

KINETIC ANALYSIS OF THE PROCESS OF THERMAL DEGRADATION OF POLY-N-VINYLCARBAZOLE AND ITS DERIVATIVES

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Abstract

Thermal studies of poly-N-vinylcarbazole and its derivatives containing -Cl, -Br, -I and -CH₃ as functional groups were carried out by means of thermogravimetry. The kinetics of the processes of thermal degradation of these polymers was examined. Kinetic parameters, i.e. apparent activation energy, reaction order and pre-exponential factor, were evaluated by using an integral method.

Keywords: kinetics, poly-N-vinylcarbazole

Introduction

Poly-N-vinylcarbazole (PNVC) and its derivatives have found broad application due to their properties, i.e. high thermal stability, electric insulation, photosensitivity and photo-conductivity comparable with that of inorganic semiconductors (Sn, ZnO) [1]. Like polymers, in response to elevated temperature or radiation PNVC undergoes gradual degradation. A complete kinetic description of this phenomenon remains complicated, since many partial reactions contribute to the overall mechanism. However, this forms an essential part of investigations of polymers, leading to a better understanding of their degradation processes.

The kinetics of the thermal degradation process in polymers has recently often been studied by means of thermogravimetry (TG) [2]. Several methods have been developed; depending on the method of solution of the basic kinetic equation, they are usually divided into differential and integral methods [3, 4].

In the present work, the kinetics of thermal degradation of PNVC and its derivatives containing halogen (Cl, Br or I) or methyl (CH₃) as functional groups was investigated.

Experimental

Materials

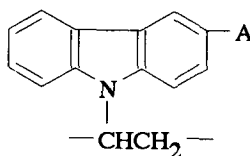
The monomers and polymers were prepared as described previously [5].

Method

Thermogravimetric measurements were carried out with a Mettler TA-2 thermal analyzer. The conditions were: heating rate, 6 deg·min⁻¹; atmosphere, argon; sample mass, 50 mg; inert material, Al₂O₃.

Results and discussion

The polymers under investigation had the general formula



where $A = \text{Cl, Br, I or CH}_3$.

Following the TG measurements, the kinetic parameters of the process of thermal degradation were evaluated by a numerical procedure based on adjustment of Eqs (1) and (2):

$$I_r = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{(1-\alpha)^n} \quad (1)$$

$$I_1 = \frac{A}{\beta_T} \int \exp\left(\frac{-E}{RT}\right) dT \quad (2)$$

where the symbols have their usual meaning.

This method has already been described in detail elsewhere [6].

The values of the activation energy (E), the pre-exponential factor (A) and the order of reaction (n) are shown in Table 1.

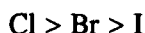
The results obtained reveal that the values of the kinetic parameters varied markedly, depending on the present substituent. In sequence of increasing E value, the investigated polymers are as follows:

chloro > bromo > iodo derivative

Table 1 The estimated values of the kinetic parameters

No.	Derivative of PNVC	$E / \text{kJ}\cdot\text{mol}^{-1}$	A / s^{-1}	n
1	PNVC	63.7	$1.19\cdot 10^5$	0.75
2	chloro	81.5	$6.09\cdot 10^4$	0.17
3	bromo	78.3	$2.36\cdot 10^6$	2.19
4	iodo	57.4	$5.97\cdot 10^3$	1.47
5	methyl	132.9	$6.21\cdot 10^8$	1.75

This is in accordance with the sequence of electronegativity for the halogens:



and suggests the characteristic influence of substituents with different electronegativities on the values of kinetic parameters. This phenomenon requires a detailed analysis, including identification of the degradation products. Such studies are now in progress.

References

- 1 J. M. Pearson and M. Stolka, *Poly(N-vinylcarbazole)*, Gordon and Breach, New York 1981.
- 2 B. Wunderlich, 'Thermal Analysis', Academic Press, New York 1990.
- 3 J. Šestak, 'Thermophysical Properties of Solids', in 'Comprehensive Analytical Chemistry', Vol. XIID, Elsevier, Amsterdam 1984.
- 4 F. Carrasco, *Thermochim. Acta*, 213 (1993) 115.
- 5 E. Trebacz, *Thermochim. Acta*, 143 (1989) 51.
- 6 J. Pielichowski, S. Kedzierski and K. Pielichowski, *Thermal Anal.*, (Submitted).
- 7 J. Pielichowski, E. Trebacz and A. Wolff, *Thermochim. Acta*, 42 (1980) 35.
- 8 I. Hamerton, J. Pielichowski and K. Pielichowski, *Polymer*, in press.
- 9 D. Dollimore, *Anal. Chem.*, 62 (1990) 44.
- 10 M. Rodriguez L. M. Leon, *Eur. Polym. J.*, 19 (1983) 585.

Zusammenfassung — Mittels Thermogravimetrie (TG) wurden eine thermische Untersuchung von Poly-N-Vinylcarbazolen und deren Derivaten mit den funktionellen Gruppen $-\text{Cl}$, $-\text{Br}$, $-\text{I}$ und $-\text{CH}_3$ durchgeführt. Die Kinetik der Vorgänge der thermischen Zersetzung dieser Polymere wurde untersucht. Kinetische Parameter wie scheinbare Aktivierungsenergie, Reaktionsordnung und präexponentieller Faktor wurden unter Einsatz der Integralmethode abgeleitet.