Thermal decomposition of tetrazole-containing polymers. Part 3. Thermolysis of poly-1-vinyltetrazole

A.I. Lesnikovich[a], S.V. Levchik[a], O.A. Ivashkevich[a], E.E. Bolvanovich[a], P.N. Gaponik[a], B.L. Korsunskii[b], S.V. Kurmaz[b], T.S. Larikova[b], V.V. Nedelko[b] and V.P. Roshchupkin[b]

[a]*Research Institute of Physico-Chemical Problems, Byelorussian State University, 220080 Minsk (Belarus)*
[b]*Research Institute of Chemical Physics in Chernogolovka, 142432 Chernogolovka (Russian Federation)*

(Received 9 April 1992)

Abstract

The thermal decomposition of poly-1-vinyltetrazole (PVT) has been studied by thermogravimetry in isothermal conditions and by DSC and thermal volumetric analysis in non-isothermal conditions. The gaseous and condensed products of thermolysis were identified.

It has been shown that nitrogen is the single gaseous product of the thermal decomposition of PVT. Cyanamide and carbodiimide fragments fixed on the polymer carbochain which are able to cyclotrimerize into triazines and isotriazines respectively were identified in the condensed phase. The kinetic curves of the thermolysis in isothermal conditions have a sufficiently long induction period and fit an equation of autocatalysis of the first order. The limiting stage of PVT thermolysis is the opening of the tetrazole rings. The activation energy of this process calculated in isothermal conditions is 148 kJ mol^{-1}; in non-isothermal conditions it is 140 kJ mol^{-1}.

INTRODUCTION

Unlike poly-5-vinyltetrazoles (the thermal decomposition of which we have studied previously [1–5]), in poly-1-vinyltetrazoles (having the general formula shown in Structure 1) heterocycles are linked to the
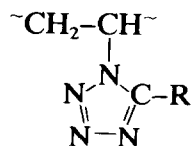
Structure 1.

Correspondence to: A.I. Lesnikovich, Research Institute of Physico-Chemical Problems, Byelorussian State University, 220080 Minsk, Belarus.

carbochain by the nitrogen atom. Therefore we believe that the mechanism of the thermolysis of poly-1-vinyltetrazoles can differ from that of poly-5-vinyltetrazoles and new polymer products with useful properties can be obtained. The thermal degradation of the simplest polymer of this type (poly-1-vinyltetrazole; R = H, see Structure 1) has been studied for the first time in this work.

EXPERIMENTAL

Poly-1-vinyltetrazole (PVT) was obtained by polymerization of the monomer, which was synthesized by the method described in ref. 6 and purified by distillation under vacuum (b.p. 363 K/1 mm Hg) in degassed water (0.5 mol l^{-1}) in the presence of $(NH_4)_2S_2O_8$ at 338 K. The precipitated polymer was separated by filtration, washed by water and dried under air and then under vacuum at 60°C. White highly dispersed powders of PVT samples, having characteristic viscosities $[\eta] = 0.94$, 1.60 and 2.31 dl g^{-1} (dimethylformamide, 393 K), were obtained at different concentrations of polymerization initiator.

The thermal decomposition of PVT was studied in isothermal and non-isothermal conditions under vacuum and in a krypton atmosphere, using a thermobalance (ATV-14) [7], by DSC in a self-generated atmosphere using a thermoanalyzer (Mettler TA-3000) in a DSC-20 cell at a heating rate of 10 K min^{-1}, and by thermal volumetric analysis (TVA) on DAGV-70-2M [8] under argon at a heating rate of 0.63–40 K min^{-1}. The experimental details are given in the previous papers [1–4]. PVT samples flash on being heated linearily under vacuum, air or inert atmosphere within 463–493 K, i.e. the decomposition due to the local overheats turns into a self-propagation regime [9]. To prevent this uncontrolled decomposition in isothermal conditions, the experiments were performed at temperatures (413–423 K) for which decomposition rate is low. To avoid flashing in non-isothermal conditions, PVT was diluted by a highly dispersed aluminium powder, having good thermal conductivity. The preliminary experiments showed that the aluminium powder did not influence the rate of PVT decomposition. In the DSC cell PVT was studied in the form of a film obtained from dimethylformamide solution in situ in a crucible and thoroughly dried under vacuum.

