Journal of Thermal Analysis, Vol. 33 (1988) 1129–1133

THERMAL PROPERTIES OF N-VINYLCARBAZOLE – DIVINYLBENZENE MACROPOROUS COPOLYMERS.

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Thermal properties of N-vinylcarbazole (NVC) – divinylbenzene (DVB) macroporous copolymers were investigated using TG, DTA methods. The copolymers contained 20, 30, 40 or 50% of DVB. The effect of the crosslinking and porosity degree on thermal stability of the copolymers was studied. With an increase of the NVC content in copolymers their thermal stability was higher.

The kinetic parameters of the thermal degradation process were estimated using numerical methods.

The studies on synthesis and properties of styrene – divinylbenzene (ST–DVB) and acrylonitryle – divinylbenzene copolymers were the subject of many works due to their wide applications in many technical fields [1–3]. Among other applications, ST–DVB copolymers can be used as stationary phase in gas chromatography [4]. In the present work we aimed to find out, if N-vinylcarbazole – divnylbenzene (NVC–DVB) macroporous copolymers would exhibit also some thermal [5] and sorption properties good enough to qualify them for such chromatographic purposes.

Experimental

The macroporous NVC–DVB copolymers were obtained using the suspension polymerization technique and in the presence of iso-amyl alcohol (toluene or *n*-decyl alcohol) toluene mixtures. Thermal studies were carried out using a Mettler TA–2 thermal analyzer. The conditions of the measurements: heating rate: 3 deg min^{-1}, sample weight: 50 mg, atmosphere: air, argon, inert material: Al_2O_3.

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Results

Thermal studies were performed for a series of NVC–DVB copolymers containing 20, 30, 40 or 50% of DVB. One could expect that at greater content of DVB, the copolymer structure would become more amorphous, while at the increase of NVC segments, the formation of some crystalline regions would be facilitated. Hence, these two contradictory tendencies should influence on thermal stability of the copolymers.

On the basis of TG measurements it was noticed that no changes of weight occured up to 290–320°, depending on the NVC : DVB ratio in the given copolymer (Fig. 1a, b).

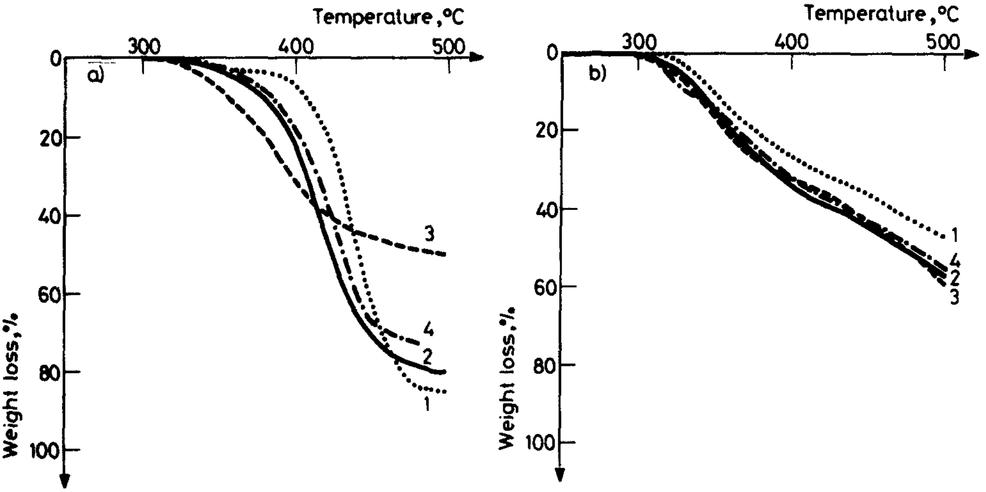

Fig. 1 TG curves of NVC-DVB copolymers.
Curves: 1 – cop. 20% DVB, 80% NVC
2 – cop. 30% DVB, 70% NVC
3 – cop. 40% DVB, 60% NVC
4 – cop. 50% DVB, 50% NVC
a – inert atmosphere,
b – oxidative atmosphere.

Generally, the copolymer containing the greater amount of NVC units exhibited higher thermal stability, except of a copolymer of (50:50) NVC : DVB, which was more stable than copolymers of 60 and 70% NVC. This fact can be explained considering the possibility of the formation of a more regular structure at such a ratio of comonomers.

The comparison of the course of thermal degradation in the oxidative and inert atmosphere led to the conclusion that in the presence of oxygen the decomposition proceeded at lower rates. It would suggest that some radical reactions involving oxygen atoms took place, which, in turn produced new sites of cross-linking and thus moderated the degradation process. The effect of porosity degree on thermal stability studied for three copolymers of the same NVC : DVB (70:30) ratio turned out to be not significant (Fig. 2a, b).

