THERMAL DECOMPOSITION OF TETRAZOLE-CONTAINING POLYMERS
Part II. Thermolysis of poly-2-*tert*-butyl-5-vinyltetrazole

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ABSTRACT

The thermal decomposition of poly-2-*tert*-butyl-5-vinyltetrazole was investigated by the gas volumetry method in an inert atmosphere and thermogravimetrically in vacuum at different heating rates. The thermolysis proceeds in two stages within the ranges 470–590 K and 610–750 K respectively. The kinetics of the first-stage decomposition under isothermal conditions between 450 and 489 K were thoroughly studied. The kinetic order of the process is close to unity, with $E_a = 165 \pm 15$ kJ mol^{-1} and $\log A = 14.4 \pm 1.1$ s^{-1}. The activation energy value calculated on the basis of non-isothermal experiments amounts to 150–165 kJ mol^{-1} for the first stage and ≈ 215 kJ mol^{-1} for the second. The compositional analysis of the volatile products and the condensed residue carried out using the methods of mass spectrometry, chromatography and IR and UV spectroscopy made it possible to propose two parallel pathways of polymer thermolysis. The first is consistent with the mechanism which was earlier substantiated for the thermolysis of poly-5-vinyl-2-alkyltetrazoles, and consists in the splitting out of a nitrogen molecule from the tetrazole ring with the formation of C,N-nitrilimine, as well as its further thermal conversion. Such a thermolysis route is implemented mainly at low heating rates. At high heating rates another decomposition mechanism is possible along with the first; it is related to removal of a *tert*-butyl substituent from the tetrazole ring with the formation of 2-methylprop-1-ene and 2-methylpropane.

INTRODUCTION

In our previous publications [1–4] we reported on the results of investigations of thermal decomposition of a number of polymers and copolymers of 5-vinyltetrazole and its 1- and 2-alkyl derivatives. We pointed out the strong dependence of thermal stability, kinetic and activation thermolysis parame-

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ters on the availability and position of the alkyl substituent in the tetrazole ring. A specific feature of thermal decomposition of 5-vinyltetrazole polymers is a noticeable growth of thermal stability when the alkyl substituent is introduced at the 2-position of the heterocycle. *A priori* one could assume that generation of tertiary nitrogen atoms in the tetrazole ring structure as a result of alkylation must lead to formation of a less thermally stable heterocyclic system and, in consequence, to reduction of the general stability of the polymers. However, these forecasts were not proved experimentally. Moreover, the rates of the reactions are noticeably reduced during transition from poly-5-vinyltetrazole (PVT) to poly-5-vinyl-2-alkyltetrazoles. In the process an increase of the effective activation energies of thermal decomposition from 30 up to 40 kJ mol^{-1} takes place. Such "abnormal" behaviour of poly-5-vinyl-2-alkyltetrazoles is explained by invoking the opportunity to transmit a part of the energy of the thermally excited tetrazole ring to neighbouring groups of atoms and the polymer carbon chain followed by its dissipation. Transmission of the surplus thermal energy takes place at the expense of low frequency torsional oscillation of the alkyl substituent [3]. This phenomenon is called the "substituent heat protection effect".

The specificity of chemical transformations of polyvinyltetrazoles due to thermal effects and the far from simple influence of substituents on the thermal stability of tetrazole rings provided the stimulus for further investigations of this class of polymer. In the present paper a comprehensive investigation of the thermal decomposition of poly-2-*tert*-butyl-5-vinyltetrazole (PTBVT) was undertaken.

