THERMAL ANALYSIS OF ACETYLCELLULOSE MODIFIED WITH BIS(2-CHLOROETHYL)1-BROMOVINYL PHOSPHONATE

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TG, DTA, pyrolytic GC and mass spectrometry methods were used to study the effect of (bis(2-chloroethyl)1-bromovinyl phosphonate on the thermal- and thermooxidative destruction of acetylcellulose. On heating the BVP-containing AC in air the initiation and intensive decomposition of the polymer was found to occur at a reduced temperature. In an inert atmosphere one can also observe a decrease in the characteristic AC decomposition with increasing BVP. The modification results in an accelerated process of dehydration and deacetylation. The effective energy of deacetylation activation (between 220 and 270 °C) decreases from 135 to 80 kJ/mol on the addition of 5.0 wt.% BVP. A comparative study of the mass spectra of the modified AC subjected to stepwise heating up to 300 °C at a rate of 10 deg/min was carried out.

Chemical modification proved to be a most suitable method for producing the desired change in polymer properties. It was shown that under certain conditions bis(2-chloroethyl)1-bromovinyl phosphonate (BVP) reacts with acetylcellulose to give a graft copolymer having short branches starting from the main macromolecule chain [1]. AC thus modified can yield materials of reduced inflammability with improved physicochemical properties [2].

The purpose of this work is to elucidate the effect of BVP on the thermal properties and regularities governing AC decomposition.

Experimental

Materials

AC acetylated to 2.28 $\bar{M}_w = 6.27 \cdot 10^5$, was used as the starting polymer.

The AC was modified by standard procedures [1] during the preparation of 100–200 μm thick films from a 4% AC solution in acetone while simultaneously adding BVP and 1% of dicumyl peroxide to the solution.

The BVP used was a clear liquid having a density of 1.6170 g/cm^{-3} at 20° and a refractive index $n_D = 1.5002$.

The boiling point of the BVP is 156–158° at 2 Torr.

Thermal analysis

The TG and DTG measurements of the sample were made in air simultaneously with the DTA curves in the temperature range 20–700° using a Mettler Thermoanalyser. The mass of the samples was 100 mg, the heating rate -10 deg/min.

In inert atmosphere the TG and DTG curves were taken with a TG thermobalance (DuPont) at a nitrogen flow rate of 50 ml/min and a heating rate of 100 deg/min. The mass of the samples was 2–4 mg.

A Setaram balance connected to a chromatograph for analysing evolving decomposition gases CO, CO_2, CH_4 and H_2 was also used. The heating rate was 5 deg/min, sample mass -50 mg.

The modified AC was subjected to thermal destruction under isothermal conditions (200–800°)—in a pyrolytic cell in helium atmosphere and the polymer decomposition products were simultaneously analysed using a Tsvet–100 chromatograph. The testing conditions were as follows: sample weight was 2–4 mg, the detector—a catharometer; the steel chromatographic column 0.4 cm in diameter and 3 m long was packed with Poropac Q carrier (80–100 mesh). The nitrogen flow rate was 0.05 l/min. The column temperature for the separation of the light gases was 50°, that of acetic acid $-140°$.

The mass spectra of the samples were taken on an AEJ MS instrument (Great Britain). The temperature in the cell positioned directly in the mass spectrometer system 1 cm from the ionization chamber was raised up to 300° at 10 deg/min. The ionizing voltage was 70 V.

The effective kinetic parameters of the polymer decomposition, based on the TG curves taken under dynamic conditions, were calculated by the method reported elsewhere [3].

