THERMAL ANALYSIS AS A METHOD OF INVESTIGATION OF POLYMER–POLYMER INTERACTION

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ABSTRACT

The method of pyrolysis gas chromatography and thermovolumetric thermal analysis has been used for the investigation of polyamic acid–poly-*N*-vinylpyrrolidone and polyimide–poly-*N*-vinylpyrrolidone mixtures in helium. The products of thermal degradation have been identified. Data of analysis of gaseous and liquid degradation products for individual polymers and mixtures indicate that the mechanism of thermal degradation of polyimide changes when poly-*N*-vinylpyrrolidone is introduced into the mixture. This change is caused by the existence of the polymer–polymer interaction between the components of the mixture.

INTRODUCTION

At present, the systems consisting of two or more polymers the macro-molecules of which are capable of interacting with each other attract considerable attention. The interpolymer complexes formed in this case [1,2] exhibit specific properties differing from those of the components forming them. Many physicochemical methods of analysis are used for the investigation of these systems [2]. However, the majority of these methods can be applied only to soluble systems. We believe, on the basis of long experience in polymer investigations by the method of thermal analysis, that this method may be successfully employed as one of the main methods (and in some cases as the only method) for the study of polymer–polymer interaction.

It has previously been established that polyamic acid, a prepolymer for the preparation of polyimides, can form stable complexes with amide solvents and, in particular, with *N*-methylpyrrolidone (*N*-MP) [3,4]. It is also known that poly-*N*-vinylpyrrolidone (high molecular weight analogue of *N*-MP) forms interpolymer complexes with polyacids [5]. It may evidently be expected that an interpolymer complex is formed between polyamic acid and poly-*N*-vinylpyrrolidone.

The present work was undertaken to study, by pyrolysis gas chromatography, the interaction occurring in the solid phase between polyamic acid (PAA) based on pyromellitic acid dianhydride and 4,4′-diaminodiphenyloxide and the corresponding polyimide (PI) on the one hand and poly-*N*-vinylpyrrolidone (PVP) on the other.

Polymer films 30–40 μm thick were used as samples. The amount of PVP introduced into the system was 0.5, 1.0 and 2.0 mol mol^{-1}. The films were subjected to pyrolysis in an apparatus which is a combination of a pyrolyzer and a Hewlett-Packard gas chromatograph. Organic products (phenol, benzonitrile, benzene and hydrocarbons) were analyzed on 10 m capillary columns with a OV-101 silicon phase.

Thermovolumetric analysis (TVA) was carried out in a modified instrument by a previously described method [6]. The samples were heated under vacuum in the 20–900°C temperature range at a rate of 5 K min^{-1}.

DISCUSSION

The interaction between polyacids (polyacrylic, polymethacrylic and other acids) and PVP yields an interpolymer complex (IPC) stabilized by a system of hydrogen bonds between the carboxy groups of the polyacid and the carbonyl groups of pyrrolidone rings [5].

$$(1)$$

It might be expected that, in general, the interaction between PAA and PVP would occur according to the same principle. However, the ortho-amic acid group which is a distinguishing feature of aromatic polyamic acids is characterized by two proton donor centres: a carboxy and an amide group. Moreover, the latter forms hydrogen bonds no less readily than the former. Hence, it is possible to stabilize the PAA–PVP polycomplex in different ways: with the participation of (A) the carboxy group alone, (B) the amide group alone and (C) both proton donor groups.

The interpolymer complex formed in a solution of PAA and PVP evidently retains the solid phase in a film as a result of cooperative interchain interaction and determines the course of subsequent intra- and intermolecular reactions.

Figure 1 shows a typical TVA curve for a film of the PAA–PVP complex. Peak I represents the elimination of bonded solvent and water in the cyclodehydration of PAA, peak II characterizes the total gas evolution

(2)

