A Study of Thermal Degradation Kinetics and Mechanism of Vinyl Acetate and Itaconic Acid Copolymers

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Synopsis

Vinyl acetate and itaconic acid copolymers, obtained by radical copolymerization using single and continuous methods of itaconic acid addition, the amount of the acid being up to 8.5 mol %, were characterized by DTA, TG, DTG, and DSC. Using IR spectroscopy for both types of copolymers, it was proved that cyclodehydration takes place in the temperature range 130–230°C. In the range 230–350°C, processes of decarboxylation of cycloanhydrous and carboxylic groups and splitting of acetic acid proceed at the same time, followed by destruction of the polyene structures formed. The rate of thermal degradation depends both on the amount and distribution of itaconic units in the macrochain. The kinetic parameters of the process were calculated.

INTRODUCTION

The thermal degradation of polyvinylacetate starts at 220–250°C.[1] The process rate does not depend on the molecular weight. The mechanism of the thermal degradation was established. Acetate group splits off the main chain in the form of acetic acid. The double bond thus formed activates the nearby acetate group, which results in the formation of polyene structures. These structures destruct at higher temperatures.

The preparation of copolymers of vinyl acetate (VA) and itaconic acid (IA) was experimentally confirmed.[2] Depending on the method of addition of the second comonomer, random copolymers (at continuous IA addition) and a mixture of copolymers and polyvinylacetate homopolymers (at single IA addition) were obtained. In the latter case macromolecules containing IA-rich segments were also obtained due to chain transfer.

The object of this study is to give an explanation regarding the influence of the amount and way of distribution of itaconic units in the macromolecule on the kinetics and mechanism of thermal degradation of VA and IA copolymers.

EXPERIMENTAL

Thermal degradation of polymer products, obtained by copolymerization of VA and IA in methanol solution at temperature of 60°C, the monomer/solvent

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ratio being 2:1, was studied. The process was initiated by bis(4-tert-butyl cyclohexyl)peroxydicarbonate (0.2%). IA was added in two different methods —single, at the beginning of the process, and continuously throughout it. The IA was in the form of methanol solution in an amount from 2 to 8.5 mol %. Copolymers were isolated by benzene extraction of the possibly formed polyvinylacetate homopolymers, followed by reprecipitation with water from methanol solution and drying at 50°C under vacuum.

Thermal investigations were performed under air on a Paulik-Erdey (Hungary) derivatograph over a temperature range of 25–245°C at heating rate of 5°C/min and on a Perkin-Elmer DSC-4 under nitrogen at a scanning rate of 10°C/min. IR spectra were recorded on Carl Zeiss' Spekord 75IR spectrophotometer using KBr tablets.

The process kinetic parameters were determined from the DSC curves by multilinear regression based on the following equation[3]:

$$\frac{dm}{dt} = K_0 \exp(-E_a/RT)(1 - m)^n$$

where K_0 = preexponential factor from the rate constant equation, m = mass of the starting polymer, E_a = energy of activation, R = gas constant, T = absolute temperature (K), and n = order of the destruction reaction. The