The solid residue and the gaseous products of decomposition were studied using IR (Specord-75-IR, pellets with KBr) and mass spectrometry (Varian-MAT-311). Kinetic parameters and a kinetic model of PVT decomposition were obtained from isothermal data using regression analysis. The dependence of the activation energy on the degree of decomposition was calculated by the isoconversion method [10].

RESULTS AND DISCUSSION

PVT decomposes in the DSC cell exothermically and smoothly in one stage at a heating rate of $10 \, K \, min^{-1}$ in the temperature interval 413–503 K (Fig. 1). The thermal effect of the decomposition is $1840 \pm 40 \, J \, g^{-1}$.

The kinetic studies in isothermal conditions were carried out within a sufficiently narrow temperature interval (413–423 K). Figure 2 shows the kinetic curves of the thermal decomposition of PVT ($[\eta] = 1.60 \, dl \, g^{-1}$) in a krypton atmosphere. Under these conditions PVT rapidly loses 1.5–2% of its weight in the initial period. Mass spectrometry of the gaseous products from the initial stage indicates that water is the major component. The presence of absorbed moisture in the initial PVT was confirmed by IR: keeping the polymer at 373–383 K leads to a decrease in the intensity of bands at 1640 and $3400 \, cm^{-1}$ without changing the characteristics of other bands, whereas the intensity of these bands increases on keeping the sample at room temperature under a damp atmosphere.

The kinetic curves of the PVT decomposition in isothermal conditions have an evident S-shape (Fig. 2). The maximum rate of weight loss corresponds to $\alpha = 0.5$. Self-heating of the samples due to exothermic reactions, or dispersion (crushing) of the matter due to thermal tensions are, apart of chemical auto-catalysis and the topochemical character of the process, the reasons for the self-acceleration of the thermal decomposition of solid materials. To ensure against artifacts, special isothermal and
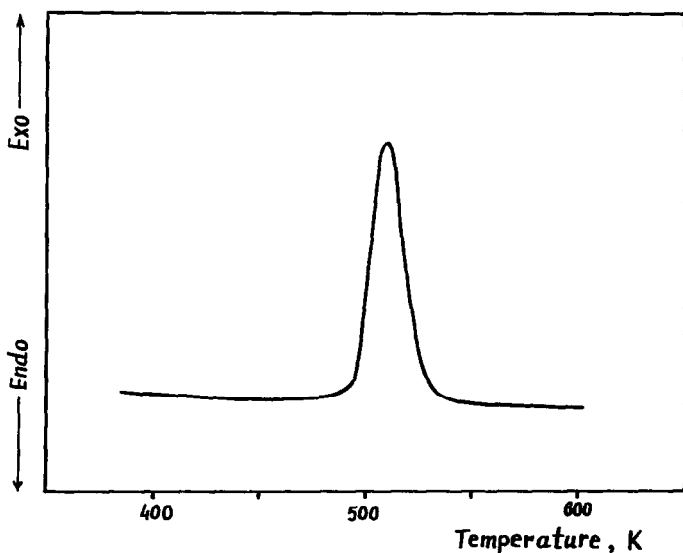

Fig. 1. DSC curve of PVT thermal decomposition in a self-generated atmosphere. Sample size was 0.7 mg, heating rate was $10 \, K \, min^{-1}$.
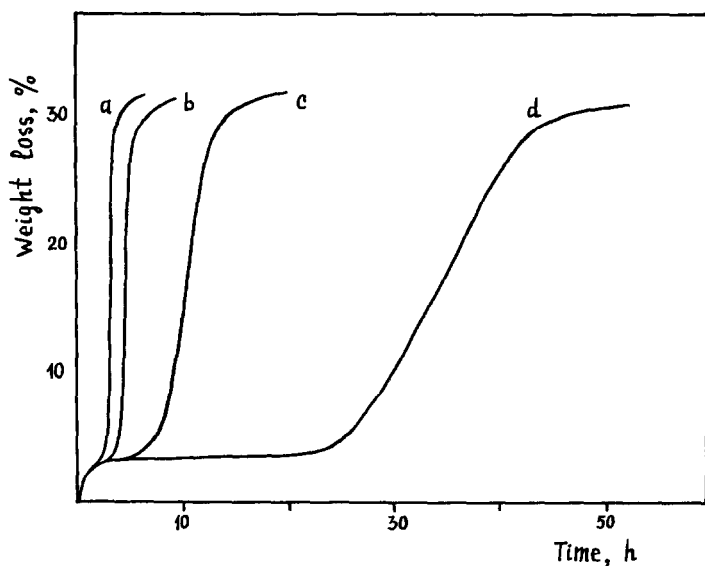
Fig. 2. Kinetic curves of PVT thermal decomposition in an inert atmosphere: (curve a) 463 K; (curve b) 460 K; (curve c) 453 K; (curve d) 443 K.