EXPERIMENTAL

2-*tert*-Butyl-5-vinyltetrazole was synthesized by deamination of 2-*tert*-butyl-5-(β-dimethylaminoethyl)tetrazole, which was obtained by the alkylation of 5-(β-dimethylaminoethyl)tetrazole with *tert*-butyl alcohol in concentrated sulphuric acid medium [5]. The monomer was purified by chromatography of a chloroform solution through a column filled sequentially with activated charcoal, silica gel L 40–100 mesh and aluminium oxide. Then the solvent was removed and 2-*tert*-butyl-5-vinyltetrazole was distilled in vacuum; b.p. = 318–319 K (3 mm Hg), n_D^{20} = 1.4702. PTBVT was obtained by radical polymerization of the monomer K$_2$S$_2$O$_8$/K$_2$S$_2$O$_5$ (2 mol l^{-1}) in degassed water in the presence of the initiating system (0.5 mol%; ratio of oxidant to reducing agent = 3 : 2) at 313 K in an argon atmosphere. The reaction mixture was poured into a saturated solution of NH$_4$Cl, and the separated polymer was filtered off, washed with water until there was no reaction for chloride ion and then dried in vacuum at 323 K until it showed no further mass change. PTBVT is a white high-dispersion powder with characteristic viscosity [η] = 0.84 dl g^{-1} (dimethylformamide, 393 K).

The thermal decomposition of PTBVT was investigated under isothermal and non-isothermal conditions by thermogravimetry in vacuum using an automatic electronic thermobalance ATB-14 [6], by differential scanning calorimetry in a self-generated atmosphere using a Mettler TA-3000 instrument and a DSC-20 cell, and also by means of an automatic gas volumeter in a helium atmosphere at heating rates of 0.63, 1.25, 2.5, 5, 10, 20 and 40 K min^{-1}. The full experimental details are described in Refs. 1 and 4. Analysis of the volatile thermolysis products was carried out by mass spectrometry (MI-1201 V instrument; energy of ionizing electrons 50 eV; accelerating voltage 5000 V) and chromatography (Chrom-5 instrument; capillary column of diameter 0.2 mm and length 50 m, dimethylsulpholane as liquid phase, flame-ionization detector, nitrogen as carrier gas).

Structural changes in the condensed residue were monitored by means of IR and UV spectroscopy using Specord-75 IR and Specord UV-VIS instruments. The calculation of the kinetic parameters of the processes investigated was done using programs based on regression analysis methods, as well as the Ozawa method [7] for the data from non-isometric experiments.

RESULTS AND DISCUSSION

Figure 1 shows kinetic curves of the PTBVT thermal decomposition obtained by means of the gas volumeter. It was found that, at high rates (10, 20 and 40 K min^{-1}) in the temperature range 533–539 K, a transition from the conventional thermal decomposition mode to that of self-propagation or flameless combustion takes place. It is interesting to note that, for all investigated poly-5-vinyl-2-alkyltetrazoles [1–3] except poly-5-vinyl-n-butyl-tetrazole (PVNBT), a similar transition is also observed, and takes place in the same temperature region within the experimental error. The dependence of the activation energy of PTBVT thermolysis on the degree of decomposi-
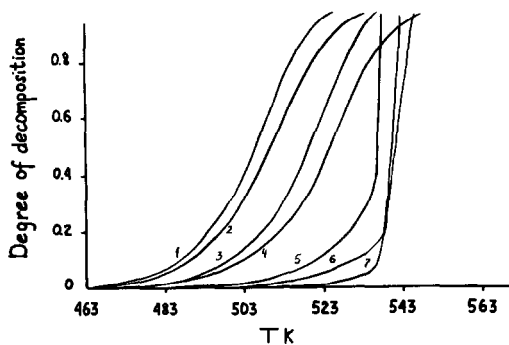

