33 Pa. The time of treatment varied depending on the rate of temperature rise (v).

For non-irradiated samples, the heating rate and hence the time of treatment of PAA films did not appreciably affect the mechanical properties of the PI. When imidization was combined with UV irradiation, the mechanical properties of the PI films differed greatly, depending on the irradiation time and on the frequency range of the light used for irradiation. Figure 4 shows the characteristic results of these mechanical tests. It can be seen that irradiation of any type leads to an increasing elastic modulus of the PI films. When the sample was irradiated with non-filtered light of the PRK-2 lamp, the elastic modulus increased with increasing treatment time, without any considerable decrease in tensile strength as compared to control samples. If the sample was irradiated with visible light (λ = 350–

600 nm), the elongation at break and the tensile strength decreased drastically with a slight increase in the elastic modulus. The best results were obtained when the PAA films were imidized with simultaneous irradiation with UV light (curve 6). In this case both the elastic modulus and the tensile strength increased. Hence, just as in the investigation of the thermal stability of the PI, it may be concluded that the mechanical properties (elastic modulus and tensile strenght) are improved if PAA films are irradiated with UV light at $\lambda = 240-400$ nm. However, when the sample is irradiated with light of any wavelength (infrared light of mercury lamp, at $\lambda = 240-400$ and $350-500$ nm), the elongation at break decreased, which might be due to the increasing number of cross-links in the PI structure. The lowest change in the elongation at break as compared with that in a control PI sample was observed for UV irradiation at $\lambda = 240-400$ nm. It is possible that in this case the change in this factor may also be due to the increasing degree of imidization of the PI, which leads to a higher rigidity of the PI films.

This investigation shows that it is possible to improve the thermal and some mechanical properties of PI materials if the stage of imidization of PAA is carried out simultaneously with UV irradiation.

References

1. L. N. KORZHAVIN, L. A. SHIBAEV, S. V. BRONNIKOV, T. A. ANTONOVA, YU. N. SAZANOV and S. YA. FRENKEL, Vysokomolekul. Soedin., 22/A (1980) 2027.
2. A. YA. ARDASHNIKOV, J. E. KARDASH and A. N. PRAVEDNIKOV, Vysokomolekul. Soedin., 16B (1974) 368.
3. G. V. BAGROV, The influence of preparing conditions of the PM polyamide acid on the physical and thermomechanical properties of the polyimide films, Leningrad, Thesis, 1975 (In Russian).
4. L. W. FROST and J. KESSE, J. Appl. Polym. Sci., 8 (1964) 1039.
5. Z. A. KABILOV, T. M. MUINOV, L. A. SHIBAEV, N. YU. SAZANOV, L. N. KORZAVIN and N. R. PROKOPCHUK, Thermochim. Acta, 28 (1979) 333.
6. Z. A. KABILOV, Mass-spectrometric study of the destructive processes in the polyarylimides Leningrad, Thesis, 1979 (In Russian).
7. A. TOIROV, D. SAIDOV, R. MARUPOV and KH. KHABIBULAEV, Zh. Prikl. Spektr., 34 (1981) 277.
8. B. RANBY and S. RABEK, Photodegradation, Photo-oxidation and Photostabilization of Polymers. Principles and applications. London, Wiley, 1975.

ZUSAMMENFASSUNG — Die allgemeinen Merkmale der Wirkung der UV-Bestrahlung auf die Imidisation von Polyamidsäuren wurde durch Einsatz der Analyse der thermischen und mechanischen Eigenschaften des erhaltenen Polyimids erläutert.

Eine optimale Methode der photothermischen Imidisation wurde gefunden, durch welche ein Produkt mit verbesserten thermomechanischen Eigenschaften erhalten wurde.

Резюме — На основе анализа термических и механических свойств полученных полимидов объяснен общий характер влияния ультрафиолетового облучения на процесс имидизации полиамидокислот. Установлен оптимальный метод фототермической имидизации при котором был получен продукт с улучшенными термомеханическими свойствами.