

THERMAL PROPERTIES OF METHYLMETHACRYLATE–*N*-VINYL CARBAZOLE COPOLYMERS

J. PIELICHOWSKI, R. CHRZĄSZCZ, E. TRĘBACZ and A. WOLFF

*Instytut Chemii i Technologii Organicznej, Politechnika Krakowska, 31-155 Kraków,
Warszawska 24 (Poland)*

ABSTRACT

Copolymers of methylmethacrylate (MM)–*N*-vinylcarbazole (NVC) were synthesized and their thermal properties were studied. The effect of NVC content on thermal behaviour of the copolymers was investigated. Based on TG and DTG analysis the kinetic parameters of the thermal degradation process were computed.

INTRODUCTION

Considering the widely known low thermal stability of polymers, many attempts have been made to synthesize materials with improved thermal properties. Such polymers can be obtained in different ways, among them: polymerization of monomers with proper chemical structure or by chemical modification of the known polymers. The copolymerization reaction also gives the possibility of the synthesis of thermally stable products if suitable co-monomers are used. The latter reaction was of interest here. We took into consideration two monomers: methylmethacrylate (MM) and *N*-vinylcarbazole (NVC). The effect of NVC content in copolymers on their thermal stability was examined. It was expected that such copolymers should have a higher thermal stability than poly-methyl-methacrylate, due to the outstanding thermal stability of poly-*N*-vinylcarbazole [1–3].

Kinetic parameters of the thermal degradation process were computed based on the numerical method of kinetic parameter estimation by the given kinetic equation [4].

METHOD

Materials

Methylmethacrylate–*N*-vinylcarbazole copolymers (MM–NVC) were synthesized via suspension copolymerization. The initiator used was AIBN.

The obtained copolymers were purified by dissolving in benzene, followed by precipitation and extraction with methanol. The samples were dried in vacuo. The content of the unreacted monomers was determined using the polarography method. The composition of MM-NVC copolymers was established based on CHN analysis.

Thermal studies

Thermal studies were carried out using a TA-2 thermoanalyser (Mettler, Switzerland). The measurements were carried out in inert (argon) and oxidizing (air) atmospheres at a heating rate of $3^{\circ} \text{ min}^{-1}$ with sample weight of 0.050 mg.

RESULTS AND DISCUSSION

Two series of TG, DTG and DTA measurements were carried out for MM-NVC copolymers containing ca. 5–48% NVC, in inert and oxidizing atmospheres, in the temperature range 25–500°C. Based on the thermograms obtained the temperatures of the beginning of weight loss and the changes of weight loss in the above temperature range were determined and are shown in Figs. 1 and 2. In air as well as in argon, the values of the weight loss varied considerably, dependent upon the copolymer composition. The maximum value of weight loss and the minimum temperature of the beginning of decomposition (T_0) was observed for poly-methyl-methacrylate.

The increase in the NVC content in copolymers caused a rise in T_0 values, while the weight loss remarkably decreased. The data calculated for some copolymers are listed below.

Copolymer (%NVC)	T_0 (°C)		Weight loss (%)	
	air	argon	air	argon
PPM	263	237	84.1	81.8
16.9	279	250	38.2	28.7
47.6	300	290	8.8	5.9

The analysis of DTG curves indicated that the temperature of the maximum decomposition rate, T_{max} , was shifted towards the higher temperature region as the content of NVC in copolymers increased, e.g.