Fig. 1. Kinetic curves of PTBVT thermal decomposition under non-isothermal conditions at various heating rates: 1, 0.63 K min^{-1}; 2, 1.25 K min^{-1}; 3, 2.5 K min^{-1}; 4, 5 K min^{-1}; 5, 10 K min^{-1}; 6, 20 K min^{-1}; 7, 40 K min^{-1}.
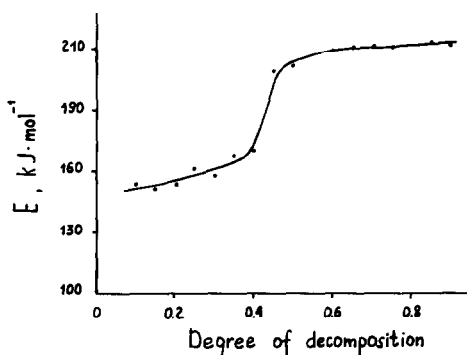
Fig. 2. Dependence of activation energy of PTBVT thermolysis on degree of decomposition.

tion calculated using the Ozawa method indicates that the polymer decomposes in two stages (Fig. 2). Up to a decomposition degree of $\alpha \approx 0.4$ the activation energy increases slightly from 150 up to 165 kJ mol^{-1}, and after this a sharp transition takes place to the region where thermolysis is characterized by an activation energy of ≈ 215 kJ mol^{-1}.

The PTBVT thermal decomposition under conditions of linear heating in vacuum also has a phasic character, which is proved by the shape of the TG curve of polymer thermolysis (Fig. 3). Comparison of the TG curves for PTBVT and its analogue with an n-butyl substituent in position 2 of the heterocycle shows the higher thermal stability of the latter. The heat of the first stage of PTBVT thermolysis measured using the DSC method between 469.7 and 586.4 K at 10 K min^{-1} heating rate amounts to 1570 ± 20 J g^{-1}. The maximal heat evolution rate corresponds to 535.6 K temperature.

The kinetics of the first stage of PTBVT thermolysis under isothermal conditions between 353 and 383 K were exhaustively measured. The kinetic order of the process is close to unity up to 80–90% conversion (the weight loss corresponding to completion of the first stage of thermolysis is taken as
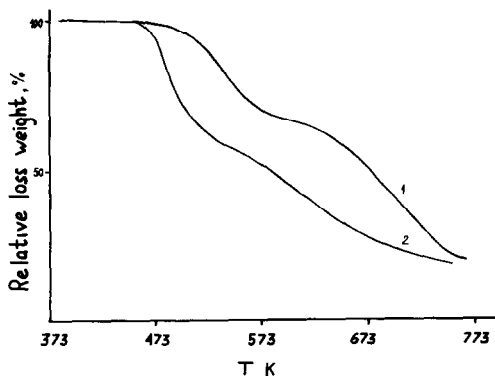

Fig. 3. Kinetic curves of thermal decomposition in vacuum: 1, PVNBT; 2, PTBVT. Heating rate of samples: 1.5 K min^{-1}; initial weight: 10.0 mg.

TABLE 1

Kinetic and activation parameters of PTBVT thermal decomposition in vacuum

T (K)	$k_{obs} \times 10^5$ s^{-1}	E_a (kJ mol^{-1})	$\log A$ (s^{-1})
453	1.41 ± 0.12		
463	3.26 ± 0.15		
473	8.97 ± 0.12		
483	19.00 ± 0.13	165 ± 15	14.40 ± 1.10
492	42.00 ± 0.19		

100%). Table 1 presents the values of the observed rate constants and Arrhenius parameters for the first stage of the PTBVT thermal decomposition.

Figure 4 shows IR spectra of the initial PTBVT and samples of this polymer subjected to thermolysis under conditions for different degrees of conversion. From comparison of the spectra one can see that, at 463 K, thermolysis for 7 h leads to reduction of the relative intensity of the absorption bands at 1040, 1320 and 1415 cm^{-1} related to the tetrazole ring vibration. In the IR spectrum of the sample subjected to thermal treatment at 483 K over 5 h these bands are effectively absent, which shows the complete opening of the tetrazole rings in the process of completion of the first stage of thermolysis (443–513 K).

Structural reorganization is an important feature of the PTBVT thermal conversion, and it leads to the inclusion of considerable quantities of *tert*-butyl groups in the structure of the modified polymer subjected to the thermolysis.

