The role of the pyrimidine ring in the main chain of polyamic acids and polyimides

4.* Influence of pyrimidine ring basicity on thermoimidization of polyamidoacids

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Thermoimidization kinetics of polypyromellitamic acids prepared from 2,5-bis(*p*-aminophenyl)pyrimidine and 4,4″-diaminoterphenyl have been investigated by IR spectroscopy. It has been shown that the activation energy for the pyrimidine-containing polymer is nearly twice as low as that for the aromatic analog. This is explained by base catalysis of cyclization of the amidoacid fragments by pyrimidine rings in polymer chains. Base catalysis facilitates the process of imidization and favors the formation of polyimidic macromolecules with a lower incidence of defects. Also, the pyrimidine rings obviously catalyze the resynthesis of amidoacid fragments from the anhydride rings and amino groups formed on the destruction of the polymer chain during thermoimidization, and ensure almost complete recovery of the macromolecules with the previous bonds.

Key words: polyimide; polypyromellitamic acid; 2,5-bis(*p*-aminophenyl)pyrimidine.

Since pyrimidine rings exhibit basic properties in polymers prepared from pyromellitic dianhydride and 2,5-bis(*p*-aminophenyl)pyrimidine (PM-PRM), the "layer-on-layer" packing of chains, typical for aromatic polyimides (PI) and for polyamidoacids (PAA), is accompanied by "shifted" packing.[2] In PAA PM-PRM, some of the pyrimidine rings seem to be bound by hydrogen bonds to the amidoacid fragments of neighboring chains. It is known that[2] the presence of bases catalyzes the process of PAA imidization. In our case, the catalytic action of mildly basic pyrimidine rings can occur when the rings approach the reactive centers (the amidoacid fragments) due to "shifted" packing of PAA PM-PRM. In this process, the spatial factors are of great importance, since thermal imidization proceeds under the conditions of increasing viscosity of the medium.[3]

The purpose of the present work was to investigate the catalytic action of the pyrimidine fragments of a macromolecule in the process of imidization of PAA PM-PRM. The study included comparison with the aromatic analog, *viz.*, polypyromellitamic acid prepared from 4,4″-diaminoterphenyl (PAA PM-TP).[1,2,4]

Experimental

Synthesis and purification of the monomers, preparation of PAA PM-PRM and PAA PM-TP, their thermal imidization,[5] and chemical imidization of PAA[6] were carried out by the known procedures. IR spectra were recorded by a UR-20 spectrophotometer in PAA films. Measurements of the PI specific viscosity [η] and of the double refraction in oleum, and the calculations of the molecular weights of PI PM-PRM and PI PM-TP were performed as described earlier.[7]

Results and Discussion

The investigation of the thermoimidization kinetics of PAA PM-PRM and PAA PM-TP was performed under isothermal conditions at various temperatures. Using the linear parts of the kinetic curves, the imidization rate constants *k*, the activation energies *E*, and pre-exponential coefficients *A* were calculated. From the calculation results shown in Table 1 it is clear that *E* of PAA PM-PRM are nearly two times lower than that of PAA PM-TP. This confirms the proposal that the pyrimidine rings of the macromolecule catalyze imidization of the amidoacid fragments of the neighboring macromolecule.

In the case of imidization of PAA PM-PRM, a lower value of *A* corresponds to a higher activation entropy.

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* For part 3, see Ref. 1.

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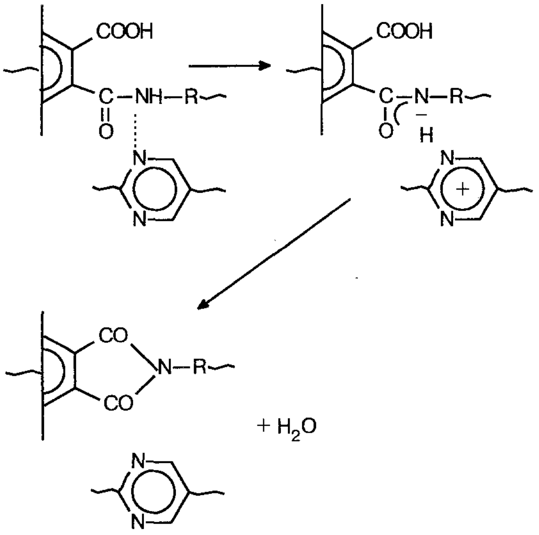
Table 1. Initial constants of thermoimidization for PAA PM-PRM and PAA PM-TP

PAA	T_{exp}/°C	k/s^{-1}	E/kJ mol^{-1}	A/s^{-1}
PM-PRM	125	0.57		
	150	1.29	43	2.5×10
	180	2.72		
PM-TP	125	0.27		
	150	1.62	71	7.3×10^4
	180	3.61		

This is probably explained by the considerable differences between the stereochemistry of the starting PAA and the activated complex of the pyrimidine-containing polymer relative to the aromatic analog.