(3)
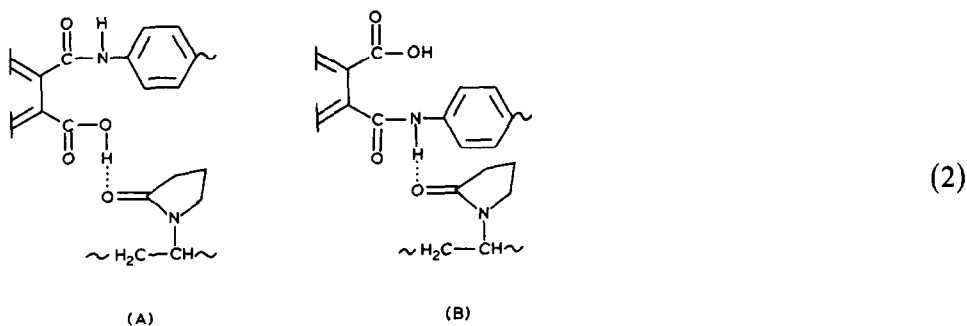
accompanying thermal degradation of PVP and peaks III and IV represent the total gas evolution in the thermal degradation of the polymer formed. A comparison of the TV curves for PAA–PVP mixtures with various compositions makes it possible to follow the effect of complexation on the processes of thermal transformations in the sample.
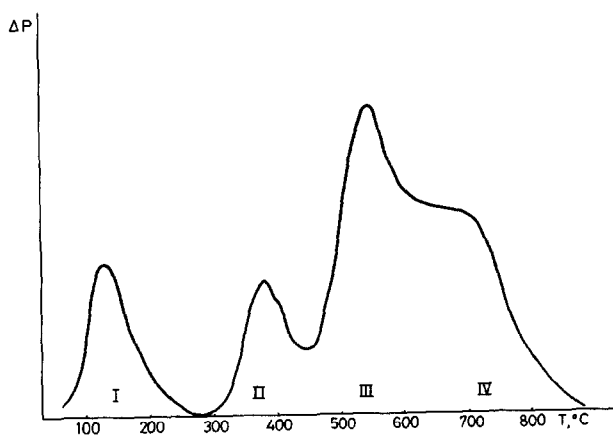

Fig. 1. TVA curve for the PAA–PVP mixture (molar ratio 1.0 : 1.0).

In the course of thermal cyclodehydration of PAA, the IPC structure should undergo considerable changes. First, as has been shown for model compounds [7], intramolecular cyclodehydration occurs only after hydrogen bonds between IPC and the solvent (in this case its high molecular weight analogue, PVP) are broken. As a result, IPC is destabilized

$$(4)$$
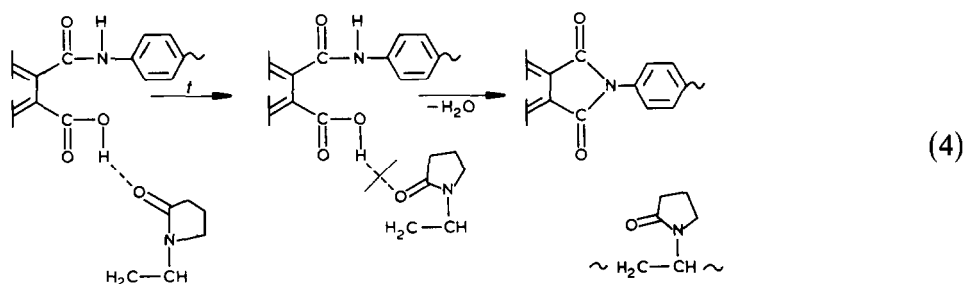
However, the interaction between PAA and PVP which is stronger than that with an amide solvent should prevent PAA cyclodehydration to an even greater degree. In fact, the TV curves of PAA (Fig. 2a) exhibit a high-temperature shift of peak I corresponding to water evolution in cyclodehydration. The greater the quantity of PVP introduced into the mixture, the more pronounced is this maximum.

After PAA undergoes cyclodehydration, proton donor groups disappear, and it is difficult to expect stabilization of the polyimide–PVP complex by the above mechanism. However, according to the TVA data, the maximum of the peak of total gas evolution in PVP degradation is observed at a slightly higher temperature for the PI–PVP complex than for pure PVP. The polyimide matrix limiting the mobility of the PVP chain fragments evidently exerts a stabilizing action on the process of its thermal degradation. This effect is observed even when the PVP content is 0.5 mol mol^{-1} of PAA (Fig. 2b) and is much more pronounced when the sample contains 2.0 mole of PVP per 1.0 mole of PAA.

The interaction with PVP, in turn, should have a certain influence on both intra- and intermolecular structure of the polyimide being formed. The process of thermal cyclodehydration of PAA in the presence of PVP can differ to a considerable extent from the usual mechanism. In this case defective structures differing from the imide structure are formed. Thus, at 100–150°C the pyrrolidone ring in the presence of the amide groups can be broken by the mechanism common to lactames (Scheme 5) [8].