Copolymer (%NVC)	T_{max} (°C)	
	air	argon
PMM	326	323
16.9	354	368
47.6	383	396

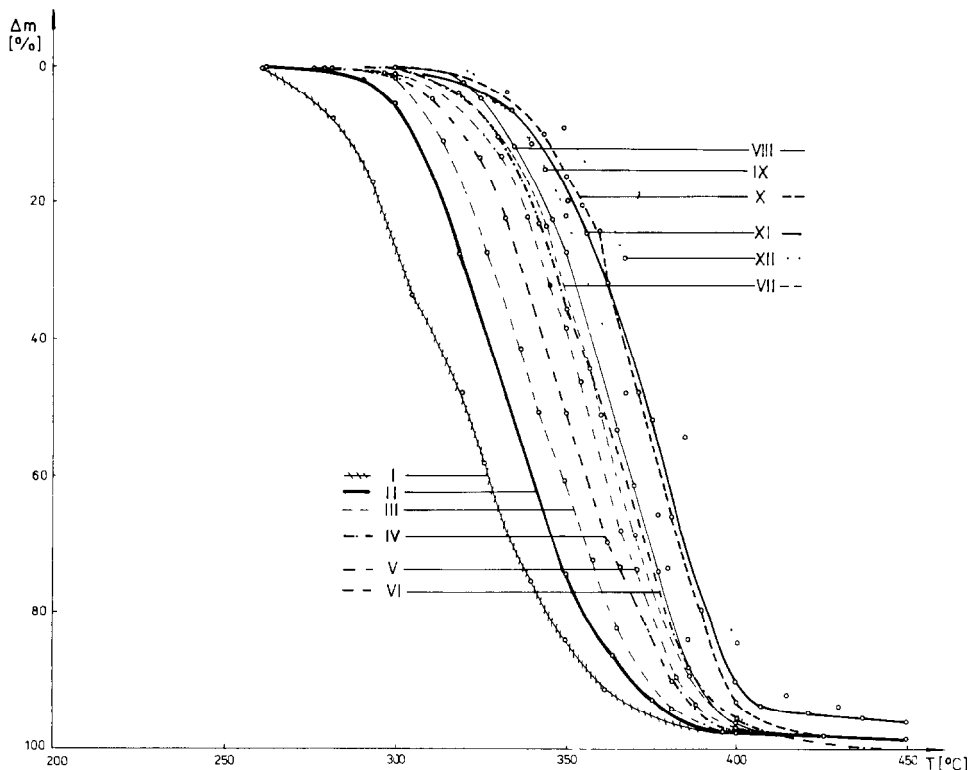


Fig. 1. Dependence of weight loss for MM-NVC copolymers in air. Content of NVC in copolymers (%): (I) PMM, (II) 4.9, (III) 8.9, (IV) 12.9, (V) 16.9, (VI) 20.8, (VII) 25.4, (VIII) 28.8, (IX) 33.9, (X) 37.0, (XI) 41.6, (XII) 47.6, (XIII) PNVC.

On the DTG curves, other less intense peaks were also observed which revealed the complexity of the given thermal degradation process.

The thermal effects taking place during sample heating registered on the DTA curves are shown in Figs. 3 and 4. In the case of PMM, the endothermal processes of melting, depolymerization and evaporation occurred at 290–350°C. For the copolymers, the endothermal changes appeared in a higher temperature range. The temperature rise was related to the introduced amount of NVC: the more NVC in the copolymer, the higher the temperatures of these effects. Such results confirmed the thermally stabilizing influence of NVC monomer units on copolymer stability.

In the case of some copolymers, exothermal changes were also noticed. These changes were probably the result of mutual interaction between NVC and MM monomer units and processes of branching or cross-linking of copolymer chains. At the present stage of work the mechanism of these reactions has not yet been evaluated.

On the basis of TG and DTG measurements, the kinetic parameters of the processes of thermal degradation and destruction of the synthesized

