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KINETICS OF THE THERMAL DESTRUCTION OF STYRENE-DIVINYLBENZENE COPOLYMERS, COMPUTED FROM THERMOANALYTICAL DATA

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The process of thermal destruction of styrene-divinylbenzene copolymers, studied in a derivatograph, proceeds in one stage, as indicated by the mass loss accompanied by a characteristic endothermic peak in the range 380–400°. The determined values of the kinetic characteristics n, E, ln A, ΔE and T_0 allow the conclusion that an increase in the divinylbenzene content of the monomer blend used to synthetize the divinylbenzene copolymers does not result in an increased thermal stability as compared to that of polystyrene.

Styrene-divinylbenzene copolymers are used as matrices to obtain various ion-exchange resins. The application of the latter materials at high pressures and temperatures obviously raises particular demands as regards their quality, including as one of their important features the thermal stability. Although the thermal stability of ion-exchange resins is not controlled only by the thermal stability of the initial copolymer, nevertheless it is undoubtedly of interest to conduct studies on the relative thermal stabilities of styrene-divinylbenzene copolymers differing in their divinylbenzene (DVB) content.

Some general questions of the thermal stability of polystyrene and of its copolymers with divinylbenzene have been studied in [1–5]. Thermal depolymerization was carried out mainly in vacuum in these studies, in the temperature range 350–450°. It was found that the volatile products of pyrolysis consist predominantly of styrene, its dimers and trimers, and the gases H_2, CH_4, C_2H_4, etc., which are presumably the products of secondary pyrolysis of the primary pyrolysis products in the furnace zone. Under static conditions, the thermal destruction of polystyrene proceeds according to an intermediate-type mechanism [1], that is, the random rupture of the macromolecule and a chain mechanism of destruction. In a carrier-gas stream and under pulse conditions, the thermal destruction of polystyrene follows a chain mechanism with a practically complete yield of the monomer [4]. The activation energy of polystyrene decomposition, calculated from differential calorimetric, thermogravimetric and mass-spectrometric data relating to the amounts of styrene and ethylene evolved, is 30 kcal/mol and is independent of the composition of the atmosphere (air, oxygen, nitrogen) [3]. In [5], the activation energies of styrene-divinylbenzene copolymers in the DVB-content range between 2 and 56% were calculated from the thermal decomposition rate in the temperature range 330−390°; the value found was 53−58 kcal/mol. Regrettably, the form of the kinetic equation and the value of the pre-exponential factor in the Arrhenius equation were not reported. To form any final conclusion regarding the thermal stability of the polymers studied solely on the basis of the numerical values of the activation energies would be incorrect, as shown in [6].

The purpose of this paper was to establish a potential correlation between the kinetic thermal stability of styrene-divinylbenzene copolymers and the amount of divinylbenzene added to the initial monomer blend. Thermogravimetric curves served as the source of kinetic information.

The kinetic values were calculated from the well-known equation

$$\mathrm{d}\alpha/\mathrm{d}t = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^{n} \tag{1}$$

and its integrated form

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^{2}}{a(E+2\,RT)} \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where α is the extent of decomposition, a is the linear heating rate, E and A are the activation energy and the pre-exponential factor in the Arrhenius equation, and n is the order of the reaction, which, according to [7], is calculated from the relationship $1-\alpha_{m} = 1.062\, n^{1/(1-n)}$. The pre-exponential factor in the Arrhenius equation was calculated by means of the equation

$$A = \frac{(1-\alpha_{m})^{1-n}}{n} \cdot \frac{Ea}{RT_{m}^{2}} \exp\left(\frac{E}{RT_{m}}\right) \tag{3}$$

where the values α_{m} and T_{m} are those corresponding to the maximum rate of the decomposition process.

The conclusions as to the relative thermal stabilities of the copolymer specimens studied were then based on the calculated temperature T_0 corresponding to the start of the reaction [8] at known kinetic parameters E and $\ln A$ and a fixed value α_0 (for instance, 0.003):

$$\alpha_0 = \frac{A}{a} \cdot \frac{RT_0^{2}}{E+2\,RT_0} \exp\left(-\frac{E}{RT_0}\right) \tag{4}$$

In addition, the thermal stabilities of the copolymers can also be compared by the value of the free activation energy [6]:

$$E = -RT_{i} \ln k = E - RT_{i} \ln A \tag{5}$$

where T_{i} is some assumed initial temperature which, for the series of reactions studied, is postulated to be constant.