This interaction with the formation of interchain imide bonds precludes the formation of the usual intramolecular imide group by the given o-amic acid group and this should lead to a decrease in the thermal stability of PI. In fact, the TV curves of the mixtures investigated exhibit a low temperature shift in peak III for the total gas evolution in the course of degradation of PI
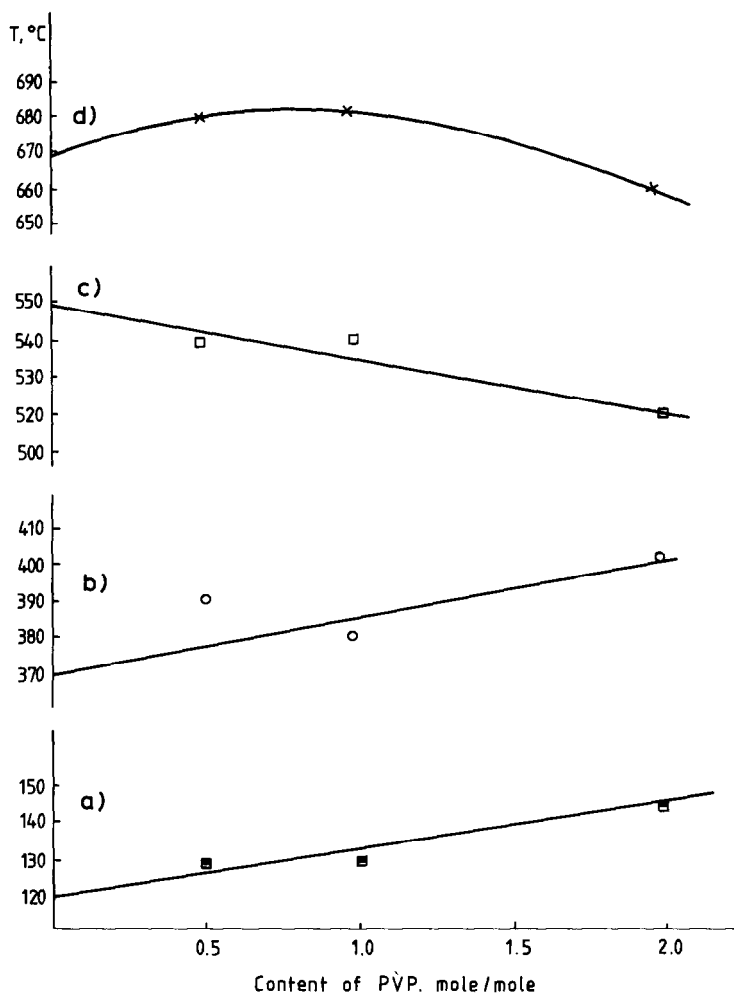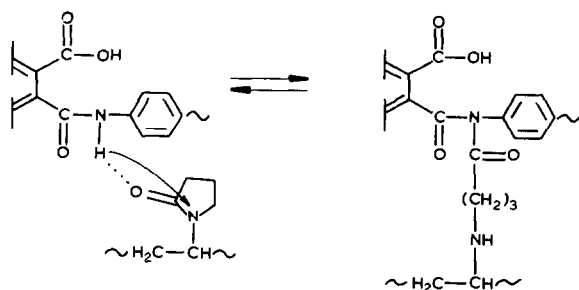
Fig. 2. Temperature of characteristic peaks vs. composition of the mixture.

(this peak is due mainly to the evolution of carbon oxides in the decomposition of "defective" and subsequently "perfect" units of the polyimide chain). The value of the shift is proportional to the initial content of PVP in the mixture (Fig. 2c).

(5)

However, the interaction according to Scheme 5 proceeds to higher conversion and can lead to the formation of a three-dimensional crosslinked structure

(6A)

(6B)
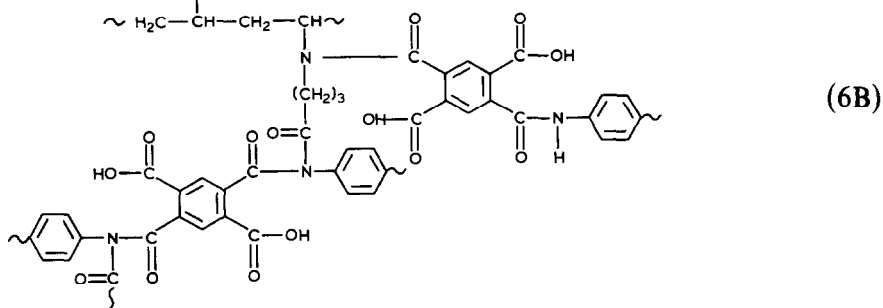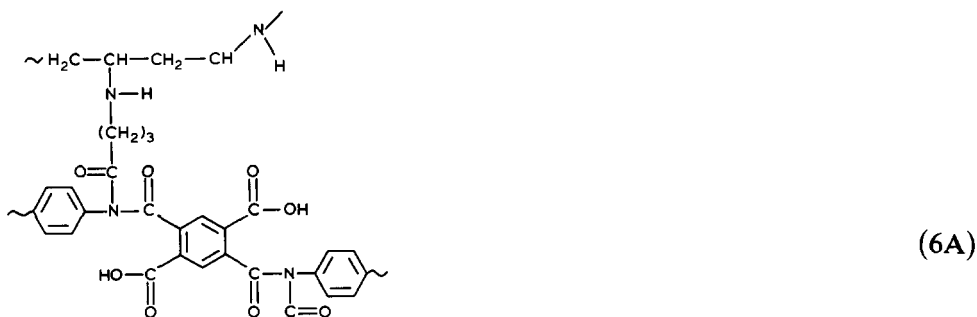
Moreover, as a result of interchain reactions with the opening of the pyrrolidone ring, secondary amino groups are formed; they can react with the terminal anhydride groups of the PAA (PI) chains forming interchain amide bonds and further increasing the structurization of the polymer system as a whole. The formation of a three-dimensional network should evidently prevent thermal degradation in the later stages of the process. In fact, peak V on the TV curves corresponding to gas evolution in this stage is displaced towards higher temperatures if PVP is present in the initial mixture (Fig. 2d). However, when 2.0 mole of PVP per 1.0 mole of PAA are present in the initial mixture, this trend is not observed. Furthermore, in this case the temperature of peak V is slightly lower even than that for pure PAA. The mechanism for the interaction between PAA and PVP in the initial mixture evidently depends on the ratio of the components, and on passing from the content of 1.0 to 2.0 mole of PVP per 1.0 mole of PAA the mechanism changes. This change affects the chemical (and possibly also the supermolecular) structure of the PI obtained by thermal treatment and hence the type of the processes of thermal degradation.