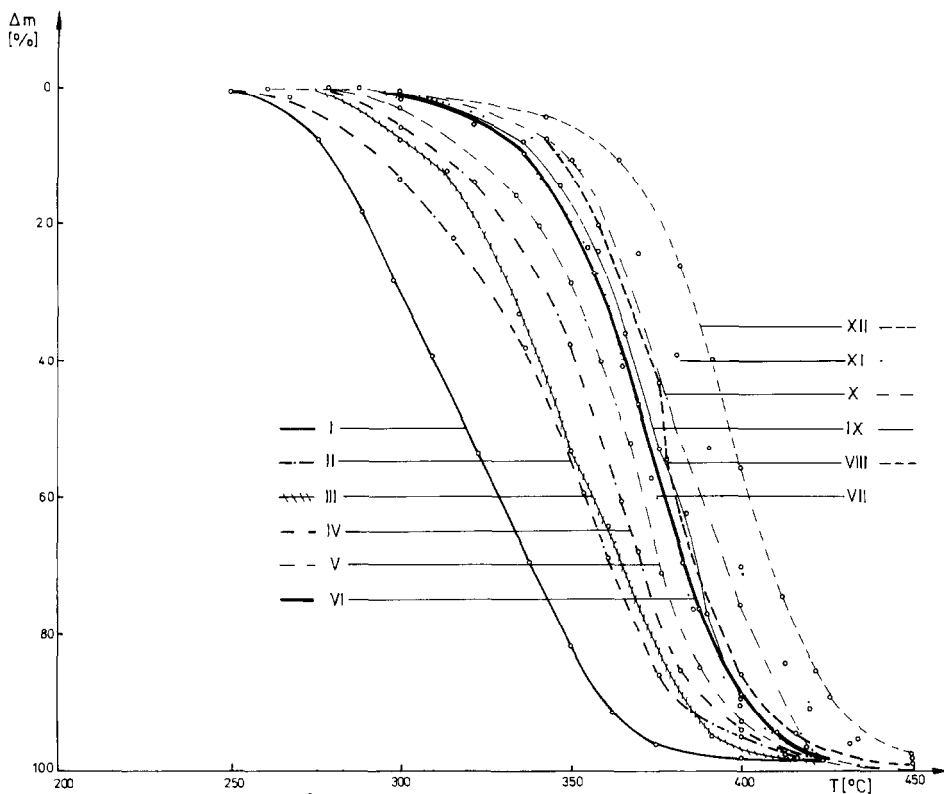


Fig. 2. Dependence of weight loss for MM-NVC copolymers in argon. For contents of NVC in copolymers, see Fig. 1.

MM-NVC copolymers were evaluated by the method of numerical estimation of the kinetic parameters of the assumed differential kinetic equation

$$\frac{d\alpha}{dt} = k_0 \exp[-E(RT)\alpha^n] \quad (1)$$

where α = weight of the active substance (mg), k_0 = frequency factor of the Arrhenius equation (min^{-1}), E = activation energy (kcal mol^{-1}), R = gas constant, T = absolute temperature (K), n = reaction order. The form of eqn. (1) is motivated by the fact that we have no detailed information on the mechanism of the thermal degradation of the MM-NVC copolymers. In such cases the form of reaction rate equations, from the numerical point of view, should be simple [4]. This statement was also confirmed by other papers [5,6], where the practical equivalency of various differential equations used for estimation of the kinetic data from TG measurements was noted.

The problem of the estimation of E , k_0 and n values was solved by the method of minimization of the sum of the absolute squared deviations of the