It is expedient to assume that the transition state of PAA PM-TP imidization involves only one amidoacidic group, and, in the case of PAA PM-PRM, this stage involves both the amidoacid fragment of one chain and the pyrimidine ring of another. Thus, a decrease in the value of *A* of PAA PM-PRM can provide indirect evidence of the partial formation of an activated complex of the amidoacid fragment with the pyrimidine ring of the neighboring chain. We believe that the pyrimidine ring can act as a base catalyst in the imidization process[5] (Scheme 1).

Scheme 1



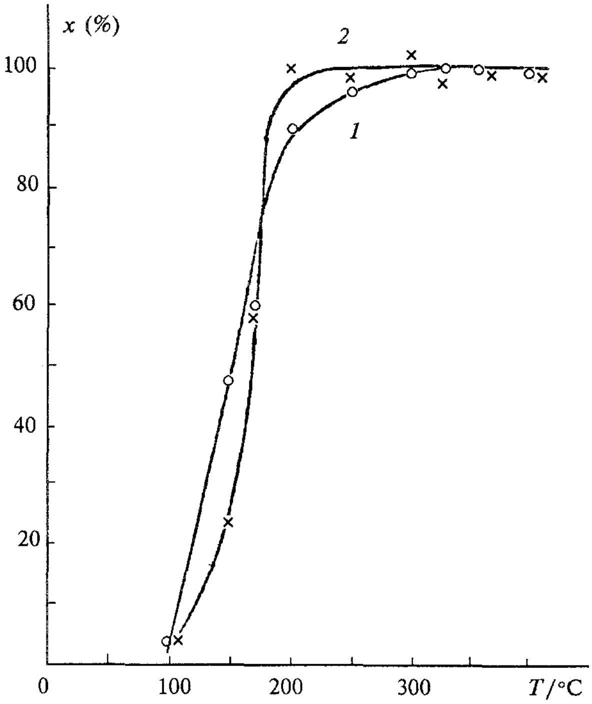


Fig. 1. Dependences of the degree of imidization ($x = D_{1780}/D_{1500}$) on temperature for PAA PM-PRM (*1*) and PAA PM-TP (*2*).

Base catalysis and the "shifted" packing of PAA PM-PRM macrochains are factors which favor the smoother occurrence of thermoimidization and influence to a great extent the imperfection of the arising polyimide. The dependences of the degree of PAA imidization (x) on temperature (Fig. 1), as well as E, also attest to the smoother occurrence of PAA PM-PRM imidization relative to that of PAA PM-TP. It is at high values of x, when the mobility of a system is already low, that the PAA PM-TP curve has a considerably greater slope than the PAA PM-PRM curve. Due to the decrease in system mobility, side-reactions become more probable than the formation of the imide ring, because the increasing rigidity of the system can prevent the realization of the conformation sterically favorable for completing imidization. In this connection, it is possible to believe that the higher the imidization rate in the last stages of the process under conditions of increased polymer rigidity, the less probable the reconstruction of the intermediate states into the spatial form favorable for closing the imide ring, *viz.*, the more probable the formation of defect structures in the PI macromolecule chain.

PI PM-TP and PM-PRM macromolecules have a "rod" form, their Kuhn segment should be endlessly long, and its decrease to limited values is naturally explained by the imperfection of the polyimide chain. The investigations by the method of double refraction[7] show that the Kuhn segment of PI PM-PRM is ~3 times longer than that for PI PM-TP: 1750 and 625 Å, respectively. Thus, PI PM-PRM is considerably less imperfect than PI PM-TP.

Using the results of measurements of specific viscosity and double refraction,[7] the molecular weights of PI

Table 2. Specific viscosities ([η] · 10^{-2}/cm^3 g^{-1}) and molecular weights M of PI PM-PRM and PI PM-TP, obtained by thermal and chemical imidization

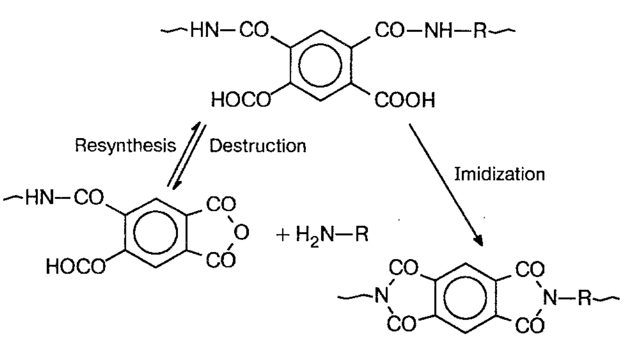
PI PM-PRM				PI PM-TP			
Thermal imidization		Chemical imidization		Thermal imidization		Chemical imidization	
[η]	M · 10^{-3}	[η]	M · 10^{-3}	[η]	M · 10^{-3}	[η]	M · 10^{-3}
2.95	14.0	3.00	14.0	1.20	10.0	4.80	22.0
2.60	12.0	2.60	12.0	0.83	7.5	2.25	16.0
2.45	11.5	2.10	11.0				

PM-PRM and PI PM-TP prepared by thermal and chemical imidization from the same PAA samples have been calculated. It is known that chemical imidization of PAA should not result in any considerable change in the molecular weight of the polymer,[8] unlike thermomidization of rigid-chain PI, after which the molecular weight decreases substantially.[9] According to this, the molecular weights of the rigid-chain aromatic PI prepared by thermoimidization are always lower than that of the same PI prepared by chemical imidization.

