Journal of Thermal Analysis, Vol. 32 (1987) 1773–1776

THERMAL PROPERTIES OF POLY-N-VINYLCARBAZOLE DERIVATIVES

E. Trębacz

INSTITUTE OF CHEMISTRY AND ORGANIC TECHNOLOGY,
POLYTECHNICAL UNIVERSITY, 31-155 CRACOW, POLAND

Thermal studies were carried out on some products of chemical modification of poly-N-vinylcarbazole (PNVC). The effect of a substituent introduced into the carbazole ring on the thermal stability of the polymers was investigated. The kinetic parameters of the thermal degradation process were computed.

DTA and DTG methods are widely used in polymer chemistry for the determination of thermal properties.

Our investigations were focused on obtaining comparative thermal characteristics of a series of PNVC polymers containing different functional groups, such as phosphone ($PO(OH)_2$) [1], chloromethyl (CH_2Cl) [2], halogen (Cl, Br, I) [3] and a group of N-vinylcarbazole-methyl methacrylate (NVC-MM) copolymers [4]. This chemical modification of PNVC was carried out in order to synthesize products higher thermal stability than that of PNVC.

The dependence of the loss of weight on temperature for the studied polymers and copolymers is shown in Figs 1–3. Data on the group of phosphorylated

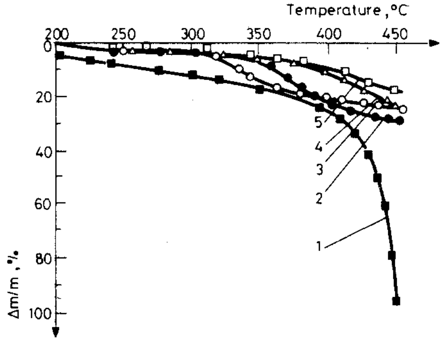

Fig. 1 Dependence of the weight loss on temperature. 1 – PNVC, 2 – phosphorylated PNVC (11.3% P), 3 – phosphorylated poly-3-vinyl-N-ethylcarbazole (6.6% P), 4 – phosphorylated chloromethylated PNVC (14.7% P). Measurement conditions: heating rate: 3 deg/min, atmosphere: argon, sample weight: 50 mg

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

derivatives are presented in Fig. 1, on the mono- and disubstituted halogen derivatives in Fig. 2, and on the NVC-MM copolymers in Fig. 3. The chloromethylated and phosphorylated derivatives turned out to be the most thermally stable compounds. The loss of weight calculated at 400° amounted to only about 5%. Such a high thermal stability could be explained by the fact that the phosphone and chloromethyl groups can undergo reactions in the higher temperature range, which lead to some crosslinking of the polymer matrix. Thus, the polymer structure becomes stiffer and more thermally stable.

In the group of halogenated PNVC derivates, the effect of the nature of the substituent introduced into the carbazole ring was marked. The thermal stability of the products in this group increased in the sequence iodo < bromo < chloro derivates, which can be attributed to the increasing dissociation energy of the

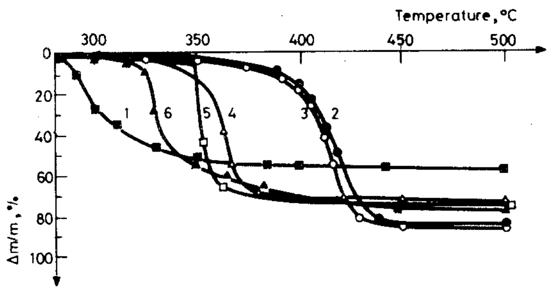

Fig. 2 Dependence of the weight loss on temperature 3 or 3, 6 halogen substituted poly-N-vinylcarbazole: 1 – 3-iodo-, 2 – 3-chloro-, 3 – 3,6-dichloro-, 4 – 3,6-diiodo-, 5 – 3,6-dibromo-, 6 – 3-bromo-. Measurement conditions: heating rate: 3 deg/min, atmosphere: argon, sample weight: 50 mg