Results and discussion

In the course of the TG, DTG and DTA curves obtained in air for the starting and modified AC (Fig. 1) a number of typical differences can be readily distinguished. The addition of BVP results in a significant reduction of the initial and active AC decomposition temperatures $T_{i.d.}$ and T_{max}, respectively.
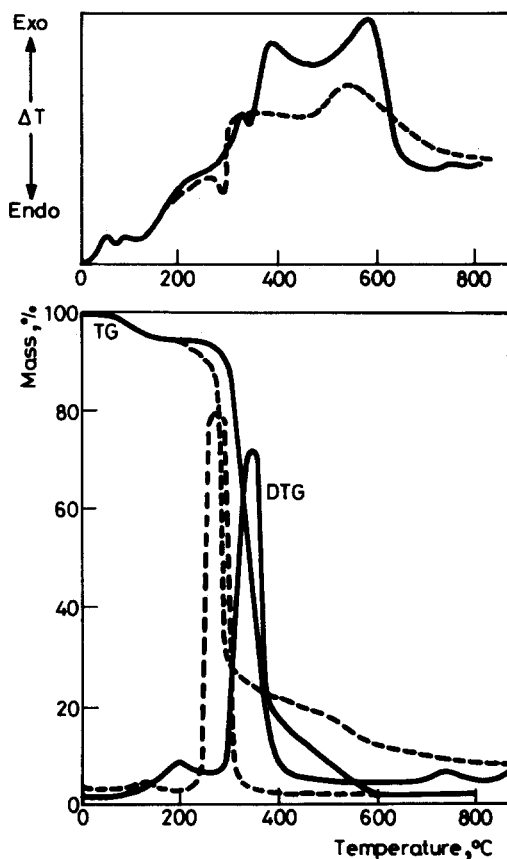

Fig. 1 TG, DTG and DTA curves for the decomposition of the starting AC (—) and AC containing 10% max BVP (– – –) in air

The AC decomposition in air involves heat evolution. As a result of the modification the exothermicity of the thermooxidative decomposition both in the low- and high-temperature region becomes lower.

Table 1 shows data on the effect of the BVP on the principal parameters of the thermooxidative AC decomposition. It is evident that the addition of 0.5 wt.%

Table 1 The effect of bis(2-chloroethyl)1-bromovinylphosphonate on the thermooxidative (in air) acetylcellulose decomposition

BVP content, wt.%	$T_{i.d.}$, °C	T_{max}, °C	W_{max}, mg/min	ω_{700}, wt.%	H, kJ/g
—	300	350	29.0	2	3.98
0.5	295	300	39.0	2	1.43
5.0	277	289	52.5	3	1.07
10.0	248	265	71.5	6	1.44
25.0	245	250	74.0	12	1.26

Notes: Heating rate = 10 deg/min, sample mass = 100 mg.

BVP to the AC with the subsequent increase in the proportion of this species up to 25.0 wt.% reduces the initial temperature of the active decomposition from 300° to 295° and 245°, respectively. In this case the W_{max} value increases from 29.0 to 74.0 mg/min. The total exothermic heat effect decreases to nearly one third of the original value.

Interestingly, on heating AC in air the heat evolution in the temperature interval between 100 and 310° is low (0.53 kJ/g). (The thermal effects were calculated by the method reported elsewhere [4]). The mass losses in this region are also insignificant. Therefore the exothermic effect can be related to polymer oxidation and, perhaps, to the partial formation of unsaturated carbon-carbon bonds resulting from the intramolecular dehydration/deacetylation reactions. The heat is evolved mainly in the course of the active thermooxidative polymer decomposition (over 300°).

In this temperature range the endothermic bond breakage and evaporation of the volatile compounds competes with the exothermic reactions consisting in the formation of unsaturated carbon bonds, crosslinking as well as the occurrence and oxidation of the carbonized products, i.e., coke.

The accelerated mass loss of the modified AC samples, the shift of the active decomposition stage towards the low temperature region is responsible for the less pronounced exothermic effects in the range below 310°. Thus, for the AC containing 25.0 wt.% BVP the specific heat evolution at 100–255° is 0.09 kJ/g, i.e., six times lower than that for the starting polymer. The total heat evolution during AC decomposition is especially distinct for the addition of 0.5–5.0 wt.% BVP.

It should be noted that in the high-temperature range the modified AC samples show a slower mass loss. Therefore the decreasing exothermic effect in this region can be attributed to the inhibiting action of the appearing phosphorus compounds on the oxidation of the carbonized decomposition product.

