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STUDIES OF THE KINETICS OF THE THERMAL DEGRADATION PROCESSES OF PHOSPHORYLATED POLYVINYLCARBAZOLE

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ABSTRACT

Thermal studies of phosphorylated derivatives of polyvinylcarbazoles were carried out by means of DTA, TG and DTG. The kinetics of the thermal degradation processes of these polymers were examined. Kinetic parameters, i.e. activation energy, reaction order and reaction rate constant, were computed using the method of numerical estimation of kinetic parameters of the assumed kinetic equation. The effect of the conditions of TG, DTG measurements on the value of kinetic parameters was studied.

INTRODUCTION

Recently, the kinetics of the thermal degradation processes in polymers have often been studied using differential thermal analysis (DTA) and thermogravimetry (TG, DTG) [1]. Several methods have been developed for calculating the kinetic parameters from the DTA, TG and DTG measurements. In the studies of polymers, the Freeman—Carroll method has been that most often used [1,2]. However, in the majority of the methods proposed, the graphical solution of a given kinetic equation was used, which took a lot of time and caused the errors of such methods of calculation. In the presented work, the problem of the kinetics of the thermal degradation processes was solved by means of the numerical method of estimation of the kinetic parameters of the assumed kinetic equation. The computations were carried out for a group of phosphorylated derivatives of poly(9-vinylcarbazole) (PVK), chloromethylated PVK and poly(3-vinyl-9-ethylcarbazole). The accuracy of this method was checked for PVK.

METHODS

I. Experimental

Materials

Phosphorylated derivatives of PVK, chloromethylated PVK and poly(3-vinyl-9-ethylcarbazole) were obtained by phosphorylation reactions using

PCl_3 and PBr_3 as phosphorylating agents in the presence of a Friedel—Craft's catalyst ($AlCl_3$ and $AlBr_3$). Phosphorylated PVK was obtained according to the method of Pielichowski and Morawiec [3]. Phosphorylated derivatives of chloromethylated PVK and poly(3-vinyl-9-ethylcarbazole) were synthesized in a similar manner. The phosphorus contents of the products were determined by the colorimetric method. The chlorine contents were determined by the Schröninger method.

Thermal studies

Thermal studies were carried out using a Thermoanalyzer TA-2 (Mettler, Switzerland). The measurements were carried out in an inert (nitrogen, argon) or oxidizing (air) atmosphere at a heating rate of 3 or 6°C min^{-1} with a sample weight of 0.018 or 0.050 g. The detailed DTA and TG conditions and the values of an active substance (α) and temperature (K) calculated on the basis of the thermograms obtained are given in Table 1.

II. Theoretical

Mathematical model

During the thermal degradation of the examined polymers other processes, such as degradation of the polymer chains, destruction of the carbazole

TABLE 1

The results of TG measurements

No.	Polymer *	Phosphorus content (wt.%)	TG measurement conditions			
			Phosphone groups per 10 monomer units	Sample weight (mg)	Heating rate (°C min^{-1})	Atmosphere
1	I	1.78	1 57	20	6	N_2
2	I	5.00	4.48	18	6	N_2
3	I	9 60	8 44	21	6	N_2
4	I	11.30	10 00	18	6	N_2
5	I	1.78	1 57	21	6	Air
6	I	5.00	4.48	18	6	Air
7	I	9.60	8.44	20	6	Air
8	I	11.30	10.00	18	6	Air
9	I	9.60	8.44	46	6	N_2
10	I	9.60	8.44	50	3	N_2
11	I	11.30	10 00	51	3	N_2
12	II	6.60	4.3	50	3	N_2
13	III	6.43	4.1	51	3	N_2

* I, Phosphorylated PVK; II, phosphorylated poly(3-vinyl-9-ethylcarbazole); III, phosphorylated chloromethylated PVK.

ring and reactions of the functional (i.e. phosphone) groups, take place in a parallel—subsequent system. The complexity of this phenomenon and the fact that the use of DTA and TG does not allow direct indentification of the reaction products, prompted the assumption of the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_0\, \mathrm{e}^{-E_a/RT}\, \mathrm{f}(\alpha) \tag{1}$$

to describe the kinetics of these changes, where α is the weight of an active substance (mg), t the reaction time (min), k_0 the reaction rate constant (min^{-1}), E_a the activation energy (cal mole^{-1}), T the temperature (K), n the reaction order, and

$$\mathrm{f}(\alpha) = \alpha^n \tag{2}$$

f(α) is a function of the composition of the reacting system that is described here by the weight of an active substance. The form of f(α) depends on the mechanism of a given reaction. In fact, when the system with several simultaneous reactions can be described quantitatively by means of only one kinetic equation, then the form of f(α) is less important. However, from the numerical point of view, it is more convenient to assume a possibly simple dependence of f(α). Therefore, the form of f(α) given by the eqn. (2) was accepted. The problem of the estimation of the parameters of the kinetic