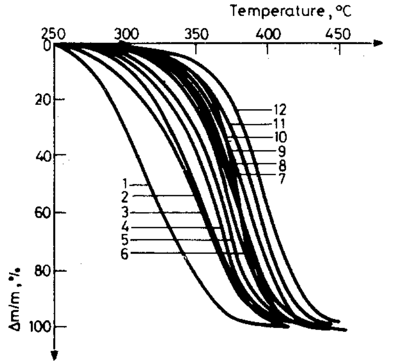

Fig. 3 Dependence of the weight loss on temperature for NVC-MM copolymers. The content of NVC in copolymers: 1 – 0%, 2 – 4.9%, 3 – 8.9%, 4 – 12.9%, 5 – 16.9%, 6 – 20.8%, 7 – 25.4%, 8 – 28.8%, 9 – 33.9%, 10 – 37.0%, 11 – 41.6%, 12 – 47.6%. Measurement conditions: heating rate: 3 deg/min, atmosphere: argon, sample weight: 50 mg

carbon-halogen bonds. However, the thermal properties of these polymers did not exceed those of PNVC in this respect.

In the case of a series of NVC-MM copolymers containing 0–48% NVC, the strong influence of the NVC content in the copolymers on their thermal properties was found, i.e. the greater the amount of NVC, the higher the thermal stability. These results were in agreement with our expectations, which were based on the comparison of the poor thermal stability of polymethyl methacrylate with the outstanding thermal properties of poly-9-vinylcarbazole.

On the basis of the TG and DTG measurements, the kinetic parameters of the processes of thermal degradation and destruction of the synthesized product were evaluated by numerical estimation of the kinetic parameters of the assumed differential equation, which was described in a previous paper [1]. The values of the activation energy (E_a), the frequency factor of the Arrhenius equation (k_0) and the reaction order (n) calculated for some modified polymers are shown in Table 1.

Table 1 Kinetic parameters for the products of PNVC chemical modification. Measurement conditions: heating rate: 3 deg/min, atmosphere: argon, sample weight: 50 mg

No	Polymer	E_a, kcal/mole	k_0, min^{-1}	n
1	Phosphorylated PNVC (11.3% P)	36.03	1.32×10^{11}	0.97
2	Phosphorylated poly-3-vinyl-N-ethyl-carbazole (6.6% P)	23.34	1.61×10^{7}	0.50
3	Phosphorylated chloromethylated PNVC (10.7% P)	17.50	2.58×10^{4}	0.40
4	Copolymer NVC-MM (47.6% NVC)	34.4	2.3×10^{11}	0.25

From the results obtained, it could be concluded that phosphorylated and chloromethylated PNVC and MM-NVC copolymers exhibited higher thermal stabilities than the unmodified ones.

References

1 J. Pielichowski and E. Morawiec, J. Appl. Polym. Sci., 20 (1976) 1803.

2 J. Pielichowski and E. Morawiec, J. Polym. Sci., Polym. Chem. Ed., 18 (1980) 729.

3 J. Pielichowski and E. Morawiec, Proceedings of the First Europ. Symp. on Thermal Analysis, p. 184, University of Salford, U.K., 20–24 Sept. 1976.

4 J. Pielichowski, R. Chrząszcz, E. Trębacz and A. Wolff, Thermochim. Acta, 94 (1985) 367.

Zusammenfassung — An chemisch modifizierten Produkten von Poly-N-Vinylkarbazol (PNVC) wurden thermische Untersuchungen durchgeführt, sowie der Effekt eines in den Karbazolring eingeführten Substituenten auf die thermische Stabilität des Polymers untersucht. Weiterhin wurden die kinetischen Parameter des Zersetzungsprozesses errechnet.

Резюме — Проведено термическое исследование производных поливинилкарбазола и изучено влияние различных заместителей в карбазольном ядре на термоустойчивость этих полимеров. Вычислены кинетические параметры реакции термического разложения исследованных полимеров.