non-isothermal experiments using PVT samples with different particle sizes (particles diameter ≈ 2, ≈ 0.3 and ≈ 0.07 mm) were performed, in addition to using samples diluted with aluminium powder. Complete independence of the behaviour of the kinetic curves from the above factors was found.

The kinetic curves were processed by the equation for autocatalytic reactions of the first order [11]

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) + k_2\alpha(1 - \alpha) \tag{1}$$

Transformation of the eqn. (1) to

$$\frac{d\alpha}{dt} \Big/ (1 - \alpha) = k_1 + k_2\alpha \tag{2}$$

results in a simple dependence of the decomposition rate on the conversion degree and enables the determination of the constants k_1 and k_2. The constant k_1 characterizing a proper noncatalytic polymer decomposition is close to zero and constant k_2 satisfies the Arrhenius equation in the form

$$k_2 \, (\mathrm{s}^{-1}) = 10^{13.7 \pm 1.0} \exp(148 \pm 9.0/RT) \tag{3}$$

(R is measured in kJ mol^{-1} K^{-1}).

A linear dependence of the logarithm of the induction period (τ_{ind}) of PVT thermal decomposition on the reciprocal of the temperature is
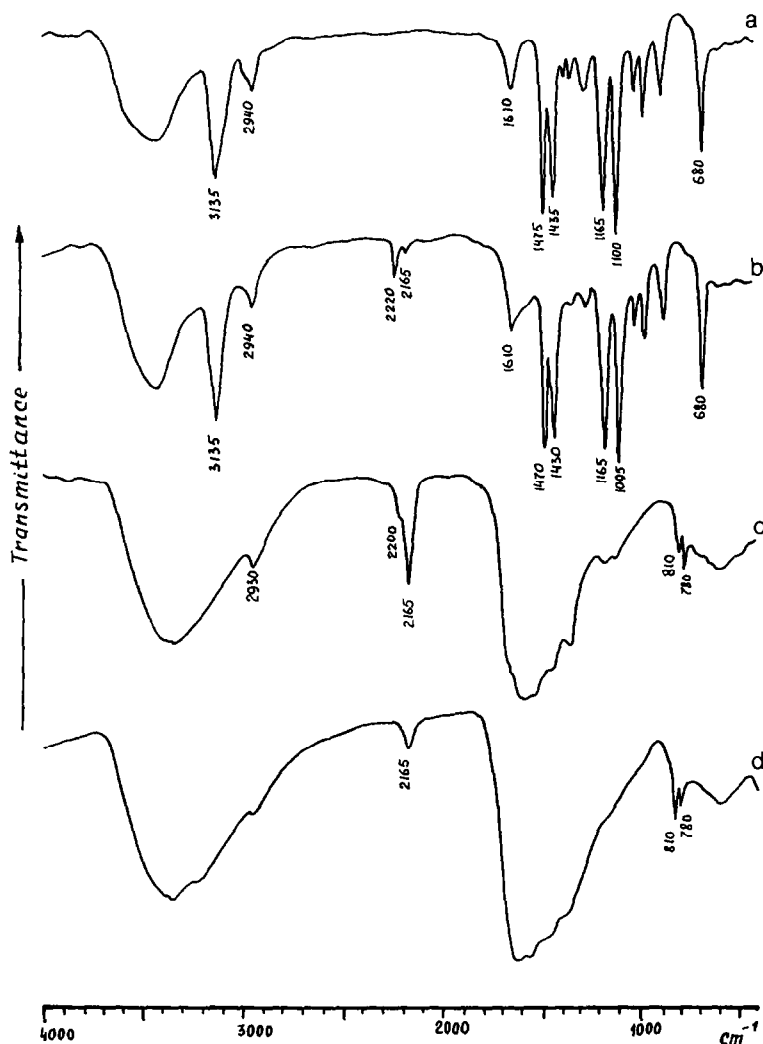
Fig. 3. IR spectra of PVT and the products of its decomposition, KBr pellets: (curve a) initial polymer; (curve b) polymer decomposed to $\alpha = 0.1$; (curve c) polymer decomposed to $\alpha = 0.75$; (curve d) product of complete decomposition of PVT.