The thermal decomposition of AC was studied in detail elsewhere [5]. In the absence of a gaseous oxidant the competing reactions of dehydration, deacetyla-

Table 2 The effect of bis(2-chloroethyl)1-bromovinyl phosphonate on the thermal decomposition of acetylcellulose in inert atmosphere

BVP content, wt.%	$T_{i.d.}$, °C	T_{max}, °c	W_{max}, wt.%	ω_{700}, wt.%
—	325	425	27.3	4.0
5.0	290	370	47.0	12.5
25.0	285	365	69.5	16.5

Note: heating rate: 100 deg/min, sample mass 2–4 mg.

tion, macromolecule chain breaking and heterocycle destruction were observed. The predominant route of the process is controlled by the conditions and energy pattern of the reactions under study.

The initiation and active decomposition temperature interval for the modified AC in inert atmosphere, as in the case of air, shifts towards lower temperatures, as compared with the initial polymer (Table 2). The decomposition of the modified AC samples in inert atmosphere is distinguished by the formation of a larger amount of the carbonized product (coke) at a high temperature. The coke yield at 700° grows most significantly as compared with the starting polymer if 5.0 wt.% BVP is added. The yield of the carbonized residue was noted to depend on the sample mass and it was also found that the diffusion and mass transfer of the decomposition products play a certain role in the way the secondary syntheses of the carbon framework occur.

Thus, for example, at a heating rate of 5 deg/min and sample mass of 50 mg the coke yield is nearly 3 times that in the case of a heating rate of 100 deg/min and a mass of 2–4 mg.

When the heating rate increases from 5 to 100 deg/min the AC begins decomposing at 325 instead of 280°.

A similar picture showing an increase in the characteristic decomposition temperatures with the heating rate is also observed for the modified AC samples. For small samples (2–4 mg) the rate of the mass loss for the AC samples containing 5.0 wt.% BVP in isothermal conditions within 250–270° is described by a first-order equation, with the constant $K = 3.7 \cdot 10^{13} \exp{(E/RT)}$, (min^{-1}), where E equals -33.4 kJ/g.

An analysis of the kinetics of water and acetic acid evolution in the decomposition of modified AC under isothermal conditions suggests that the modification favours the intramolecular reactions of substituent elimination and formation of unsaturated carbon-carbon bonds.

As can be seen from Fig. 2, the deacetylation rate at 250° for the AC containing
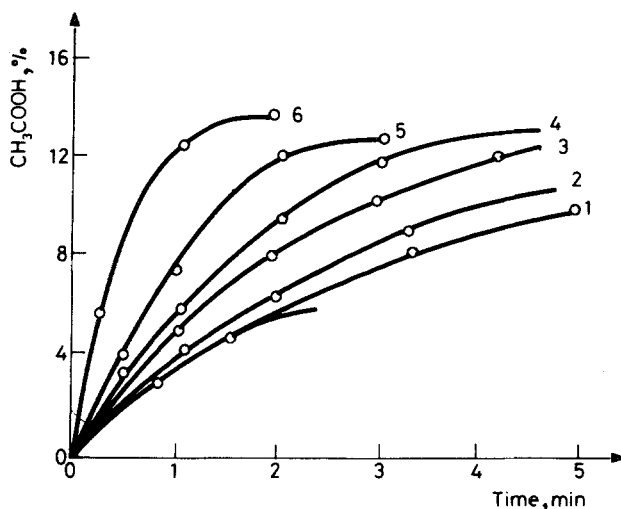
Fig. 2 Kinetic curves for acetic acid evolution when heating AC containing 50 wt.% BVP in air.
1 – 250 °C, starting AC; 2 – 220 °C; 3 – 235 °C; 4 – 250 °C; 5 – 260 °C; 6 – 270 °C

5.0 wt.% BVP is higher than that for the initial polymer. The effective energy of AC deacetylation as a result of the modification decreases from 135 to 80 kJ/mol.

Along with the substituent elimination from the modified AC, during isothermal decomposition there occurs also an accelerated breaking of the main polymer bond and the heterocycles to give rise to carbon oxides. On heating the modified AC at a rate of 5 deg/min carbon oxides began appearing at temperatures 40–50° lower than for the starting AC (Table 3).

Typically, the temperature marking the onset of the intensive hydrogen evolution, which is usually involved in the aromatization of the AC decomposition products, as a result of this modification also shows a drop from 470° to 420°.