This is indicated by the presence of absorption bands at 1237 and 1375 cm^{-1} related to *tert*-butyl group deformation vibrations in the PTBVT IR spectrum with completely destroyed heterocycles (Fig. 4, curve 3). A small shift of the maxima of these bands to lower frequency points to the new
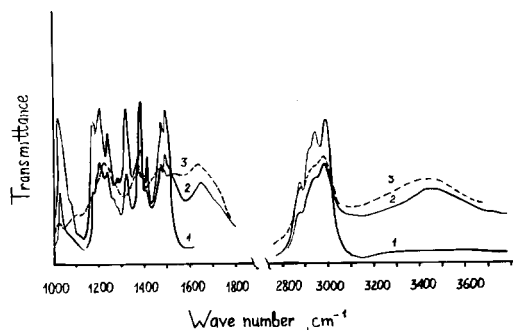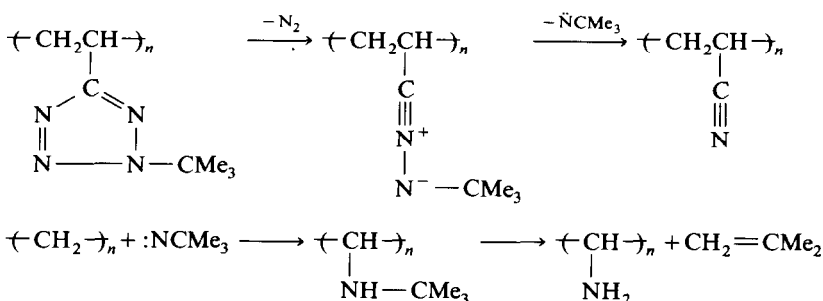

Fig. 4. IR absorption spectra of PTBVT and products of its thermal conversion: 1, initial polymer; 2, thermolysis product after heating at 463 K for 7 h; 3, product after heating at 483 K for 5 h.

$$+CH_2CH\rightarrow_n \xrightarrow{-N_2} +CH_2CH\rightarrow_n \xrightarrow{-\ddot{N}CMe_3} +CH_2CH\rightarrow_n$$

(with pendant groups: tetrazole ring $\overset{C}{\underset{N-N-CMe_3}{N\diagdown\diagup N}}$; then $\overset{C}{\underset{N^- -CMe_3}{\overset{|||}{N^+}}}$; then $\overset{C}{\underset{N}{|||}}$)

$$+CH_2\rightarrow_n + :NCMe_3 \longrightarrow +CH\rightarrow_n \underset{NH-CMe_3}{|} \longrightarrow +CH\rightarrow_n \underset{NH_2}{|} + CH_2{=}CMe_2$$

Scheme 1

localization of the *tert*-butyl group in the polymer. Analysis of IR spectra of the initial and thermolysed PTBVT samples, taking into account an insignificant change in intensity of the bands at 2980 and 2935 cm^{-1} related to stretching vibrations of C–H bonds in methyl and methylene groups [8], leads one to assume that approximately half the *tert*-butyl groups contained in the initial PTBVT are introduced to C–H links of the polymer carbon chain in the process of the initial stage of thermolysis. (The evaluation is based on the assumption that the first stage of thermolysis is accompanied only by opening of heterocycles and involves no scission of C–C bonds of the macrochain.) Such a migration of the *tert*-butyl groups can take place within the earlier proposed mechanism of thermal decomposition of poly-5-vinyl-2-alkyltetrazoles [1–3], as in Scheme 1.

The emergence of the absorption band at 3450 cm^{-1} in the IR spectrum of thermolysed PTBVT, which is characteristic of N–H bond vibration, may confirm the assumption of *tert*-butyl group transfer to the carbon chain in the form of a nitrene. In addition, the fact that the weight loss at the first stage of PTBVT decomposition (Fig. 3) corresponds exactly to elimination of one nitrogen molecule speaks for the validity of the above mechanism.