Some assumptions in the mechanism of interaction between PAA and

PVP and its influence on the type of thermal transformations of PAA could be made on the basis of the pyrolysis gas chromatography (PGC) data for the mixtures investigated.

The chromatograms of both the individual polymers (PAA and PVP) and the investigated systems as a whole show a considerable amount of pyrolysis products (Fig. 3) many of which have not been identified. Hence, only the most characteristic and reliably identified products were used in subsequent investigations. Thus, in the pyrolysis of PI large amounts of benzene, phenol, benzonitrile and C_1-C_3 aliphatic hydrocarbons are evolved (the latter compounds are also observed in the pyrolysis of PVP) as well as considerable amounts of carbon monoxide and dioxide.

Preliminary analysis showed that the temperature ranges of the pyrolysis of PI and PVP do not overlap (Fig. 4). The pyrolysis of PVP proceeds in the 400–500°C range, whereas that of PI takes place in the 600–900°C range.

The evolution of phenol in the PI pyrolysis is usually considered to be related to the degradation of the diamine fragment (diphenyl oxide) [9]. Figure 5 shows that the introduction of PVP into the system has very little influence on the type of evolution of this product. Even if the polymer–polymer interaction occurs, it does not affect the diamine component of PI.

It should be noted that if PVP is introduced into the system in the amounts 0.5 and 1.0 mole per one mole of PI with subsequent treatment at 380°C the presence of PVP in a previously thermally treated (imidized) sample is not detected, as is indicated by the evolution of aliphatic hydro-
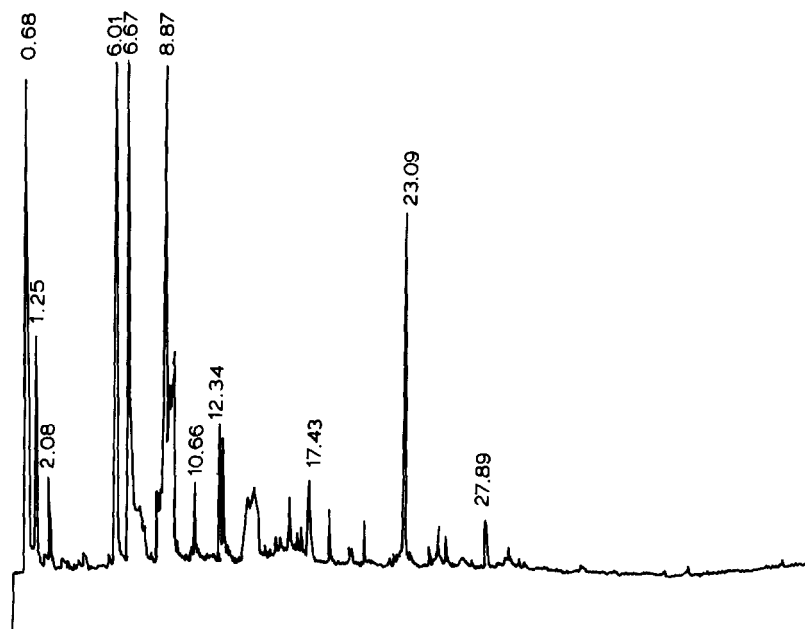