The data given in Table 2 show that the molecular weight of PI PM-TP obtained by the thermal method is, as expected, nearly twice as low as that of PI PM-TP prepared by chemical imidization. In the case of PI PM-PRM, however, the type of imidization is not important: the molecular weight and [η] are practically the same.

According to existing conceptions, a decrease in the molecular weight of PAA at the beginning of their hermal conversion to PI is a result of the reversible destruction of the amide bonds in the macromolecules, i.e., the main process of imide cycle closure is accompanied by a side-reaction yielding polymers with a lower molecular weight, which have terminal anhydride and amine groups. Thermal action at higher temperatures results in resynthesis of the amidoacid units at these erminal groups succeeded by imidization (Scheme 2).

Scheme 2



Accordingly, when PAA of various structures undergo thermal treatment, the destruction and resynthesis of macromolecules is accompanied first by a decrease, and then by an increase in the deformation and strength characteristics of the polymers in the course of thermoimidization. It is believed[3,8] that the absence of a minimum in the curves reflecting the dependence of the properties on the degree of imidization under the

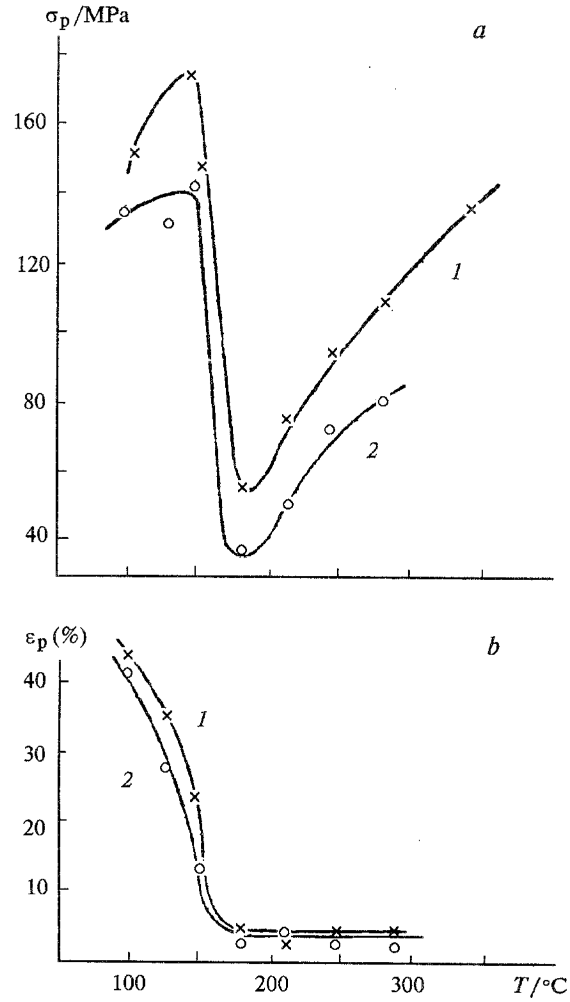


Fig. 2. Changes in the strengths (*a*) and extensions (*b*) during the rupture of PAA PM-PRM (*1*) and PM-TP (*2*) films in the process of thermal imidization.

conditions of chemical cyclization, attest to conservation of the molecular weight of the polymer in this process.

Fig. 2 exhibits the changes in the physico-mechanical properties of PM-PRM and PM-TP polymers in the course of heating PAA. It is clear that PM-PRM restore the strength properties of the polymer to a greater extent than PM-TP. The way in which the value of σ_p changes attests to the fact that the molecular weight first drops and then increases.

The more effective restoration of the mechanical properties of the pyrimidine-containing polymer in the course of thermoimidization can be explained by the influence of the pyrimidine fragment of the chain. When the pyrimidine ring is in close contact with the reactive amidoacid group, where the rupture of the macromolecule occurs to yield the terminal anhydride cycles and amino groups, the former can act as a basic catalyst in the process of resynthesis (see Scheme 2). In this case, the conditions are realized under which resynthesis of the macromolecules includes more complete restoration of the molecular weight of the pyrimidine-containing PI relative to the totally aromatic PI.

Thus, the pyrimidine ring influences considerably the process of thermoimidization: not only is its energetic barrier decreased by this ring, but there is also more rapid and complete resynthesis of PAA partly damaged by thermocyclization. All of these processes lead to PI of greater molecular weight and more perfect chemical structure.

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