On the other hand, the chromatographic data and mass spectrometric analysis of the composition of the gaseous products of PTBVT decomposition at 493 K during 1 h indicate the possibility of direct separation of the *tert*-butyl substituent from the tetrazole ring. According to the chromatographic data, during PTBVT thermolysis 2-methylprop-1-ene and 2-methylpropane are formed (except for nitrogen) and their ratio amounts to $\approx 4:1$. This finding agrees with the mass spectrometric data (Fig. 5). The basic groups of peaks correspond to the fragmentation of 2-methylprop-1-ene ($m/e = 56$) and 2-methylpropane ($m/e = 58$) [9,10]. Under conditions of maximum instrumental resolution, separation of the peak at $m/e = 28$ into two components with $m/e = 28.013$ (nitrogen molecular ion) and $m/e = 28.054$ (C_2H_4 fragment) was achieved. The corresponding data are given in Fig. 6. Under similar conditions of PVNBT thermolysis nitrogen is the dominating decomposition product (Fig. 5a); its production is accompanied by the formation of only small quantities of *n*-butane and but-1-ene.
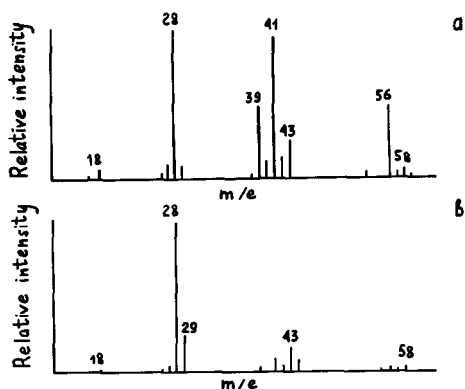
Fig. 5. Mass spectra of volatile products of thermal decomposition: (a) PTBVT, (b) PVNBT. Thermolysis temperature: 493 K; thermolysis time: 1 h.

The qualitative difference in composition of the thermolysis products of PTBVT on one hand and PVNBT (as well as other poly-5-vinyl-2-al-kyltetrazoles) on the other indicates the possibility in the case of PTBVT of the implementation of another thermal decomposition mechanism. This hypothesis is also based on noticeable differences in the activation parameters of the initial stage of thermolysis of PTBVT and other polyvinyltetrazoles [3]. The respective data are given in Table 2.

The presence of 2-methylpropane along with 2-methylprop-1-ene in the decomposition products proves that homolytic breakage of the N–C bond between the quaternary carbon atom of the substituent and the nitrogen atom takes place with the formation of tert-butyl radicals, the disproportionation of which leads to the formation of the above products. On the other hand, the fact that the yield of 2-methylprop-1-ene during the thermolysis is substantially higher than that of 2-methylpropane leads to the assumption that breakage of the N–C bond between the substituent and the heterocycle may be accompanied by migration of the methyl hydrogen atom to the nitrogen atom of the tetrazole ring, as in Scheme 2.
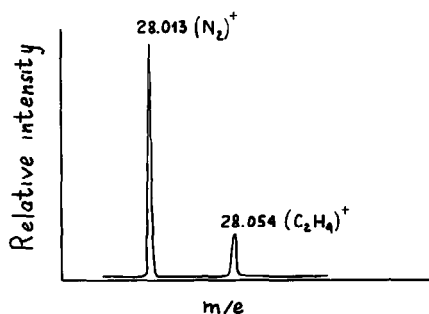

Fig. 6. Resolution of total peak with m/e 28 in mass spectrum of volatile products of PTBVT decomposition at 493 K and 1 h thermolysis time.