In Figs 4 and 3 are shown mass spectra of the BVP, a modified AC sample and high-boiling decomposition products appearing in the course of heating of the

Table 3 The effect of BVP on the thermal destruction and products of acetylcellulose decomposition

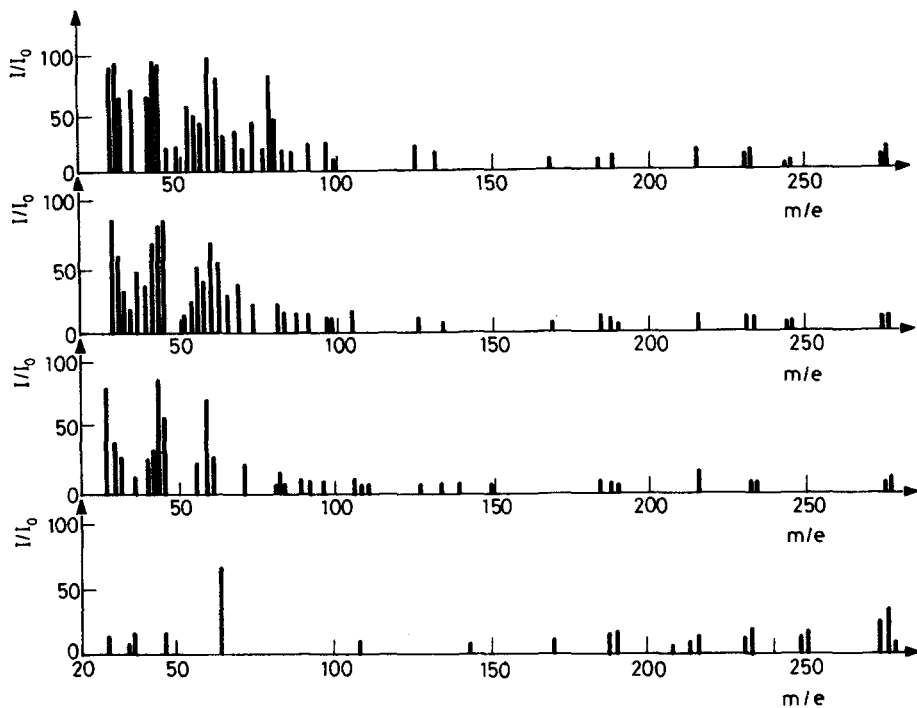| BVP content, wt.%	$T_{i.d.}$, °C	Amount of coke residue (700 °C), wt.%	Initial temperature of gas evolution, °C				Total amount of gases produced, mol/base-mol			
			CH_4	H_2	CO	CO_2	CH_4	H_2	CO	CO_2
—	270–280	15.0	300	460	300	300	0.47	0.92	0.61	1.66
0.5	195–200	22.0	300	410	260	280	0.25	0.61	1.49	0.38
5.0	120–125	70.0	355	440	250	240	0.03	0.17	0.62	0.22
25.0	125–130	74.0	385	440	240	240	0.03	0.65	0.65	0.30

Fig. 3 Mass spectra of BVP (a) and containing 5.0 wt.% BVP when heated to: b – 200 °C; c – 250 °C; d – 300 °C
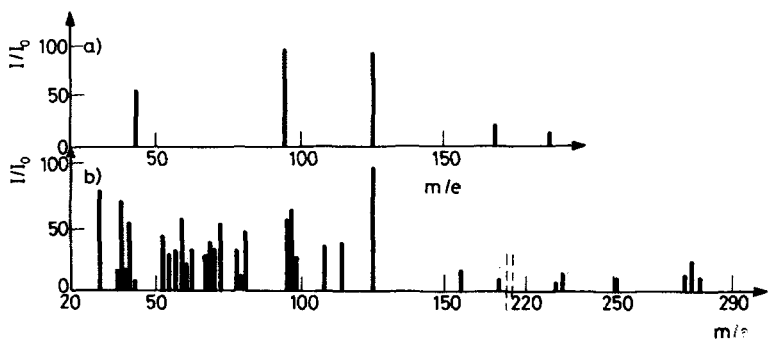

Fig. 4 Mass spectra of high-boiling destruction products of AC (a) and modified AC (b) at 300 °C in inert atmosphere

modified AC in inert atmosphere at 300° for 15 min. For comparison a mass spectrum of high-boiling initial AC decomposition products, obtained under similar conditions, is presented. At the high instrument sensitivity the BVP mass spectra show the presence of BVP microions (m/e 309–311) as well as chloroethyl radical ions (m/e 63) and ions appearing as a result of the elimination of the chlorine, bromine atoms and one or two chloroethyl, vinylbromide or chloroethoxy groups from the BVP.