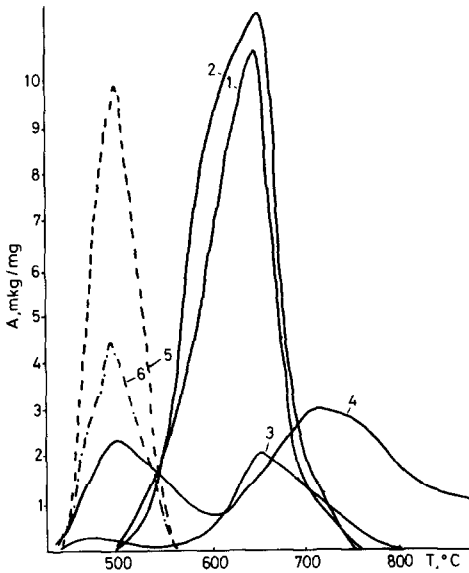Fig. 3. Pyrochromatogram of the PI–PVP mixture (1.0 mole : 2.0 mole).

Fig. 4. Products of pyrolysis of PI–PVP mixture (1.0 mole : 2.0 mole)—1–4 and PVP 5,6: 1—phenol, 2—benzonitrile, 3—benzene, 4,6—aliphatic hydrocarbon, 5—unidentified products.

carbons only in the temperature range characteristic of PI (Fig. 6). In the course of thermal treatment up to 380°C, PVP which did not undergo intermolecular interaction with PAA evidently undergoes complete thermal
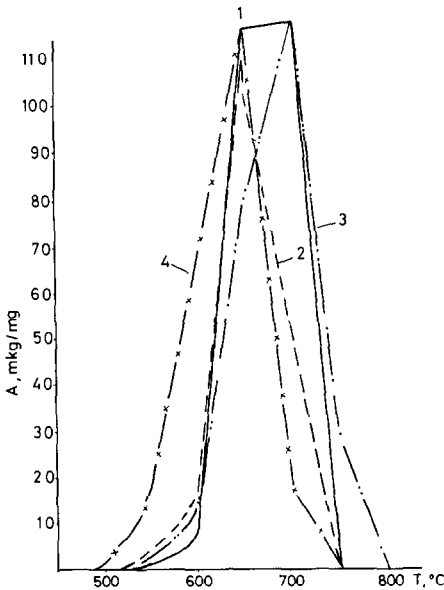

Fig. 5. Phenol yield in the pyrolysis of the PI–PVP mixture and the initial polymers: 1. PI; 2. PI + 0.5 mole of PVP; 3. PI + 1.0 mole of PVP; 4. PI + 2.0 mole of PVP.

degradation and is eliminated from the sample in the form of volatile products. The thermal structures shown in Schemes 5 and 6 also undergo degradation, which is probably due to the homolytical degradation of aliphatic fragments. However, the interchain network formed at lower temperatures is probably restored as a result of homolytical processes occurring in the sample. In this case the formation of graphite-like polycyclic systems forming the basis of the carbonized residue after the PI pyrolysis should proceed more readily
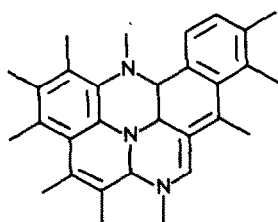
$$(7)$$

The fraction of carbonized residues after pyrolysis up to 900°C (TVA) is actually much larger for samples containing initially 0.5 and 1.0 mole of PVP per mole of PAA than for samples which did not contain PVP (Table 1). However, the fraction of carbonized residue of a sample which contained 2.0 mole of PVP per mole of PAA is slightly lower than for PI obtained in the absence of PVP. In this case intermolecular bonds are presumably either not formed at all or their number is negligible.

It is important that, even after imidization at 380°C, a considerable quantity of PVP remains in the film. This is indicated by a marked evolution
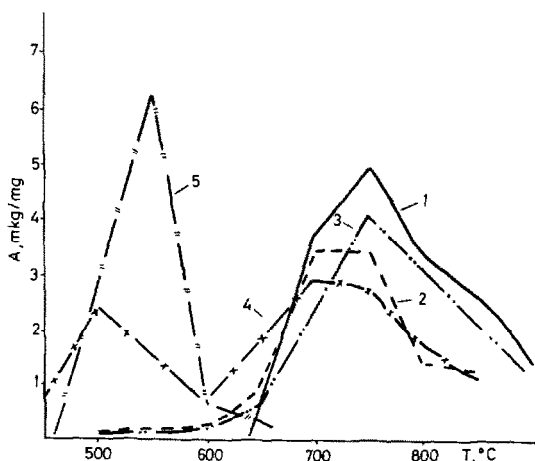

Fig. 6. Yield of aliphatic hydrocarbons in the pyrolysis of the PI–PVP mixture and the initial polymers: 1. PI; 2. PI + 0.5 mole of PVP; 3. PI + 1.0 mole of PVP; 4. PI + 2.0 mole of PVP; 5. PVP.