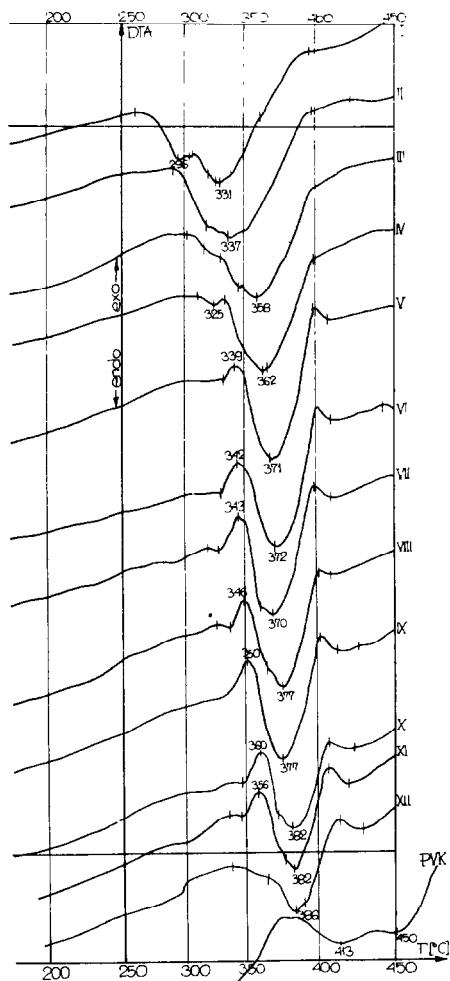


Fig. 3. DTA curves of MM-NVC copolymers in air. For contents of NVC in copolymers, see Fig. 1.

measured and computed values from numerical integration of eqn. (1)

$$F = \sum_{i=1}^n (\alpha_i^z - \alpha_i^0)^2$$

where α_i^z , α_i^0 are the measured and computed values of the active substance (mg), respectively. The details on the minimization methods were given in a previous paper [4]. The detailed TG measurement conditions and the values of an active substance, α , and temperature, T , calculated on the basis of the thermograms are given in Tables 1 and 2.

The course of the changes of the estimated E , k_0 and n values for the studied copolymers are presented graphically in Figs. 5–7. The accuracy of the method of kinetic parameter estimation is satisfactory. The worst objective function F -values were received for data Nos. 1 and 11 (in the presence

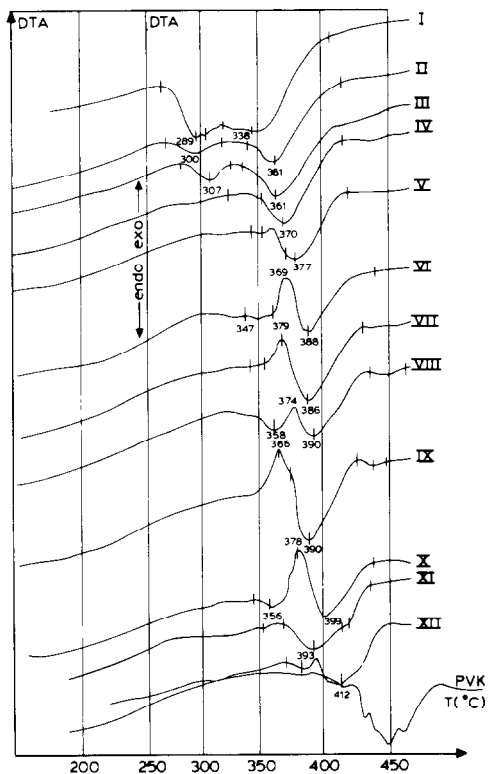


Fig. 4. DTA curves of MM-NVC copolymers in argon. For contents of NVC in copolymers, see Fig. 1.

of argon) and for data Nos. 1 and 8 (in oxidizing atmosphere). However, absolute deviations, α_i^z and α_i^0 , are not greater than ± 0.7 mg (see Table 3) corresponding to a maximum relative deviation of $\pm 1.5\%$. Moreover, these values correspond well with the accuracy of reading of α_i^z values from a thermogram, which is not better than ± 0.5 mg.

The estimated values of kinetic parameters vary considerably for the degradation process taking place in inert and oxidative atmospheres. For the series of measurements carried out in argon, the E and k_0 values increased for the copolymers containing greater amounts of NVC, while in the presence of air these values decreased, e.g.