observed (Fig. 4). The dependence fits the correlation equation

$$\lg(\tau_{\text{ind}}) = \frac{9259}{T} - 19.60 \tag{4}$$

(correlation coefficient $r = 0.992$).

The dependence of the activation energy on the degree of PVT decomposition in non-isothermal conditions calculated from TVA data is shown in Fig. 5. The effective activation energy practically does not change (decreases negligibly from 144 to 136 kJ mol^{-1}) throughout the
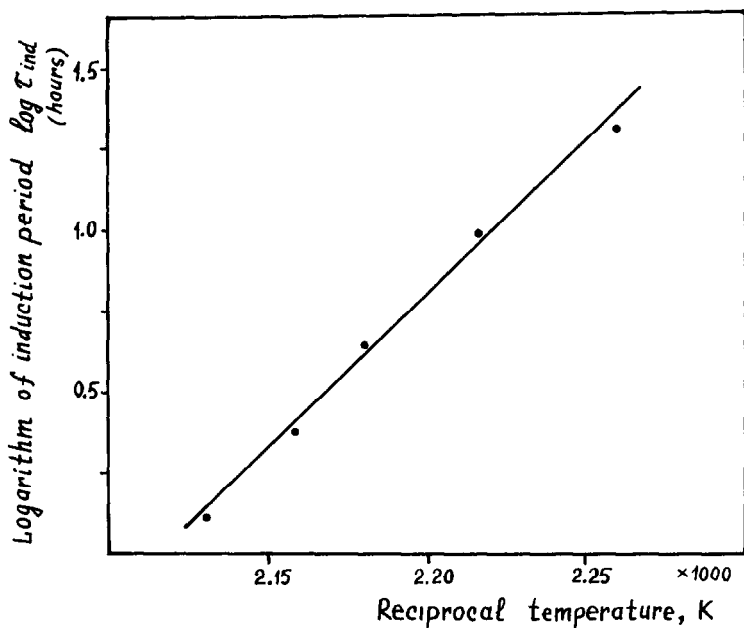
Fig. 4. Temperature dependence of the induction period of PVT thermal decomposition in isothermal conditions.
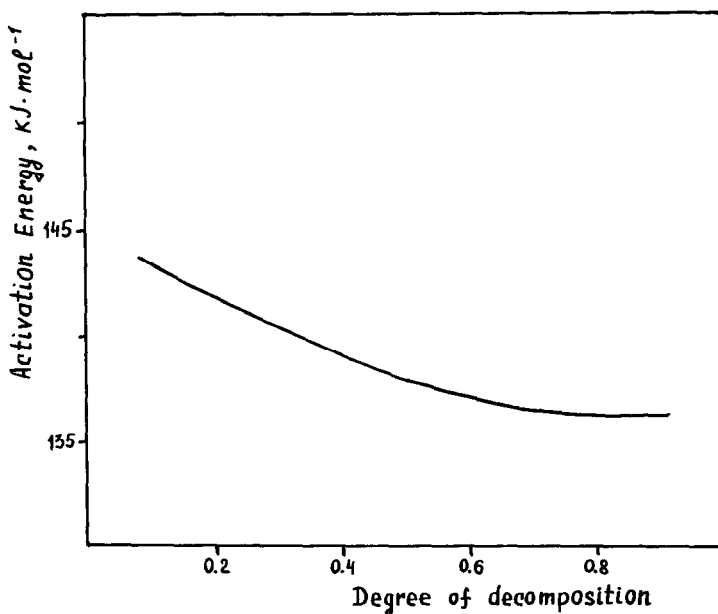

Fig. 5. Dependence of the activation energy on the degree of PVT decomposition, calculated from non-isothermal data by the Ozawa method.

experimental interval, which is in favour of PVT thermolysis being a simple single-stage process. In spite of some experimental differences in the methods of performing thermolysis, the activation energies calculated in non-isothermal ($E_{av} = 140 \pm 4 \, kJ \, mol^{-1}$) and isothermal ($E = 148 \pm 9 \, kJ \, mol^{-1}$) conditions correspond well.