Experimental

The studies were carried out with a standard derivatograph (MOM, Hungary). The specimens were placed in the standard platinum crucibles of the instrument fitted in platinum-platinorhodium thermocouples. The specimens were compacted by tapping the crucibles several times. The polymers were used in the form of granules (0.1 – 0.3 mm fraction). The mass of the specimens was around 200 mg. The reference standard was aluminium oxide previously heated to 1000°. In the general case the copolymers were heated up to 500° at a rate of 5°/min. The sensitivity of the instrument was 1/10 for DTA and 1/5 for DTG. The specimens studied contained 1, 4, 6, 8 or 20% divinylbenzene, with pure polystyrene for comparison. Before thermal analysis, the polymers were conditioned by treatment with a 10% alkali solution, washing with water to neutrality and drying in a desiccator above calcium oxide.

Results and discussion

A typical example of the thermoanalytical curves obtained in the thermolysis of styrene-divinylbenzene copolymers is shown in Fig. 1. The thermal destruction process usually takes place in one stage as indicated by the mass loss, accompanied

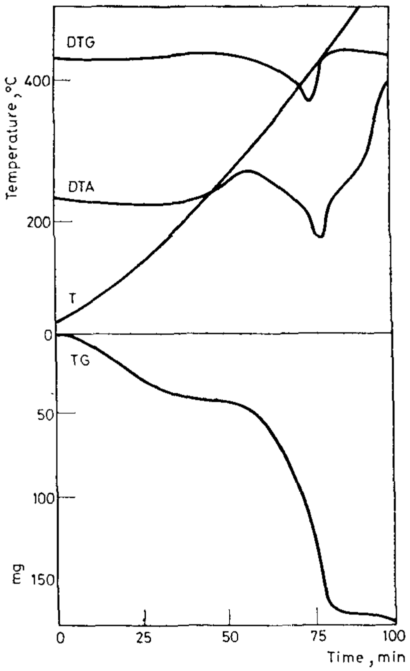

Fig. 1. Thermoanalytical curves of the thermal destruction of a styrene-divinylbenzene copolymer containing 1% DVB. The sample was previously kept in dichloroethane

by an endothermic peak in the DTG curve in the range 380–400°. This value corresponds to the literature data from studies performed with isothermal heating in vacuum or inert atmospheres. The above equations were used to calculate the formal order of reaction n, the activation energy of thermal destruction E, the pre-exponential factor of the Arrhenius equation A, and the characteristic activation values ΔE and T_0. All data are listed in Tables 1 and 2.

Table 1

Kinetic parameters of the thermal destruction of styrene-divinylbenzene copolymers under non-isothermal conditions. $a = 5°/\text{min}$

Polymer	n	E kcal/mol (kJ/mol)	ln A	T_m, K	T_0, K	ΔE at $T_i = 473$ K kcal/mol (kJ/mol)
Polystyrene	0.45	22.2 (92.9)	10.28	674	518	12.5 (52.3)
	0.35	25.0 (104.6)	12.17	684	537	13.5 (56.5)
	0.32	23.0 (96.2)	10.61	685	528	13.0 (54.4)
1% DVB	0.53	26.0 (108.8)	13.61	663	528	13.1 (54.8)
	0.73	26.6 (111.3)	13.88	669	534	13.5 (56.5)
	0.65	25.0 (104.6)	12.66	668	527	13.0 (54.4)
3% DVB	0.30	20.0 (83.7)	8.22	687	513	12.2 (51.0)
	0.59	22.0 (92.0)	10.39	664	511	12.2 (51.0)
	0.43	22.0 (92.0)	10.37	665	511	12.2 (51.0)
6% DVB	0.22	16.0 (66.9)	5.23	680	482	11.0 (46.0)
	0.26	18.3 (76.5)	6.92	676	502	11.8 (49.4)
	0.20	17.6 (73.6)	6.50	680	494	11.5 (48.1)
8% DVB	0.32	13.0 (54.4)	2.92	674	452	10.2 (42.7)
	0.32	15.0 (62.8)	4.53	675	471	10.7 (44.8)
	0.26	15.0 (62.8)	4.53	676	472	10.7 (44.8)
20% DVB	0.48	18.0 (75.3)	7.25	661	486	11.1 (46.4)
	0.65	18.0 (75.3)	7.28	660	485	11.1 (46.4)
	0.40	15.0 (62.8)	4.79	661	464	10.5 (43.9)

From the data, the following conclusions may be drawn. At a heating rate of 5°/min, the temperature T_m (where the rate of non-isothermal transformation is highest) remains constant, independently of the initial amount of divinylbenzene. This finding, according to [9], should lead to a compensation effect between the activation parameters ln A and E. In fact, all experimental values of E and ln A fit fairly well into a narrow band in the plot of ln A *vs.* E.