Data for kinetic computations

T_1	α_1^z	T_2	α_2^z	T_3	α_3^z	T_4	α_4^z	T_5	α_5^z
583	15.00	620.0	14.50	658.0	13.00	695.5	9 20	733 0	4.0
568	1.45	576.7	1.33	585.5	1.15	594 2	0.92	603.0	0.70
613	8.10	630.5	7.90	648.0	7.10	665.5	5.60	683.0	3.60
625	0.80	631.7	0.71	635.5	0.65	639.2	0.55	643.0	0.45
593	6.00	608.0	5.80	623.0	5.20	638.0	4 20	653.0	2 50
573	1.30	580 0	1.20	588.0	1.05	665.5	0.85	603.0	0.60
533	2.45	553.0	2.36	573.0	2.25	593.0	2.07	613.0	1.15
643	3.60	668.7	3.35	694.5	2.75	720 2	2.00	746.0	1.50
573	21.00	596.7	20.00	620.5	18.70	644.2	15.0	668.0	9.00
573	21.80	591.7	21.30	610.5	20.30	629.2	17.8	648.0	9.80
573	11.60	593.0	11.10	613.0	10 50	633.0	8.60	653.0	5.30
542	46.00	558.7	45.30	575.5	45.00	592.2	44.1	609.0	42.0
623	44.00	648.0	43.00	673.0	41.20	698.0	38.9	723.0	35.3

equation, i.e. the calculation of k_0, E_a and n, was solved by the method of minimalization of the sum of the absolute squared deviations of the measured and calculated values from the numerical solution of eqn. (1). For the computations, the program MINUITS was used to optimize a non-linear objective function F of n variables without constraints [4]. In this method, the following subroutines were used to solve the problem: SIMPLX (Nelder's and Meade's method) and MIGRAD (Davidon's method). Each of these methods can be used separately or in combination with the other two methods, depending on the form of the objective function F and the type of problem. More detailed information concerning the method used for the estimation of the parameters of the model was given in an earlier paper [5]. To solve the kinetic equation, eqn. (1), the numerical fourth-order Runge—Kutta method of integration with automatic choice of step size, MERSON [6], was used. The objective function F is a factor which determines the quality of the identification carried out. In numerical computations, the form of the function F

$$F = \sum_{i/1}^{n} (\alpha_i^z - \alpha_i^0)^2 \qquad (3)$$

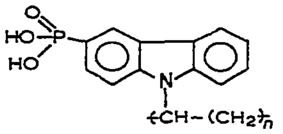
was taken where α_i^z, α_i^0 are the measured and computed values of an active sustance, respectively. The value n denotes the number of α value levels for which the absolute deviations was minimalized. In a given case, three intermediate values of α_i and a final value were considered, so n was equal to 4. The complexity of the changes which occur during thermal degradation meant that the estimated values of k_0, E_a and n could not be identified with the real values of the kinetic constants of this process. However, it can be accepted that the values obtained under the given conditions (accuracy of the TG method, the method of reading data from thermograms, a simplified kinetic description) give the best estimation.

The effects of chemical structure of the compounds used and the conditions of the TG measurements on the estimated value of kinetic parameters are discussed below.

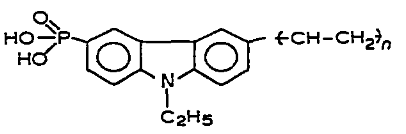
RESULTS AND DISCUSSION

The effect of chemical structure

Three types of phosphorylated derivatives of polyvinylcarbazoles were taken into consideration: phosphorylated PVK (I), phosphorylated poly(3-vinyl-9-ethylcarbazole) (II) and phosphorylated chloromethylated PVK (III).



I



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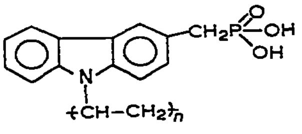

III

The results of thermal studies on these polymers are compiled in the Table 1 (nos. 11—13).

Of the changes which take place during thermal degradation, some are common to all the group of polymers studied, i.e. the formation of anhydride systems and crosslinking by means of phosphone groups [7]. Since the differences in activation energy values are mainly influenced by degradation and destruction reactions of a polymer matrix, phosphorylated chloromethylated PVK would undergo degradation reactions relatively easily because of the lower stability of the bond between the phosphonemethylene group and the carbazole ring compared with direct substitution of the phosphone group in the carbazole ring. In the case of poly(3-vinyl-9-ethylcarbazole) (II), degradation would most probably start with changes in the ethyl group.

According to the computed values of the kinetic constants, phosphorylated PVK (I) was the most thermally stable compound, which was to be theoretically expected (Table 2).