Mass spectrometry of the gaseous products shows that the nitrogen is the single volatile product of both smooth decomposition and of flashes. Its quantity in all cases exactly corresponds to the elimination of one molecule of N_2 by each tetrazole ring.
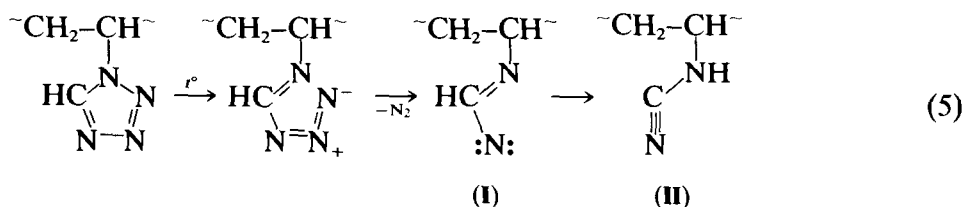
Information on the dynamics of conversions in the condensed phase is obtained from IR spectra taken at different degrees of conversion. The slow heating of PVT at $0.63 \, K \, min^{-1}$ up to a degree of decomposition of $\alpha \approx 0.1$ leads to diminution of the integral intensities of absorptions at $3135 \, cm^{-1}$ (v(C–H) of cycle) [12] and $2940 \, cm^{-1}$ (v_{as}(C–H) of the carbochain methylene groups, which remains invariable) (Fig. 3, curves a, b). Because the above absorptions are characteristic, their relative intensities can be taken as a measure of the degree of the heterocyclic opening on thermolysis. Simultaneously, some new absorption bands appear in the IR spectra. The most intense one, with a maximum at $2220 \, cm^{-1}$, can be attributed to v(C≡N). The pair of new bands at 2165 and $1345 \, cm^{-1}$ correspond to antisymmetric and symmetric absorptions of the carbodiimide fragments –N=C=N–.

Further heating of PVT up to a degree of decomposition of $\alpha = 0.75$ leads to the complete disappearance of the band at $3120 \, cm^{-1}$ (Fig. 3, curve c). Furthermore, the characteristic bands of deformation vibrations at 810 and $780 \, cm^{-1}$ of the triazine and isotriazine rings [13] appear in the spectra at a sufficiently high degree of PVT conversion.
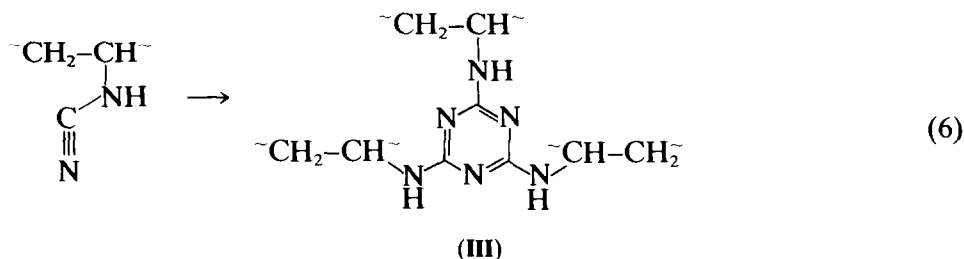
At the initial stage of thermolysis (Fig. 3, curve b) the band at $2220 \, cm^{-1}$ is rather intense, but on increasing the degree of decomposition (Fig. 3, curve c) the intensity of this band diminishes. Simultaneously, the intensity of the band at $2165 \, cm^{-1}$ increases considerably. In final stages of PVT thermal decomposition (Fig. 3, curve d) the band of the cyanamide groups completely disappears, whereas the band of carbodiimide fragments remains, but with some decrease in intensity. The intensity of the band of deformation vibrations of isotriazine rings at $780 \, cm^{-1}$ also decreases, whereas the intensity of that for triazine at $810 \, cm^{-1}$ increases.