The mass spectra of the modified AC heated to 200° contain acyl and acetyl ions (m/e 43 and 59, respectively) as well as carbon oxide ions (m/e 28 and 44, respectively). Ketone and oxymethyl molecule ions (m/e 42 and 31, respectively) are present as well. With increasing temperature the intensity of the peaks with m/e 168, 126 and 95 grows. These peaks can be assigned to the ions of dehydrated and partially deacetylated anhydro-glucopyranose derivatives. Moreover, the decomposition products showed the presence of HCl and HBr peaks with m/e 36, 37 and 80, 81, respectively.

The mass spectrum of high-boiling decomposition products of the modified AC, condensing at room temperature, as distinct from that of the similar product of the starting AC, contains BVP ions. The peak with m/e 81 (HBr) is distinguished by high intensity. This suggests that at 300° the BVP units undergo active destruction and evaporation. In the carbonized residue of the modified AC, formed upon polymer destruction in inert atmosphere at 430° for 15 min, phosphorus was found to be practically absent.

The mass spectra of the high-boiling modified AC decomposition products also show the presence of ions of dehydrated and partially deacetylated glucopyranose anhydroderivatives (m/e 126, 95, respectively).

Thus, the process of substituent elimination is accompanied by the breakage of the macromolecular AC chains.

The data obtained suggest that the products of the thermal decomposition of BVP-modified AC undergo the same reactions that take place during the decomposition of the starting polymer. However, the dehydrohalogenated BVP units within the Ac macromolecular structure as well as the mesomeric and steric effects of these units influence the elimination of side glycopyranose cycle substituents. It is known [6] that protic and aprotic acids exert a promoting effect on the monomolecular sugar and cellulose dehydration.

The heterolytic decomposition of the macromolecular modified AC chains occurs by the law of chance to give rise to high molecular mass fragments. Their depolymerization is hindered by formation of unsaturated groups prone to mutual interactions. Thus the modification under study favours the reactions of crosslinking and carbonization as well as the appearance of less inflammable decomposition products.

Conclusions

Various methods of thermal analysis were used to study the destruction of BVP-modified acetylcellulose. The modification is shown to favour the water and acetic acid elimination as well as the formation of a nonvolatile carbonized residue.

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Zusammenfassung — Mittels TG-, DTA-, Pyrolyse-GC- und MS-Methoden wurde der Einfluß von bis(2-chlorethyl)-1-bromvinylphosphat auf den thermischen und thermooxidativen Abbau von Azetylzellulose untersucht. Bei Erhitzen der BVP-haltigen AZ an Luft findet die Initiierung und die intensive Zersetzung des Polymers bei niedrigeren Temperaturen statt. In inerter Atmosphäre kann man mit zunehmendem BVP-Gehalt außerdem ein Absinken des charakteristischen AZ-Zerfalles beobachten. Die Veränderung verursacht die Beschleunigung von Dehydratation und Deazetylierung. Die effektive Energie für die Aktivierung der Deazetylierung (zwischen 220 und 270 °C) sinkt bei Zusatz von 5.0 Gew.-% BVP von 135 auf 80 kJ/mol. Außerdem wurde bei stufenweisem Aufheizen auf 300 °C und bei einer Aufheizgeschwindigkeit von 10 grd/min eine vergleichende Untersuchung der Massenspektren der modifizierten AZ durchgeführt.

Резюме — Предложен численный метод расчёта составов сосуществующих растворов по заданной зависимости состава одного из них от температуры. Термодинамические свойства фаз могут при этом быть неизвестными. В отличие от ранее использовавшихся подходов допускается применение на промежуточных стадиях расчёта фиктивных термодинамических функций веществ. Возможности метода показаны на примерах построения кривых солидуса на фазовых диаграммах двухкомпонентных систем калий-рубидий, калий-цезий, цезий-рубидий из экспериментальных данных о ликвидусе.