Thermal properties of phosphorylated poly(vinyl carbazole)*

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It was confirmed that the prepared phosphorylated polymers of poly(vinyl carbazole) are characterized by a considerably higher thermal stability and lower weight losses at 600°C in comparison with poly(vinyl carbazole). Moreover, a dependence between the phosphorus content in polymer and the loss of weight was observed. The activation energy of thermal decomposition of phosphorylated poly(vinyl carbazole) (11.3% P) calculated by Freeman—Carrol's method is 287 kJ mol^{-1}

Было подтверждено, что полученные фосфорилированные полимеры поливинилкарбазола характеризованы относительно высшей термостойкостью и низшей убылью веса при температуре 600°C в сравнении с поливинилкарбазолом. Далее было найдено, что убыль веса зависит от содержания фосфора в полимере. Энергия активации термической деструкции фосфорилированного поливинилкарбазола (11,3 % P), вычислена с помощью метода Фримана и Карола, равна 287 кДж моль$^{-1}$

Recently, chemical modification of polymers has been intensively investigated. The phosphorylation reaction is one of the ways of modification. The phosphorylated polymers contain cationic groups and they are fire-retardant.

Many works are devoted to phosphorylation process of styrene polymers and copolymers [1—3]. Recently, we have studied the phosphorylation reaction of poly(vinyl carbazole) and interesting polymers containing one phosphonic group in each carbazole ring were obtained [4, 5]. The obtained polymers exhibit outstanding thermal stability and ion-exchange properties [4]. Thermal properties seem to be very interesting and they are the subject of this work.

Experimental

The phosphorylation reaction of poly(vinyl carbazole) was carried out with phosphorus trichloride in the presence of aluminium trichloride at 78°C, according to [4]. The phosphorus content in polymers was determined using photocolorimetric method [6]. Thermal analysis of modified polymers was made on a Thermal Analysator TA-2 (Mettler, Switzerland). The determinations were carried out in the temperature range 25—600°C at the heating rate of 6°C/min, in air and nitrogen [7]. Alumina calcined at 1000°C was used as reference material.

Table 1

Thermal properties of phosphorylated poly(vinyl carbazole) in air

No.	Phosphorus content %	Temperature range for initial loss of weight °C	Corresponding loss of weight %	The beginning of decomposition (1% loss of weight) °C	Loss of weight (°C)		
					400	500	600
1	1.78	50—100	1.9	320	33	59.5	90.5
2	5.0	50—90	1.67	300	22	44.0	61.0
3	9.6	50—90	2.5	320	22.5	35.0	50.0
4	11.3	60—100	4.45	310	21.1	33.0	44.5
5	0	80—180	2.87	230	19.5	90.0	95.2

Table 2

Thermal properties of phosphorylated poly(vinyl carbazole) in nitrogen

No.	Phosphorus content %	Temperature range for initial loss of weight °C	Corresponding loss of weight %	The beginning of decomposition (1% loss of weight) °C	Loss of weight (°C)		
					400	500	600
1	1.78	60—190	3.1	310	23.0	77.0	78.0
2	5.0	50—130	3.9	340	23.3	28.0	33.4
3	9.6	70—125	4.75	340	24.0	53.8	56.2
4	11.3	70—110	3.34	350	17.7	23.9	38.8

Results and discussion

Thermal properties of poly(vinyl carbazole) and its phosphorylated derivatives containing 1.78, 5, 9.6, and 11.3% P were examined in the air and in nitrogen atmosphere. Results of these investigations are summarized in Tables 1 and 2 and shown in Fig. 1. Table 1 shows the results of thermal studies of the phosphorylated poly(vinyl carbazole) in air. The observed temperature for the initial loss of weight
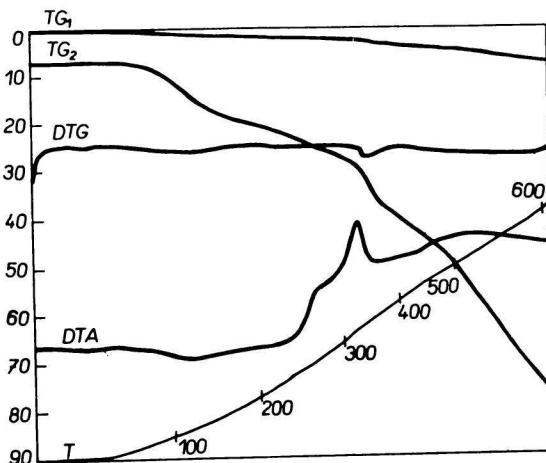

Fig. 1. DTA, TG, and DTG curve of phosphorylated poly(vinyl carbazole) (in nitrogen).