All the obtained data suggests that the cracking of the tetrazole ring with elimination of a nitrogen molecule occurs at the initial stage of PVT thermal decomposition. As for poly-5-vinyltetrazoles [2–4], the isomerization of the corresponding heterocycle in azidoazomethyne, which splits off a nitrogen molecule and forms nitrene, is likely to take place during PVT thermolysis. The nitrene is stabilized by isomerization into

cyanamide

$$
\begin{array}{ccccc}
\sim CH_2-CH\sim & \sim CH_2-CH\sim & \sim CH_2-CH\sim & \sim CH_2-CH\sim \\
\underset{N-N}{\overset{N}{HC\diagdown N}} \xrightarrow{\ r^\circ\ } \underset{N=N_+}{\overset{N}{HC\diagup N^-}} \xrightarrow[-N_2]{} \underset{:N:}{\overset{N}{HC\diagup}} \longrightarrow \underset{N}{\overset{NH}{C\diagup}} & & & & (5) \\
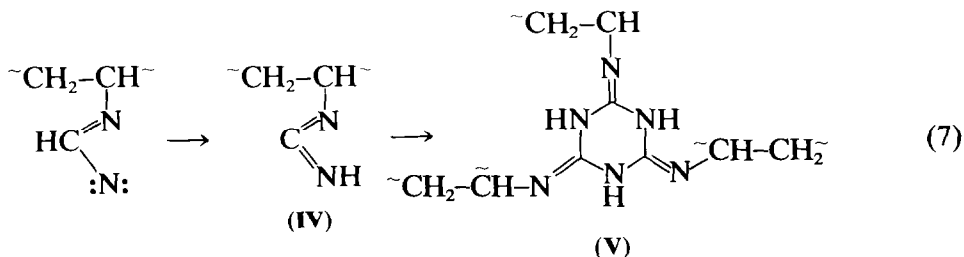& & \mathbf{(I)} & \mathbf{(II)}
\end{array}
$$

Therefore, the IR spectra of the residue from the initial stage of thermolysis (Fig. 3, curve b) mainly contains, together with the absorptions of the initial PVT, a band at 2220 cm^{-1} which is characteristic of the cyanamide group. Further conversions of the solid residue leading to the final products might be a polymerization, with formation of a triazine ring [14]

$$
\begin{array}{cc}
\sim CH_2-CH\sim & \\
\underset{N}{\overset{NH}{C\diagup}} \longrightarrow & \text{(triazine ring structure } \mathbf{(III)}) \qquad (6)
\end{array}
$$

having the characteristic absorption at 810 cm^{-1} (Fig. 3, curve c).

The accumulation of polymer product with non-substituted carbodiimide fragments in side chains is hardly probable in the initial stage of thermolysis because of their instability [15]. However, one cannot exclude their formation as intermediates, and hence further trimerization to an isotriazine ring [16]

$$
\begin{array}{cccc}
\sim CH_2-CH\sim & \sim CH_2-CH\sim & & \\
\underset{:N:}{\overset{N}{HC\diagup}} \longrightarrow & \underset{\mathbf{(IV)}}{\underset{NH}{\overset{N}{C\diagup}}} \longrightarrow & \text{(isotriazine ring structure } \mathbf{(V)}) & (7)
\end{array}
$$

The isotriazine structures are identified by an absorption at 780 cm^{-1} in the IR spectrum of the condensed products (Fig. 3, curve c).

Besides the mechanisms of nitrene (**I**) stabilization discussed above (eqns. (5) and (7)), reactions of proton removal or proton implantation in C–H bonds [17] are also characteristic of the nitrene. The probable site of

attack by **I** is the tertiary carbon atom in a carbochain of products **III** and **V**, which has a labile hydrogen atom

