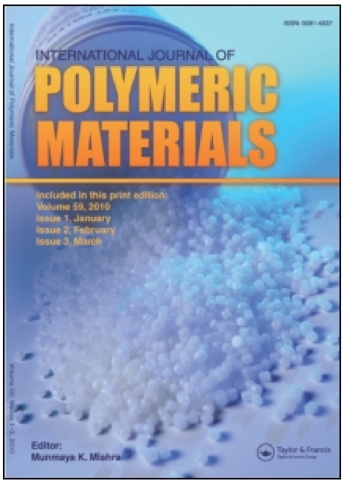

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Thermal Analysis of Products Obtained upon Ozonolysis of Polybutadiene Rubbers in Solution

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The thermochemical properties of ozonides, prepared from two polybutadiene rubbers of different structure, are studied via differential scanning differential scanning calorimetry. An estimation is made of the enthalpy of the thermal decomposition (≈370 kJ/mol), the activation energy (90–120 kJ/mol) and the reaction order (≈0.73). On the basis of the differences in the respective values of some parameters characteristic of the kinetics of the thermal decomposition, it is suggested that the cis-ozonide species exhibit higher thermal stability in comparison with the trans-form.

KEY WORDS Ozonolysis, polybutadiene, thermal analysis

INTRODUCTION

It is well known that ozonides are the major product of olefin ozonolysis in solution. The formation of other compounds containing peroxide bonds is also possible during the reaction: polymer ozonides, dimere and polymer peroxides.[1] By contrast with different types of organic peroxides, the thermochemical properties of the above-mentioned compounds have not been investigated practically. This work describes a study of the thermal decomposition of products of the peroxide type obtained upon ozonolysis of two polybutadiene rubbers of different structure in solution.

EXPERIMENTAL

Commercial samples of SKD and Diene 35 NFA rubbers are used. Their structure, determined by means of 1H NMR spectroscopy, is as follows (%): (i) SKD - 1,4 cis - 93; 1,4 trans - 3; 1,2 - 4; (ii) - Diene 35 NFA - 1,4 cis - 47; 1,4 trans - 42; 1,2 - 11.

Polymer solutions of 10 ml volume and 1 g/100 ml concentration of CCl_4 are ozonized in a bubbling reactor at 293 K to a 17–20% conversion of the C═C bonds. An ozone-oxygen gas mixture with ozone concentration of 1.10^{-4} mol/l is passed through the solution at a rate of 1.6×10^{-3} l/s. After finishing the reaction, the solvent is removed by evacuation.

The differential scanning calorimetry (DSC) study is performed on a Mettler FP 800 instrument in a stream of Ar at the rate of 60 ml/min.

The values of the activation energy E and the reaction order n of the thermal decomposition are estimated from the slope and the intercept, respectively, of the dependence (1) suggested by V. Gorbachev[2]:

$$\frac{\ln h/h_s}{\ln(1 - \alpha)/(1 - \alpha_s)} = (E/RT_s)\frac{T - T_s}{T \ln(1 - \alpha)/(1 - \alpha_s)} + n \tag{1}$$

where α_s is the conversion degree, h is the peak height and T is the temperature in K. The s index refers to values of the DSC peak maximum.

RESULTS AND DISCUSSION

The thermal decomposition of ozonolysis products is studied in the 323–453 K range. Practically no thermal effects are detected in the thermogram with the nonozonized samples. In our previous studies of ozonolysis of polybutadiene elastomers it has been shown that ozonides are mainly formed under the conditions applied to SKD and Diene NFA ozonolysis. The amounts of other products of the peroxide type are negligibly small in comparison with those of the ozonides.[3,4]

The presence of only one peak in the DSC thermograms of the two rubbers, even at low heating rates, is also a serious argument in favor of the claim that considerable quantities of functional groups, possessing different thermochemical properties from those of the 1,2,4-trioxalanes, are missing. Therefore, it is reasonable to expect that the results of the DSC study presented in Table I are mainly concerned with the thermochemical properties of the ozonides. It is seen that the respective values of ΔH_1 with SKD are about 25% higher than those with Diene NFA. These results correlate with reference data according to which the ozonide yield from the cis-double bonds is higher in comparison with that from the trans-

TABLE I

DSC analysis of products obtained upon ozonolysis of polybutadiene rubbers

Rubber heating rate (°C/min)	SKD			Diene 35 NFA		
	1	2	5	1	2	5
ΔH_1 (kJ/mol O_3)	274	338	355	216	260	276
ΔH_2 (kJ/mol ozonide)		370	370			
T_s (K)	402.3	409.3	420	398.7	406.2	417
α_s	0.65	0.67	0.68	0.65	0.70	0.75
E (kJ/mol)	99.9	105.5	121	91.2	93.7	109.6
n	0.71	0.73	0.79	0.73	0.73	0.73

double bonds.[1] If the respective values of ΔH_1 are used together with the ratio ozonide (mol)/reacted ozone (mol) $\approx$ 0.89, determined by chemical analysis upon the SKD ozonolysis,[3] one find that 1 mole of ozone gives about 0.67 moles of ozonides with Diene NFA. Recalculation of the ΔH_1 values relative to the amounts of ozonides allows us to evaluate the enthalpy of the thermal decomposition of the 1,2,4-trioxalanes ($\Delta H_2 \approx$ 370 kJ/mol).

It is seen in Table I that $n \approx 0.73$. The values of E are between 91 and 121 kJ/mol, while those of T_s are in the 398–420 K range. Concerning the samples of SKD, one can note that the values of E are about 9–11% and of T_s about 3 K higher than the respective values of Diene NFA. Discussing these differences, we bear in mind that two isomer forms of the ozonides occur: cis and trans. According to the current ideas about the mechanism of ozonolysis, cis C=C bonds give predominantly cis-ozonides whereas more trans-ozonides are formed from trans C=C bonds.[1] Furthermore, this tendency is enhanced by increasing the volume and number of the substituents. Therefore it is quite possible that the differences in T_s and E, indicated above, are due to a higher thermal stability of the cis-1,2,4-trioxalane.

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