Copolymer (%NVC)	Activation energy, E (kcal mol ⁻¹)		Frequency factor, k_0 (min ⁻¹)	
	air	argon	air	argon
4.9	75.25	18.79	5.11×10^{21}	2.39×10^7
20.8	52.35	32.28	2.26×10^{15}	2.22×10^{11}
47.6	39.15	34.44	1.73×10^{13}	1.96×10^{11}

TABLE 1
 Data for kinetic computations: α (mg); T (K); sample weight, 50 mg; heating rate, 3° min^{-1} ; atmosphere, air

Copolymer No.	NVC content (%)	α_1^i	T_1	α_2^i	T_2	α_3^i	T_3	α_4^i	T_4	α_5^i	T_5
1	4.9	49.0	536.0	48.7	553.25	47.6	570.5	38.3	587.75	24.9	605.0
2	8.9	49.6	535.0	49.2	556.5	48.0	578.0	36.1	599.5	19.8	621.0
3	12.9	48.7	549.0	48.4	567.5	46.2	586.0	37.2	604.5	23.2	623.0
4	16.9	48.9	552.0	48.7	570.75	47.2	589.5	40.7	608.25	25.9	627.0
5	20.8	48.8	549.0	48.6	569.5	47.1	590.0	40.0	610.5	25.9	631.0
6	25.4	50.0	554.0	49.5	572.5	48.0	591.0	41.5	609.5	28.0	628.0
7	28.8	49.8	573.0	48.6	590.5	44.6	608.0	35.2	625.5	19.1	643.0
8	33.9	48.6	573.0	48.1	590.0	45.3	607.0	37.2	624.0	23.0	641.0
9	37.0	48.2	573.0	49.7	592.25	45.1	611.5	35.2	630.75	20.2	650.0
10	41.6	47.2	556.0	46.6	580.0	44.2	604.0	34.0	628.0	17.5	652.0
11	47.6	46.8	573.0	46.1	593.75	43.5	614.5	35.8	635.25	17.8	656.0

TABLE 2
 Data for kinetic computations: α (mg); T (K); sample weight, 50 mg; heating rate, 3° min^{-1} ; atmosphere, argon

Copolymer No.	NVC content (%)	α_1^i	T_1	α_2^i	T_2	α_3^i	T_3	α_4^i	T_4	α_5^i	T_5
1	4.9	48.0	513.0	47.1	541.5	41.8	570.0	34.0	598.5	18.2	627.0
2	8.9	48.9	534.0	47.9	558.25	41.8	582.5	33.3	606.75	16.8	631.0
3	12.9	49.2	511.0	48.4	542.75	46.0	574.5	38.8	606.25	18.7	638.0
4	16.9	49.0	523.0	48.5	552.5	46.5	582.0	39.5	611.5	20.4	641.0
5	20.8	48.9	523.0	48.0	555.25	46.6	587.5	40.5	619.75	15.7	652.0
6	25.4	49.4	523.0	49.0	555.5	47.1	588.0	39.7	620.5	16.0	653.0
7	28.8	48.2	523.0	48.0	553.5	47.0	584.0	42.9	614.5	20.9	645.0
8	33.9	49.0	552.0	48.8	577.5	46.5	603.0	38.6	628.5	17.8	654.0
9	37.0	48.6	523.0	48.4	556.0	47.5	589.0	43.6	622.0	27.2	655.0
10	41.6	48.1	523.0	47.8	558.25	46.3	593.5	41.2	628.75	21.1	664.0
11	47.6	49.0	535.0	48.9	568.5	47.5	602.0	43.5	635.5	24.0	669.0