$$\text{(chemical structures)} \longrightarrow$$

$$\text{(VI)} \quad + \quad \text{(VII)} \tag{8}$$
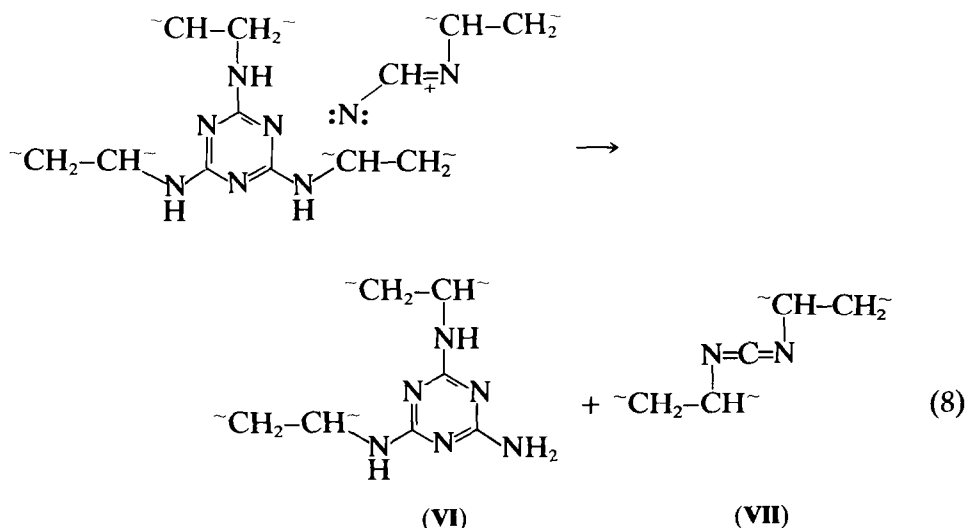
Because the generation of triazine and isotriazine structures (**III** and **V** respectively) is observed in the condensed phase, the poor lability of the polymer chains may cause tension in the –NH– bridge links connecting heterocycles and carbochains, and their breaking when attacked by nitrene. Then the proton transfer and the formation of carbodiimide cross-links between polymer chains (IR absorption at 2165 cm^{-1}) that are stable up to high temperatures take place. The isomerization of isotriazine heterocycles into more stable triazine ones [14], obvious from the relative absorption intensities at 810 and 780 cm^{-1} (Fig. 3, curves c and b), is observed on increasing the temperature.

Unlike tetrazole [18] and poly-5-vinyltetrazole [4], nitrogen is only detected in the gaseous products of PVT thermolysis, which is evidence of a uniform mechanism for the opening of the tetrazole ring, throughout the conversion of PVT. The activation energy does not depend on the degree of decomposition (Fig. 5) and is close to values calculated for tetrazole (150 kJ mol^{-1}) [19] and poly-5-vinyltetrazole (140 kJ mol^{-1}) [4] at the stage when tetrazole cycle splitting and nitrogen elimination become limiting (eqn. (1)).

We relate the autocatalytic character of PVT thermal decomposition to the topochemical development of the reaction zones in the solid polymer particles. We recently showed [20] that molecules of 1-vinyltetrazole associate by hydrogen bonds between the most strongly electron-donating nitrogen atoms in position 4 of the ring and hydrogen atoms connected to carbon atoms of the ring. We assume that the PVT macromolecules are also strongly associated, which is confirmed by the limited solubility of the polymer (PVT is soluble only in dimethylformamide among the well-

~CH₂–CH—CH₂–CH~   ~CH₂–CH~

[Structure 2 diagram]
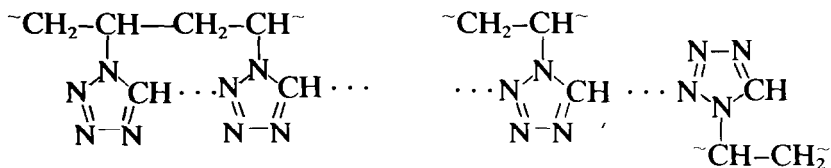
Structure 2.

known solvents). Therefore, irrespective of whether intra- or inter-molecular interaction takes place, as shown in Structure 2, the breaking of hydrogen bonds must precede the tetrazole ring splitting and elimination of the nitrogen molecule. Thus, it is evident that the system of hydrogen bonds in PVT exerts a stabilizing effect upon the thermal properties of the heterocycle.

The heating of polymers [21], as a rule, leads to the weakening and subsequent complete destruction of the hydrogen bond system. At the comparatively low temperatures at which PVT thermal decomposition has been studied (Fig. 2), the weakening and breaking of hydrogen bonds may not occur simultaneously throughout the entire volume of the amorphous polymer particle, but may occur first in the places where tensions due to the reciprocal allocations of the polymer chains arise. Such places are the potential nucleus for the subsequent development of the reaction and their number increases during the induction period. If their concentration or size exceed critical values, the mechanism of tetrazole ring opening and nitrogen elimination comes into operation. As a result the tensions increase, particularly due to reactions (6) and (7), and the thermolysis self-accelerates. The overlap of reaction zones, and reaction (8), contributing to a weakening of the tensions in the polymer matrix, are responsible for the slowing down of the thermolysis during the final stages of conversion. Thus, it is obvious that PVT thermolysis, besides the purely chemical factors responsible for the thermal stability of the tetrazole ring, is dependent on topochemical factors responsible for the initiation and development of reactions in solids.