The effect of the number of phosphone groups

The effect of the number of phosphone groups introduced into a polymer matrix on the values of the kinetic parameters was studied on the grounds of the data compiled in the Table 1 (nos. 1—8). These measurements were carried out in an inert (nitrogen) and an oxidizing (air) atmosphere, so allowing a simultaneous assessment of the effect of the type of carrier-gas on the course of the thermal degradation kinetics to be made. The results of these computations are shown in Table 3. Based on these data it can be concluded that, in the inert and oxidizing atmospheres, the thermal stability of the polymers studied is maximum with 8.44 phosphone groups per 10 monomer units. However, the respective values of k_0 and E_a in the oxidizing atmosphere are considerably higher. This is connected with some thermal

TABLE 2

The effect of the chemical structure of the phosphorylated derivative on the values of the kinetic parameters

	Polymer *		
	I	II	III
Phosphorus contents (wt.%)	11 30	6.60	6.43
Atmosphere for TG measurements	N_2	N_2	N_2
Sample weight (mg)	51	50	50
Heating rate ($^\circ$C min^{-1})	3	3	3
Activation energy, E_a (cal mole^{-1})	36028.0	23361.9	17500.0
Absolute rate constant, k_0 (min^{-1})	1.320×10^{11}	1.617×10^7	2.587×10^4
Reaction order, n	0.975	0.503	0.400

* I, Phosphorylated PVK, II, phosphorylated poly(3-vinyl-9-ethylcarbazole); III, phosphorylated chloromethylated PVK.

TABLE 3

The effect of phosphone group content of poly-9-vinylcarbazole on the values of the estimated parameters

Phosphone groups per 10 monomer units	Atmosphere for TG measurements					
	Nitrogen			Air		
	Activation energy, E_a (cal mole^{-1})	Absolute rate constant, k_0 (min^{-1})	Reaction order, n	Activation energy, E_a (cal mole^{-1})	Absolute rate constant, k_0 (min^{-1})	Reaction order, n
1.57	20269.1	4.958×10^5	0.550	30000.0	4.325×10^9	0.530
4.48	27951.2	4.640×10^9	0.500	40025.3	1.006×10^{14}	0.745
8.44	38500.0	7.254×10^{11}	0.739	43978.1	1.606×10^{15}	0.661
10.00	30208.1	5.990×10^9	0.997	25036.5	3.269×10^6	1.100

oxidative destruction processes. At a phosphone group content of 8.44, the reaction order ranges from 0.5 to 0.75 in both atmospheres, while at a content of 10 phosphone groups per 10 monomer units, the reaction order reaches 1 and the values of k_0 and E_a are considerably lower.

The effect of TG measurement conditions

It has happened quite often in thermal studies that the thermograms obtained under various conditions of measurement were different and this automatically meant that calculations based on such thermograms were also different. It was therefore interesting to check the effect of TG measurement conditions on the kinetics of the thermal degradation of phosphorylated polyvinylcarbazoles. Changes in the type of atmosphere, heating rate, and sample weight were considered. The computations were carried out on the data for phosphorylated PVK containing 9.6% phosphorus (Table 1, nos. 3, 9, 10). The results of the computations are presented in the Tables 3 and 4. It is seen that a twofold increase in the sample weight caused about a 25%

TABLE 4

The effect of TG measurement conditions on the estimated values of the parameters

Computations were carried out for the sample of phosphorylated poly(9-vinylcarbazole) containing 9.6% phosphorus

	Effect of sample weight		Effect of heating rate	
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Sample wt. (mg)	21	46	46	50
Heating rate (°C min^{-1})	6	6	6	3
E_a (cal mole^{-1})	38500.0	28878.4	28878.4	47318.7
k_0 (min^{-1})	7.254×10^{11}	$6\ 375 \times 10^8$	6.375×10^8	3.794×10^{15}
n	0.739	0.919	0.919	0.589

TABLE 5

Comparison of α values obtained from eqn. (1) with values calculated from the thermograms at various temperatures

α (mg)	Atmosphere									
	Nitrogen					Air				
	583.0 K	620.5 K	658.0 K	695.9 K	733.0 K	643.0 K	668.7 K	694.5 K	720.2 K	746 K
From TG	15 0	14.50	13.0	9.20	4.00	3.60	3.35	2.75	2.0	1.50
From eqn. (1)		14.38	12.81	9.41	3.92		3.44	2.88	2.18	1.29

decrease in the activation energy. Furthermore, reduction of the heating rate from 6 to 3°C min^{-1} resulted in about a 60% increase in the activation energy. Thus, any change of TG measurement conditions had an appreciable influence on the values of the kinetic parameters. It follows that the proper way to obtain the most credible results would be to carry out the measurements and estimations of the parameters for a given sample under different conditions of T, heating rate and sample weight and then to take an average value of the kinetic parameters from the obtained computations. The accuracy of the method of the parameter model estimation was shown using data (Table 1, nos. 1 and 8) which had maximum absolute deviations between the measured and computed values of α. The comparison of the measured and computed values of an active substance weight is given in Table 5. In case of data for material with a phosphorus content of 1.78 wt.%, the maximum deviation of $(\alpha_i^z - \alpha_i^o)$ for a temperature of 695.5 K was 0.21 mg which corresponded to a relative deviation of 2.3%. For material with a phosphorus content of 11.3 wt.%, the maximum value of $(\alpha_i^z - \alpha_i^o)$ for a temperature of 746 K was also 0.21 mg, which corresponded to a relative deviation of 14%.

CONCLUSIONS

The numerical method for the estimation of kinetic parameters presented here gives a significant reduction in the effort and time required for the calculations and an increase in precision over the traditional Freeman—Carroll method. The values obtained for the kinetic parameters of PVK are in good agreement with those determined by Barrales-Rienda and Gonzales-Ramas [8].

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