TABLE 2

Arrhenius parameters of thermal decomposition of poly-5-vinyltetrazole and its 2-alkyl derivatives

Polymer	E_a (kJ mol^{-1})	log A (s^{-1})
Poly-5-vinyltetrazole	164 ± 7	13.8 ± 0.8
Poly-5-vinyl-2-methyltetrazole	196 ± 6	16.8 ± 0.6
Poly-5-vinyl-2-n-propyltetrazole	203 ± 8	17.6 ± 1.2
Poly-5-vinyl-2-n-butyltetrazole	189 ± 7	16.0 ± 0.8
Poly-5-vinyl-2-tert-butyltetrazole	165 ± 12	14.1 ± 1.1
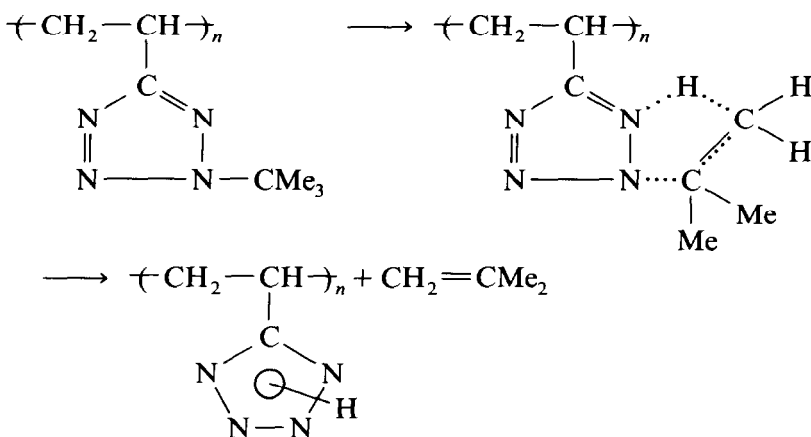
Scheme 2

The opportunity for formation of a transient configuration favourable to such a conversion is confirmed by the data from the quantum-chemical calculation of the geometric structure of the 2-tert-butyl-5-vinyltetrazole molecule (Fig. 7), which we carried out by the SCF MO–LCAO method in AM-1 approximation [11]. This calculation method can be used for evaluation of the spatial structure of tetrazole derivatives, as is proved by our comparisons of estimated and experimental geometric parameters for 2-methyl-5-vinyltetrazole obtained by gas electron-diffraction examination [12]. The minimum estimated N · · · H distances (Scheme 2) between hydrogen atoms of the tert-butyl group and nitrogen atoms of the ring in positions 1 and 3 amount to 2.734–2.737 Å, which corresponds closely to the sum of the van der Waals radii of nitrogen and hydrogen atoms (2.7 Å).

We have no experimental proof of the formation of unopened tetrazole rings deprived of the substituent, but emergence of a 1640 cm^{-1} band and a 3050–3350 cm^{-1} wide absorption region in the IR spectrum of partially thermolysed PTBVT can be related to vibrations of associative N–H bonds of the tetrazole ring free from the substituent.

It is interesting to note that, in the case of PVNBT, the mass spectrometric method records only trace quantities of but-1-ene in the thermal decom-
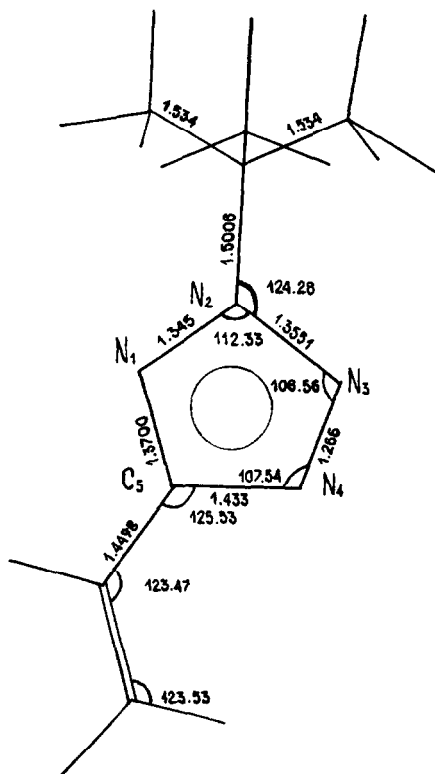
Fig. 7. Geometric structure of *tert*-butyl-5-vinyltetrazole according to quantum-chemical calculation data.