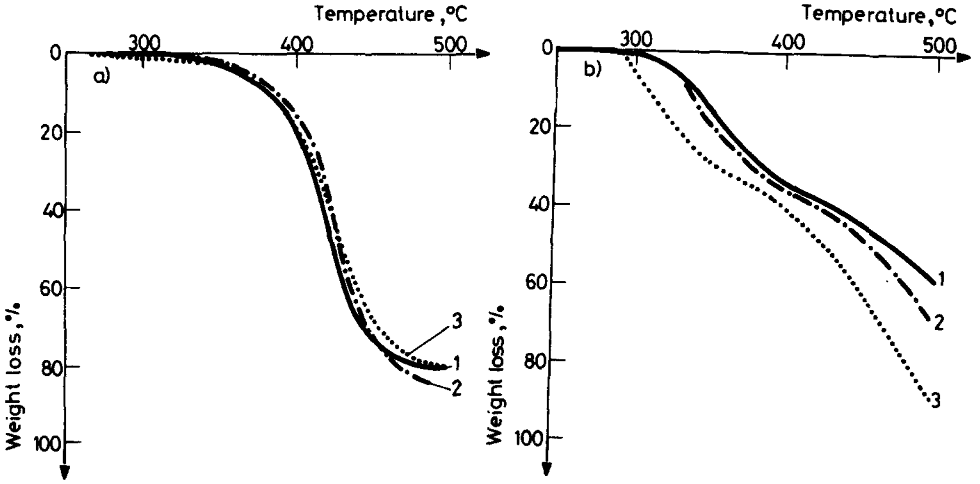

Fig. 2 TG curves of NVC-DVB (70:30) copolymers obtained at the presence of diluents:
1 – iso-amyl alcohol:toluene = 1:2
2 – *n*-decyl alcohol:toluene = 2:1
3 – iso-amyl alcohol:toluene = 2:1
a – inert atmosphere,
b – oxidative atmosphere.

The kinetic parameters of thermal degradation process i.e. activation energy, frequency factor and reaction order were estimated using the numerical methods [6]. The estimated values are compiled in Table 1.

Table 1 Kinetic parameters of thermal degradation process of NVC-DVB copolymers.

No	Copolymer	Activation energy, kcal/mol		Frequency factor, min^{-1}		Reaction order		FCN*	
		air	argon	air	argon	air	argon	air	argon
1	20% DVB, 80% NVC	42.77	52.26	$3.68 \cdot 10^{14}$	$1.4 \cdot 10^{15}$	0.3	0.9	0.198	0.232
2	30% DVB, 70% NVC	31.18	32.07	$4.85 \cdot 10^{8}$	$1.00 \cdot 10^{10}$	2.0	0.3	0.155	0.022
3	40% DVB, 60% NVC	30.36	30.81	$4.302 \cdot 10^{8}$	$2.15 \cdot 10^{8}$	1.8	1.6	0.071	0.090
4	50% DVB, 50% NVC	29.80	34.43	$3.97 \cdot 10^{8}$	$1.25 \cdot 10^{10}$	1.5	0.8	0.22	0.141

*FNC $= \sum_{i=1}^{n} (\alpha_i^z - \alpha_i^o)^2$ α^z, α^o – calculated and computed values of the conversion degree.

Conclusions

The NVC–DVB macroporous copolymers are thermally stable up to 290–320°, this temperature range being somewhat higher in comparison to ST–DVB copolymers. The increase of NVC content in a copolymer improves its thermal stability.

The copolymers synthesized exhibit also good sorption properties thus implying their possible use as the stationary phase in chromatography.

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Zusammenfassung – Die thermischen Eigenschaften von makroporösen N-Vinylcarbazol (NVC)-Divinylbenzen (DVB)-Copolymeren mit 20, 30, 40 oder 50% DVB wurde mittels TG-DTA untersucht. Der Einfluss des Vernetzungsgrades und der Porosität auf die thermische Stabilität der Copolymeren wurde ermittelt. Mit steigendem NVC-Gehalt nahm die thermische Stabilität der Copolymeren zu. Kinetische Parameter des thermischen Abbaus wurden unter Verwendung numerischer Methoden abgeschätzt.

РЕЗЮМЕ — Используя методы ТГ и ДТА, исследованы термические свойства макропористых сополимеров N-винилкарбазола с 20, 30, 40 и 50% дивинилбензола. Изучено влияние перекрестного сшивания и степени пористости на термоустойчивость сополимеров. Найдено, что увеличение в сополимерах содержания N-винилкарбазола, вызывает их большую термоустойчивость. Установлены кинетические параметры процесса термического разложения сополимеров.