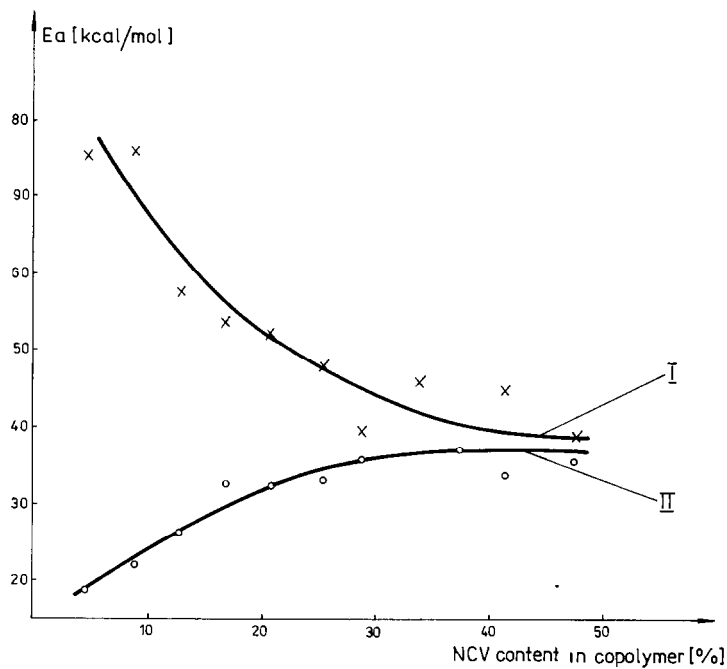


Fig. 5. Dependence of the E values on the content of NVC in MM-NVC copolymers. (I) In air, (II) in argon.

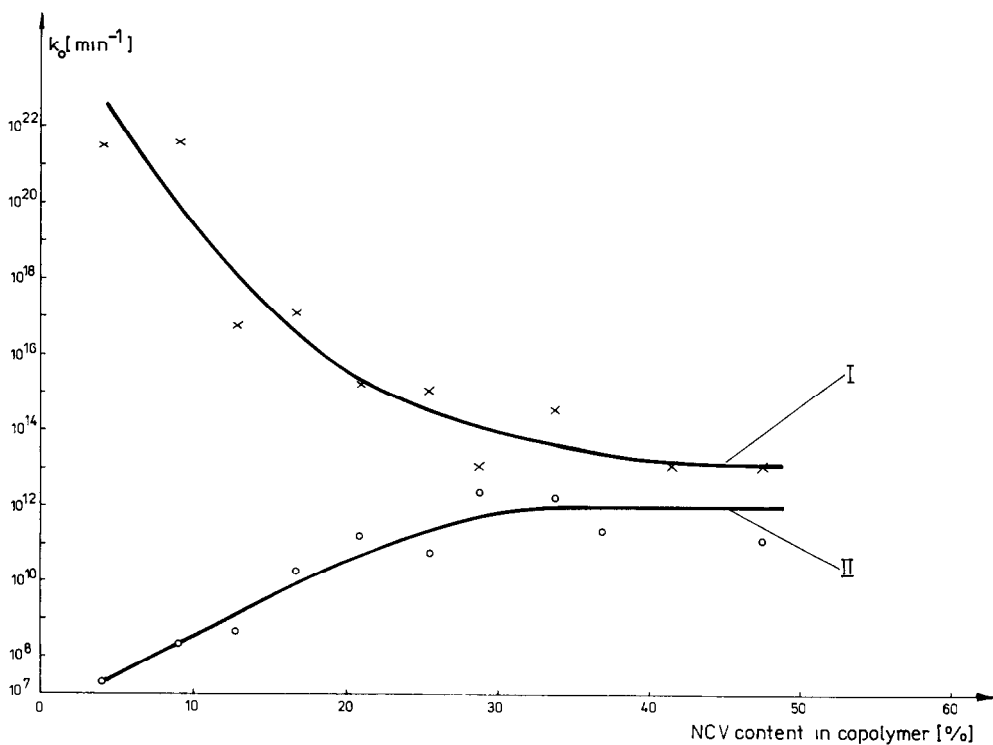


Fig. 6. Dependence of k_0 values on the content of NVC in MM-NVC copolymers. (I) In air, (II) in argon.