REFERENCES

1 V.V. Nedelko, V.P. Roshchupkin, T.S. Larikova, L.N. Shumakova, N.A. Afanas'ev, B.L. Korsunsky, A.N. Pavlov, E.V. Fronchek and G.V. Korolyov, Vysokomol. Soedin. Ser. B, 28 (1986) 681, (in Russian).

2 V.V. Nedelko, V.P. Roshchupkin, T.S. Larikova, G.G. Asatryan, G.V. Asatryan, N.A. Afanas'ev, E.V. Fronchek and G.V. Korolyov, Vysokomol. Soedin. Ser. A, 29 (1987) 2088, (in Russian).

3 V.V. Nedelko, V.P. Roshchupkin, T.S. Larikova, S.V. Kurmaz, N.A. Afanas'ev, E.V. Fronchek and G.V. Korolyov, Vysokomol. Soedin. Ser. A, 31 (1989) 1726, (in Russian).

4 S.V. Levchik, E.E. Bolvanovich, A.I. Lesnikovich, O.A. Ivashkevich and P.N. Gaponik, Thermochim. Acta, 168 (1990) 211.

5 V.V. Nedelko, V.P. Roshchupkin, S.V. Kurmaz, T.S. Larikova, A.I. Lesnikovich, O.A. Ivashkevich, S.V. Levchik, E.E. Bolvanovich and P.N. Gaponik, Thermochim. Acta, 179 (1991) 209.

6 P.N. Gaponik, O.A. Ivashkevich and M.M. Degtyarik, USSR Pat. 1028669, 1983.

7 L.N. Gal'perin and Yu.R. Kolesov, Izmer. Tekhn., 4 (1971) 23, (in Russian).

8 A.I. Lesnikovich, O.A. Ivashkevich, V.A. Lyutsko, G.V. Printsev, K.K. Kovalenko, P.N. Gaponik and S.V. Levchik, Thermochim. Acta, 145 (1989) 195.

9 A.I. Lesnikovich, S.V. Levchik, K.K. Kovalenko and V.G. Guslev, Thermochim. Acta, 81 (1984) 245.

10 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.

11 R. Schmid and V.N. Sapunov, Non-Formal Kinetics in Search for Chemical Reactions Pathways, Verlag Chemie, Weinheim, 1982.

12 M.M. Degtyarik, P.N. Gaponik, V.N. Naumenko, A.I. Lesnikovich and M.V. Nikanovich. Spectrochim. Acta, Part A, 43 (1987) 349.

13 D.W. Kaizer, G.A. Peters and V.P. Wystrach, J. Org. Chem., 18 (1953) 1610.

14 V.A. Pankratov and A.E. Chesnokov, Usp. Khim., 58 (1989) 1528, (in Russian).

15 F. Kurrer and K. Douraghi-Zadeh, Chem. Rev., 67 (1967) 107.

16 N. Grassie and G.A. Perdomo Mendora, Polym. Deg. Stab., 10 (1985) 267.

17 T.F. Goryainova, Yu.A. Ershov and R.M. Livshits. Khim. Vys. Energ., 9 (1975) 99, (in Russian).

18 A.I. Lesnikovich, O.A. Ivashkevich, G.V. Printsev, P.N. Gaponik and S.V. Levchik, Thermochim. Acta, 171 (1990) 207.

19 S.V. Vyazovkin, A.I. Lesnikovich and V.A. Lyutsko, Thermochim. Acta, 165 (1990) 17.

20 P.N. Gaponik, O.A. Ivashkevich, V.I. Biba, V.N. Naumenko and T.N. Andreeva, Vesti Akad. Nauk Belarusi, Ser. Khim. Nauk, (1990) 55, (in Russian).

21 I.S. Kochneva and V.P. Roshchupkin, Vysokomol. Soedin. Ser. A, 33 (1991) 2235 (in Russian).