position product mixture under similar conditions (see Fig. 5). This indicates a minimum contribution of the reaction route with direct substituent separation in the initial stage. This fact has a natural statistical explanation: if, in PTBVT, all nine hydrogen atoms of the substituent are equally capable of forming a configuration favourable for the transition state, then in the case of PVNBT the number of such atoms is two. We assume that the formation in thermolysed PTBVT of fragments with heterocyclic structure deprived of substituents and not possessing high thermostability under the thermolysis conditions can lead to a sequence of chemical conversions which is similar to that proposed earlier for PVT [3]; see Scheme 3.

One should be aware of the fact that both pathways of PTBVT thermal decomposition include the stage of formation of nitrile groups. The existence of an intense absorption region from 1500 to 1600 cm^{-1} indicates the formation of sections of conjugated bonds $(C=N)_n$ as a result of ring formation by nitrile groups similar to that taking place in polyacrylonitrile thermolysis [13].

Additional data on the development of a conjugated bond system in the process of PTBVT thermal decomposition were obtained by examination of the electronic absorption spectra. Figure 8 shows absorption spectra in the
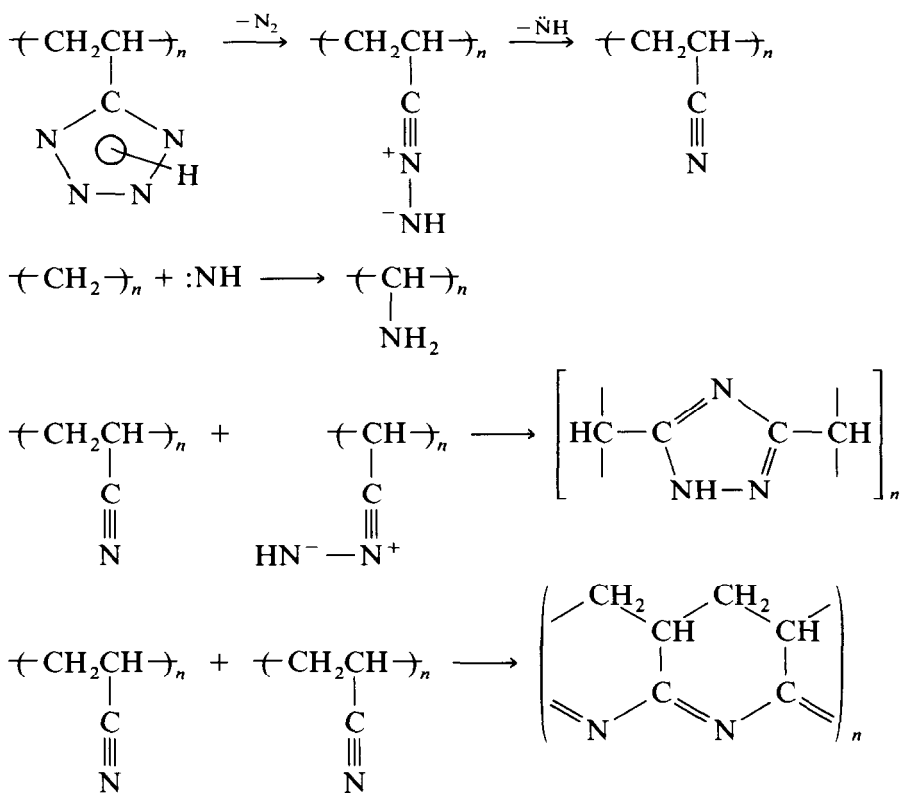
Scheme 3