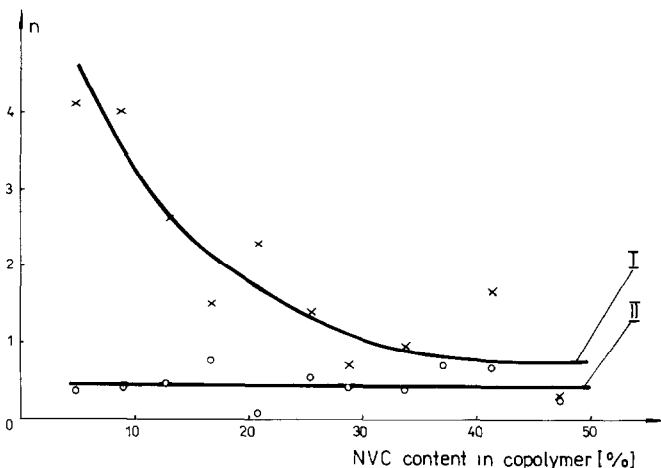


Fig. 7. Dependence of n values on NVC content in MM-NVC copolymers. (I) Air, (II) argon.

In the case of reaction order, n , values, the situation is slightly different, because in the presence of argon, the value of n is approximately constant, while in the oxidative degradation process, this value decreases with an increase in NVC content in the copolymer (see Fig. 7). The reason for such a distinct course of changes of E and k_0 values for the studied process is the different mechanism of thermal decomposition in inert and oxidative atmospheres. In an inert atmosphere mainly the depolymerization reactions predominate, then in the higher temperature range some destruction processes, while in the presence of air, the thermal oxidation processes become significant. It is a well-known fact that poly(*N*-vinylcarbazole) and poly-methylmethacrylate belong to the group of polymers which depolymerize on heating [1,2,7]. According to the above statement, it can be expected that MM-NVC copolymers would decompose in a similar manner, however, the other reactions resulting from mutual interaction of both co-monomers would be also possible.

Considering the stability of MM and NVC radicals it was confirmed that NVC radicals are more stable, because of their higher resonance energy than those of MM [8]. Therefore, the decomposition process is slower as the NVC content in copolymers increases and the overall activation energy is higher. Instead, in the presence of oxygen, the effect of the introduced NVC monomer units on the course of the degradation reaction is different. The increase in the number of NVC molecules in the polymer chain, which are more susceptible to the action of oxygen than MM molecules, due to the presence of tertiary carbon atoms, would facilitate the thermal decomposition process and lead to a decrease in E and k_0 values. Such a decrease of the energetic barrier of the process does not influence the thermal resistance of the copolymers studied, determined as the change of percentage weight

TABLE 3
 Examples of measured α_i^z values from thermograms and computed α_i^0 values

Atmosphere = Argon		Air				
h3%NVC =	4.9	47.6	4.9	33.9		
Data No. =	1	11	1	8		
	T (K)	α_i^z	α_i^0	T (K)	α_i^z	α_i^0
1	513	48.0	-	536	49.0	-
2	541.5	47.1	46.4	553.2	48.7	48.1
3	570	41.8	42.4	570.5	47.6	46.9
4	598.5	34.0	33.8	587.7	38.3	38.5
5	627	18.2	18.2	605.0	24.9	24.9
F-value	0.542	0.916		0.602		0.558

loss with temperature (see Figs. 1 and 2). This phenomenon could be explained satisfactorily if more detailed information about the products of decomposition were available.

CONCLUSIONS

The obtained MM-NVC copolymers exhibited an improved thermal stability in comparison to PMM. It was stated that with increasing NVC content in copolymers a considerable decrease in percentage weight loss was observed and at the same time the values of the temperature of maximum decomposition rate and the range of thermal endo and exo effects were shifted towards the higher temperature region.

The dependence of E , k_0 and n values on the content of NVC in copolymers was not accidental, proving the different mechanism of thermal decomposition of MM-NVC copolymers in inert and oxidative atmospheres. Further investigations should be done to evaluate this mechanism in detail. The accuracy of the computations of the changes in weight of the active substance was at least good, if the deviations of the measured, α_i^z , and computed values, α_i^0 , were in the range of the reading accuracy of α_i^z from the thermogram.

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