TABLE 1

Fraction of carbonized residue of samples in the pyrolysis up to 900°C

PI–PVP	Solid residue (%)
0.5 mol mol^{-1}	66.6
1.0 mol mol^{-1}	60.6
2.0 mol mol^{-1}	52.1
PI	54.0

of hydrocarbons in the temperature range characteristic of PVP (Fig. 6). This gas evolution cannot be related to the degradation of PI since the source of aliphatic hydrocarbons during pyrolysis is provided by aromatic rings the decomposition of which proceeds at much higher temperatures. Hence, in this case PVP remained in the sample in a considerable amount even after thermal treatment up to 380°C. The evaluations based on the PGC data show that this amount is 0.4 mole of PVP per mole of PI (Table 2).

Marked differences in the structure of the samples containing different amounts of PVP are also manifested in the degradation processes with the formation of benzonitrile. It is known that the main amount of benzonitrile evolved from PI results from the opening of the imide ring proper [9,10]. The preliminary opening of the ring should lead to a decrease in the benzonitrile fraction among the pyrolysis products because after the breaking of the amide bond this product is evolved in a much lower quantity [11]. As can be seen from Fig. 7, the evolution of benzonitrile in the pyrolysis of the systems in which 0.5 and 1.0 PVP mole per 1.0 mole of PI is present is observed in the same temperature range as for pure PI. A slightly smaller amount of benzonitrile in these cases is an additional evidence for the formation of interchain bonds during pretreatment under the influence of PVP. When 2.0 moles of PVP per 1.0 mole of PI are introduced into the system, the amount

TABLE 2

Calculation of residual PVP content in samples after imidization

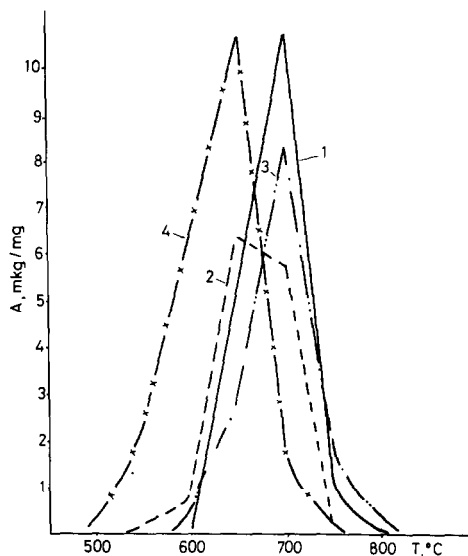| PVP content before imidi- zation mol mol^{-1}	Mass of volatiles in the PGC of the imidized sample below 600°C	PVP content in the imidized sample
PVP : PI 0.5 : 1.0	0.19	0.015 mol mol^{-1}
PVP : PI 1.0 : 1.0	0.15	0.02 mol mol^{-1}
PVP : PI 2.0 : 1.0	4.88	0.38 mol mol^{-1}

Fig. 7. Yield of benzonitrile in the pyrolysis of the PI–PVP mixture and the initial polymers:
1. PI; 2. PI + 0.5 mole of PVP; 3. PI + 1.0 mole of PVP; 4. PI + 2.0 mole of PVP.

of isolated benzonitrile does not differ from that for pure polyimide but the entire peak of evolution is displaced by 50°C towards lower temperatures. Hence, in this case preliminary opening of the imide ring does not occur but the thermal stability of the imide structure proper is somewhat lower. Finally, approximately identical amounts of benzene (product of degradation of the aromatic part of the polyimide chain) and phenol (the source of which is diphenyloxide, the residue of the amine component of polyimide) in all the cases investigated (Figs. 5 and 8) indicated that the interaction with
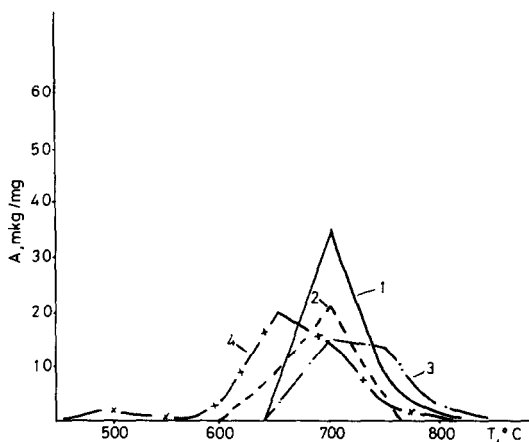

Fig. 8. Yield of benzene in the pyrolysis of the PI–PVP mixture and the initial polymers: 1. PI; 2. PI + 0.5 mole of PVP; 3. PI + 1.0 mole of PVP; 4. PI + 2.0 mole of PVP.