for both poly(vinyl carbazole) and the phosphorylated derivatives varies from 50 to 100°C. The initial loss of weight is connected with evaporation of water and solvents from polymer and varies from 1.67 to 4.45%. The beginning of polymer decomposition defined as 1% loss of weight was observed at about 300°C for
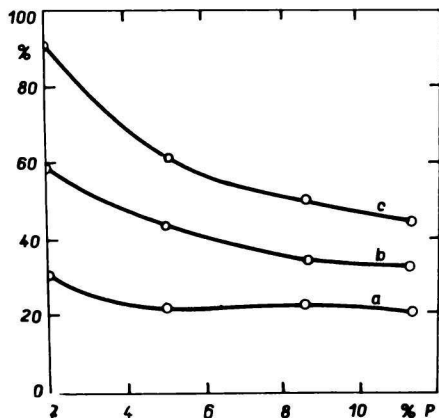

Fig. 2. Dependence of the weight losses (%) of phosphorylated poly(vinyl carbazole) on phosphorus content at 400°C (*a*), 500°C (*b*), and 600°C (*c*) (in air).

phosphorylated poly(vinyl carbazole), this value being much higher than the temperature 230°C determined for poly(vinyl carbazole). The comparison of weight losses of polymers at 400, 500, and 600°C in air is very interesting, *e.g.* at 600°C poly(vinyl carbazole) has the highest loss of weight and phosphorylated poly(vinyl carbazole) containing 11.3% P has the lowest one. The dependence of weight losses at 400, 500, and 600°C in air on phosphorus content in polymer is
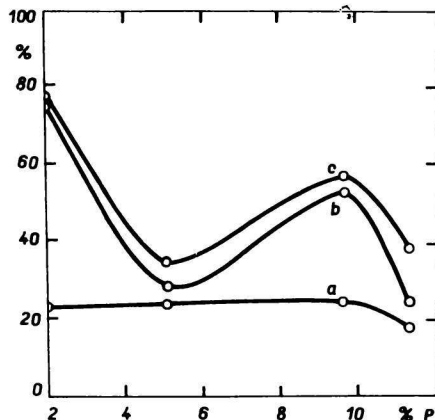

Fig. 3. Dependence of the weight losses (%) of phosphorylated poly(vinyl carbazole) on phosphorus content at 400°C (*a*), 500°C (*b*), and 600°C (*c*) (in nitrogen).

shown in Fig. 2. The results of thermal studies of modified poly(vinyl carbazole) in nitrogen atmosphere are shown in Table 2 and Fig. 3. Under these conditions the temperature ranges are considerably wider and the corresponding weight losses are higher. This fact is connected probably with the greater amount of the evaporated solvent. On the other hand, some differences in the results of the tests which were carried out in air and nitrogen are due to the fact that in air the effects of oxidation and destruction are overlapped, while in nitrogen only destruction effects take place. We do not suggest any mechanism of these processes, since it was not the aim of our work.

Generally, the temperature of the beginning of polymer decomposition increases with increasing phosphorus content in the polymer. Further investigations were carried out in order to determine the thermal decomposition energy for phosphorylated poly(vinyl carbazole). We have calculated this value for the polymer containing the greatest amount of phosphorus (11.3%) because of its highest thermal stability. The thermal decomposition energy was calculated by Freeman—Carrol's method [8—10], using the following equation

$$\frac{\Delta \log \beta \, dc/dT}{\Delta \log (1-c)} = n - \frac{E\Delta 1/T}{2.3R\Delta \log (1-c)},$$

where T — temperature, K,

n — order of reaction,

R — gas constant,

c — degree of decomposition $1 - w/w_0$,

w — weight of sample,

w_0 — weight of sample before heating, g,

β — heating rate, °C/min.

Subsequently the dependence

$$\frac{\Delta \log \beta \, \mathrm{d}c/\mathrm{d}T}{\Delta \log (1-c)} \quad vs. \quad \frac{\Delta (1/T)}{\Delta \log (1-c)}$$

$$\text{element } A \qquad\qquad \text{element } B$$
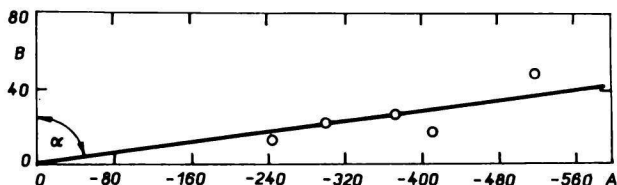

Fig. 4. Graphical interpretation of Freeman—Carrol's equation.

was graphically plotted (Fig. 4). The value of the decomposition energy was calculated by means of the formula $E = -2.3R$ tg α (Fig. 4). The activation energy of thermal decomposition of phosphorylated poly(vinyl carbazole) amounts to 287 kJ mol^{-1}

References

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