Table 1 indicates that the initial temperatures T_0 of the transformation and the free activation energy values show a general weak trend to decrease with increasing DVB content. It may therefore be stated that – although increasing DVB content slightly improves the mechanical strength of the granules and reduces their swelling in solvents – no increase in thermal stability will be attained.

The dependence of the thermal destruction of the copolymers on the rate of heating was also studied. The copolymers with 8 and 20% DVB displayed a slight shift of the DTG and DTA curves towards a higher temperature T_m and a lower formal order of reaction n, but the value of ΔE remained practically unchanged (Table 2). With the procedure reported in the literature [10, 11] for determination of the kinetic parameters from the linear relationship $\ln a/T_m^2$ *vs.* $1/T_m$ (where a is the heating rate), somewhat lower results are obtained: 13 kcal/mol for the copolymer with 8% DVB, and 11.4 kcal/mol for the copolymer with 20% DVB. It should be noted, however, that according to [12] the cited calculation procedure is correct, strictly speaking, only for the parallel translation of the thermoanalytical curves with increasing linear heating rates, that is, without change in the mechanism of the transformation or the form of the kinetic equation $f(\alpha) = (1-\alpha)^n$ used, which is not the case in the thermolysis of styrene-divinylbenzene copolymers (cf. Table 2).

Table 2

Kinetic parameters of the thermal destruction of styrene-divinylbenzene copolymers at various heating rates

Heating rate °/min	n	E kcal/mol (kJ/mol)	$\ln A$	T_m, K	T_0, K	ΔE at $T_i = 473$ K kcal/mol (kJ/mol)
	Styrene copolymer with 8% DVB					
1	0.42	19.0 (79.5)	6.97	641	481	12.4 (51.9)
5	0.32	15.0 (62.8)	4.53	675	470	10.7 (44.8)
10	0.27	12.6 (52.7)	3.07	687	454	9.7 (40.6)
15	0.24	18.6 (77.8)	7.88	703	513	11.1 (46.4)
24	0.10	16.8 (70.3)	6.55	719	509	10.5 (43.9)
	Styrene copolymer with 20% DVB					
1	0.61	22.0 (92.0)	9.31	646	499	13.2 (55.2)
5	0.48	18.0 (75.3)	7.25	661	486	11.1 (46.4)
10	0.22	13.9 (58.1)	4.02	692	470	10.1 (42.2)
15	0.12	14.8 (61.9)	4.74	715	489	10.3 (43.1)
24	0.13	15.0 (62.8)	5.17	726	497	10.1 (42.2)

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ZUSAMMENFASSUNG — Der in einem Derivatographen untersuchte thermische Zersetzungsvorgang von Styroldivinylbenzolkopolymeren verläuft in einer Phase, welche durch Massenverlust angezeigt und durch einen charakteristischen endothermen Peak im Bereich von 380 . . . 400° angewiesen wird. Die ermittelten kinetischen Charakteristika n, E, $\ln A$, ΔE, T_0 gestatten die Schlußfolgerung, daß die Zunahme des Divinylbenzolgehalts in dem zur Synthese der Divinylbenzolkopolymeren verwendeten Monomergemisch im Vergleich zu der des Polystyrols, keine erhöhte Thermostabilität herbeiführt.

Резюме — Процесс термической деструкции стирол-дивинилбензольных сополимеров в системе дериватографа протекает по убыли веса в одну стадию и сопровождается эндоэффектом в области температур 380 ÷ 400°C. Определены кинетические характеристики (n, E, $\ln A$, ΔE, T_0) на основании которых сделано заключение, что увеличение содержания дивинилбензола в исходной смеси при синтезе дивинилбензольных сополимеров не ведет к повышению их термостабильности по сравнению с полистиролом.