PVP affects only the *o*-amic acid group proper without changing the aromatic backbone of the macromolecule of polyamic acid. Figure 9 shows data on the yield of carbon oxides which are the main products of polyimide degradation. These results indicate that the amount of CO_2 present in the PI–PVP mixture greatly exceeds that in the initial polyimide. Since the formation of CO_2 is usually considered to be related to the destruction of "defective" structures, this fact confirms again our suggestion that the imperfection of structure increases as a result of interaction with PVP.

When PVP is introduced in the molar ratio of 2.0 : 1.0, water is eliminated in large amounts. This is probably caused by the thermal degradation of PVP present in the system. The presence of water at these very high temperatures leads to the development of thermohydrolytic processes and, as a result, the evolution of large amounts of CO_2 is observed. This is evidently the explanation for the lower thermal stability of the polymer structure in this mixture than in polyimide alone. Hence, the main differences between the behaviour of the samples upon thermal treatment are as follows

| 0.5 and 1.0 mole of PVP per mole of PAA	2.0 mole of PVP per mole of PAA
(1) In the cyclodehydration of PAA interchain bonds are formed with the participation of PVP and amic acid groups of PAA, and the number of imide rings decreases	In the cyclodehydration of PAA interchain bonds are not formed, and the number of imide rings does not change
(2) No PVP remains in the sample after cyclodehydration (380°C)	0.4 mole of PVP per mole of PI remains after cyclodehydration

These differences clearly indicate that the mechanism of polymer interaction is affected by the composition of the mixtures.

This fact may be interpreted as follows.

The formation of IPC is usually possible if the macromolecules participating in it are complementary. Chemical and structural complementarities are distinguished [12]. In most cases IPC are formed as a result of the chemical complementarity of interacting marcromolecules. This type of IPC between PAA and PVP has been described above and probably exists at the PVP/PAA ratios of 0.5 : 1.0 or 1.0 : 1.0.

In the formation of IPC one type of macromolecule behaves as the matrix and the other type behaves as side "daughter" chains. This assignment is evidently tentative and depends on many factors including the quantitative ratio of the components. We believe that at the above PVP/PAA ratios the macromolecule of PAA plays the part of the matrix, whereas the PVP chains are attached to the matrix by analogy with a "lightning fastener". However, beginning from a certain ("critical") value of the PVP : PAA ratio (according to our data, this value is approximately 2 : 1) the types of interaction between the IPC components change. Now the macromolecules of PVP play

the part of the matrix and those of PAA become side ("daughter") chains. Moreover, the principle of the IPC structure changes: apart from chemical complementary structural complementarity also appears and involves all the system rather than individual chains. In this case the IPC does not consist of linear pairs of macromolecules but is constructed according to the principle of "weaving"
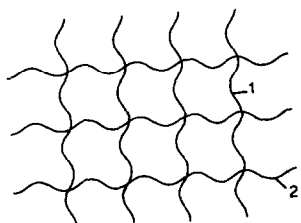
This structure leads to steric hindrances for interchain interactions with the formation of bridge bonds which, in the above cases, are formed according to Schemes 5 and 6. The intramolecular cyclodehydration of PAA is correspondingly facilitated, and linear polyimide chains are formed (as is experimentally observed). Furthermore, in this case there arises a possibility of the formation of the PI–PVP complex as a result of structural complementarity. This has been realized as shown experimentally. In fact, in the formation of supermolecular structure of PI, layer chain packing appears and the "parquet" structure is formed [13] (Fig. 10). In this structure the
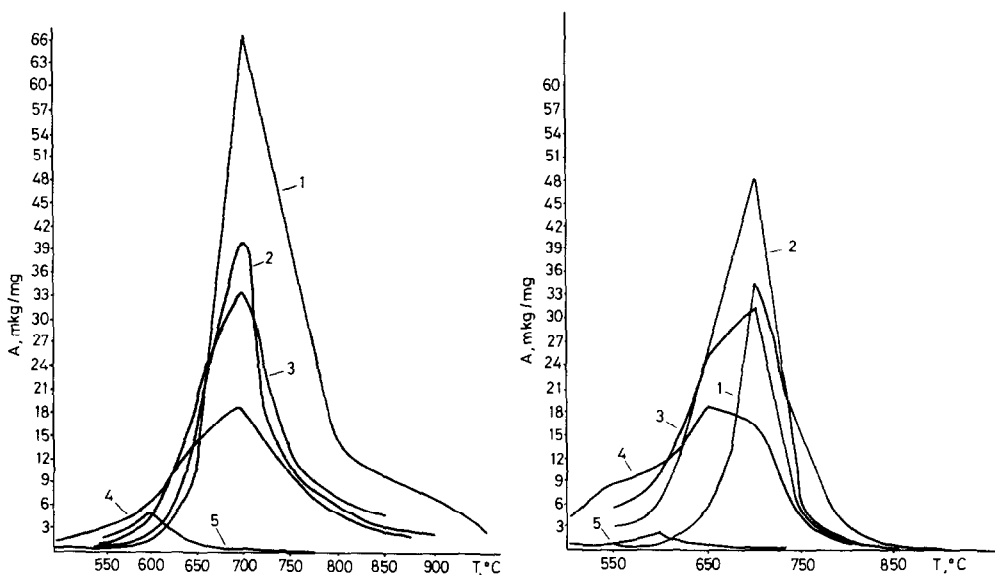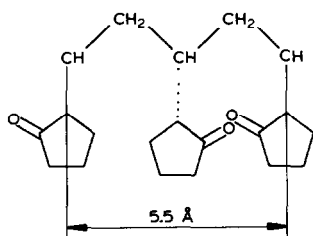