UV and visible regions of the PTBVT film prior to and after heating at 483 K for different periods of thermostatic operation. A clear absorption band with its maximum near 47 800 cm^{-1}, corresponding to a π-electron transition of the tetrazole ring, is observed in the initial polymer spectrum. Even brief heating of the polymer sample, which causes an extent of conversion of heterocycles of several per cent accompanied by intensity reduction of this
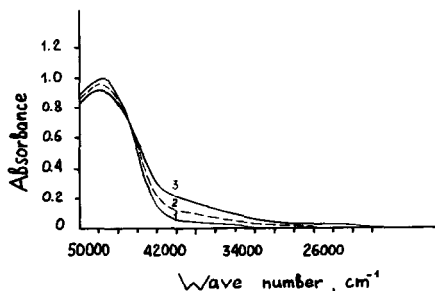

Fig. 8. Electronic spectra of PTBVT absorption: 1, initial polymer film; 2, thermolysis product after heating at 473 K for 0.5 h; 3, product after heating at 473 K for 1 h.

bands, leads to the emergence of a continuous absorption region extending from 45000 cm^{-1} to the visible region as far as 22000 cm^{-1}. The development of absorption over such a wide region can be rationally explained by the formation of sequences of conjugated π-bonds $(C=N)_n$ having a wide length distribution. If one takes into account the fact that the electron transition frequency is in inverse proportion to the conjugation chain length, then the emergence of absorption in the low-frequency region even at the earlier thermolysis stages can be considered as evidence of the fact that PTBVT decomposition has a "micro-mesh" character; that is, the decay of one heterocycle induces opening of the neighbouring ones and thus creates conditions for the formation of extended conjugation sections $(C=N)_n$. It is quite probable that such a "quasi-chain" mechanism of thermal decomposition is attributable to the polymeric nature of the investigated substance, and forms a basis of the susceptibility of PTBVT and, as is shown above, other polyvinyltetrazoles to decomposition transition processes in the mode of self-propagation or thermal explosion.

One possible reason for the lower thermal stability of PTBVT in comparison with PVNBT and other poly-5-vinyl-2-alkyltetrazoles, which also displays itself particularly in reduced effective energy of activation, is the existence of steric hindrance between the heterocycle and the *tert*-butyl substituent. The data from quantum-chemical calculation of the geometric structure show that the N–C bond length between the ring nitrogen atom and the carbon atom of the *tert*-butyl group is substantially larger (by 0.0422 Å) than the analogous parameter for 2-methyl-5-vinyltetrazole, in the molecule of which steric tension between the ring and the substituent is absent. We can note here that the AM-1 method exactly replicates the geometric structure of the *tert*-butyl group [14]. The effect of steric stresses can manifest itself in several ways: both through promotion of direct separation of the nitrogen molecule and of the *tert*-butyl substituent by the mechanisms discussed above. It is probable that the observed difference in the effective energies of activation of PTBVT and PVNBT thermolysis is attributable to
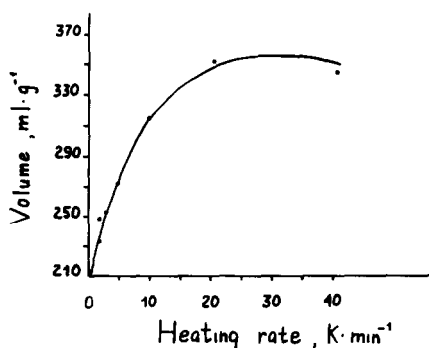

Fig. 9. Dependence of specific gas production during PTBVT thermolysis on heating rate.

the above factors. It is quite difficult to evaluate the individual contribution of each of the proposed mechanisms; however, taking into account the fact that, as the heating rate increases, the total gaseous volume grows considerably (Fig. 9), one can assume that the thermolysis mechanism taking place mainly at low heating rates involves nitrogen molecule separation from the ring.

When the heating rate rises another thermolysis route is possible alongside the first; this is related to separation of the *tert*-butyl substituent from the PTBVT tetrazole ring.

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