Fig. 9. Yield of carbon oxides, (a) CO and (b) CO_2, in the pyrolysis of the PI–PVP mixture and the initial polymers: 1. PI; 2. PI + 0.5 mole of PVP; 3. PI + 1.0 mole of PVP; 4. PI + 2.0 mole of PVP; 5. PVP.

interplanar distance is close to 5.5 Å. The pyrrolidone rings (if alternate rings are counted) are located at the same distance [14]

(9)

The transverse dimensions of the pyrrolidone and the imide rings are also close to each other, which suggests the following structure of IPC (Fig. 11).

The stabilization of the complex, as in the ordered PI structure, is due to the dipole–dipole interaction between the carbonyl groups of neighbouring chains [15]. However, the pyrrolidone ring contains only one carbonyl group and, hence, the interaction in IPC is slightly weaker than in pure PI. Nevertheless, this interaction ensures the existence of IPC up to very high temperatures (380°C). In the IPC pyrolysis, the PVP macromolecules are the first to undergo degradation (as was to be expected). After PVP is eliminated
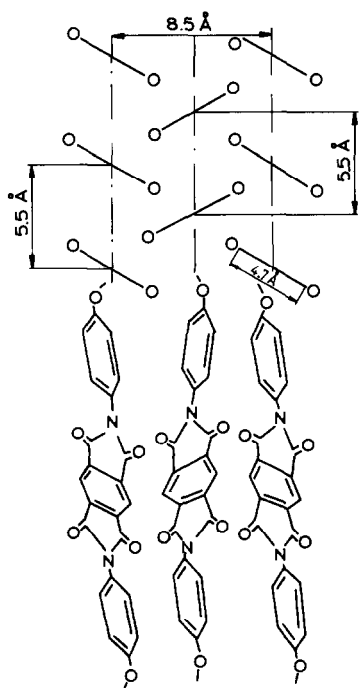

Fig. 10. Scheme of the supermolecular structure of polyimide with layer chain packing and the formation of the "parquet" structure.
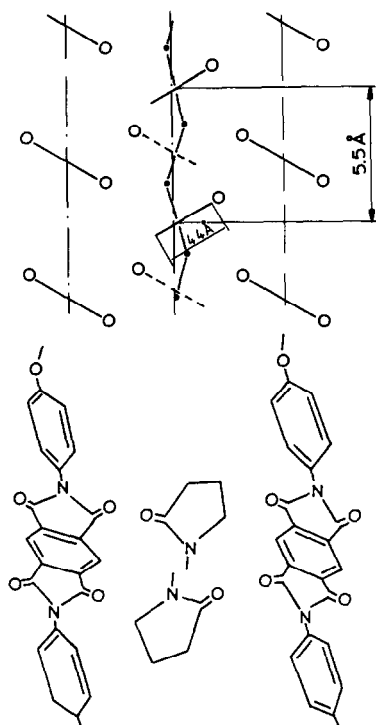
Fig. 11. Scheme of assumed structure of the PI–PVP interpolymer complex.

from the sample, the supermolecular structure of PI is characterized by a great number of defects, and as a result thermal stability decreases slightly. As to the fate of the "extra" pyrrolidone ring in the PVP molecule, it might be suggested that this ring is either located in IPC on the other side of the aliphatic chain as a result of bending distortions of this chain induced by the requirements of the minimum free energy of IPC or is eliminated during the formation of IPC at 200–300°C, which is usual for PVP [8].

Hence, the data of thermal analysis indicated that the mechanism for the formation of IPC between the polyamic acid and poly-*N*-vinylpyrrolidone depends on the ratio of the components of the complex. Naturally, in order to specify these assumptions it is necessary to apply some traditional methods. However, the information based on thermal analysis is quite independent and would be difficult to obtain by other methods.

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