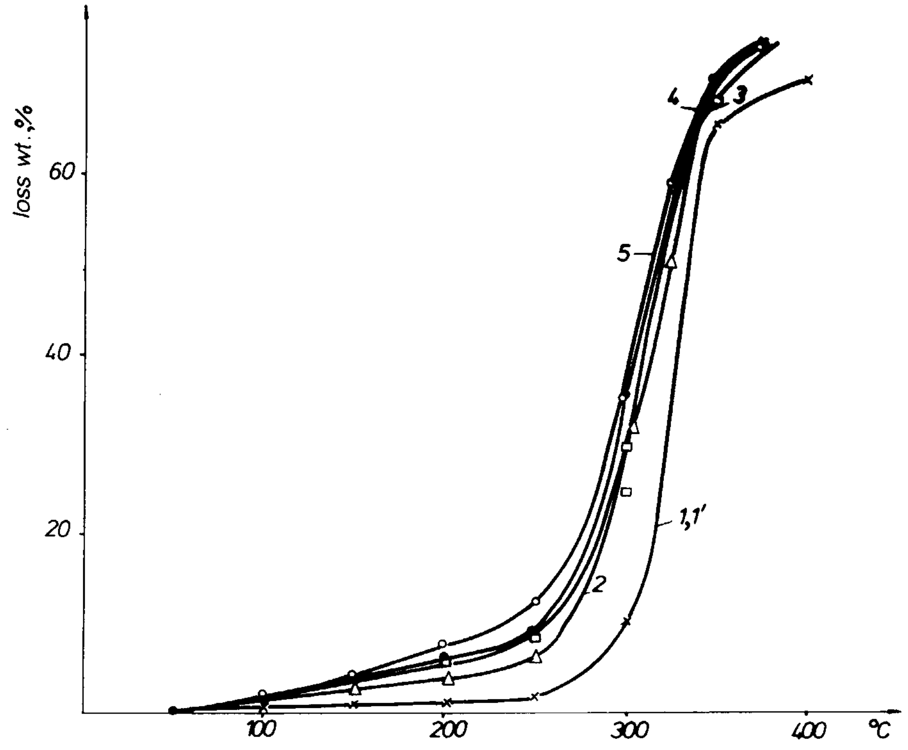
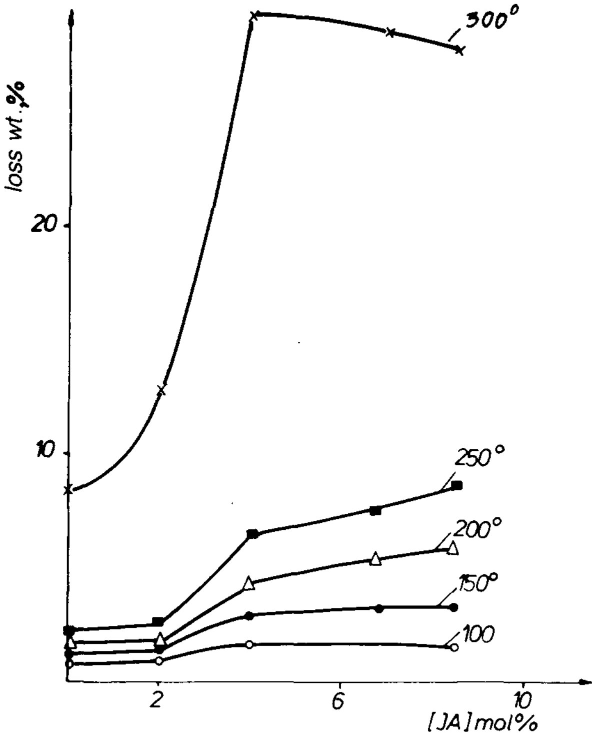


Fig. 1. Polymer weight loss vs. temperature (1) without IA; (2, 3) single addition of 4.5 and 8.5 mol % IA, resp.; (4, 5) continuous addition of 4.5 and 8.8 mol % IA, resp.



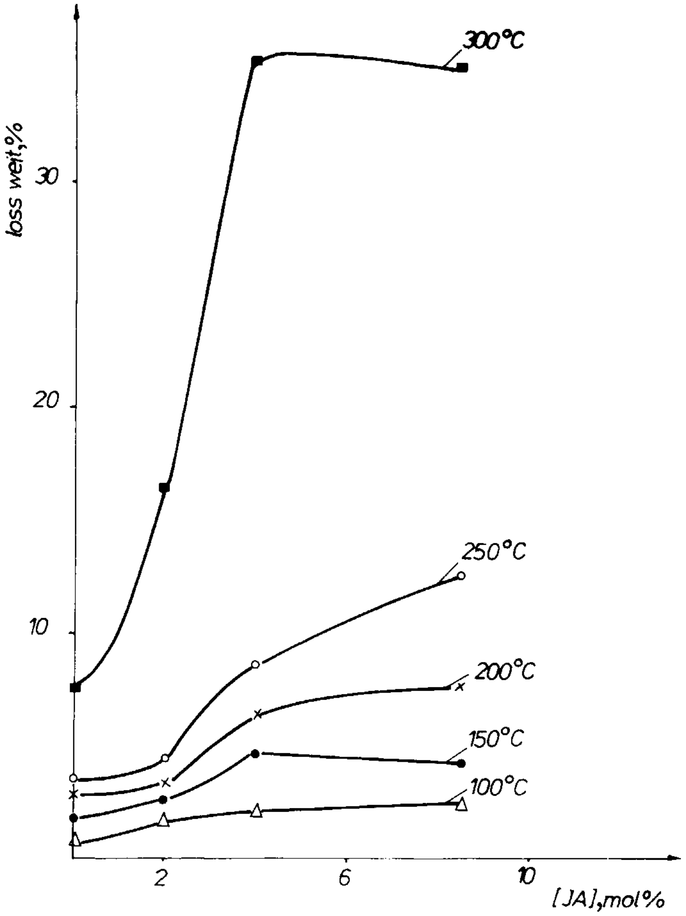
(a)

Fig. 2. Dependence between weight losses and IA amount at 100, 150, 200, 250 and 300°C: (a) single IA addition; (b) continuous IA addition.

variation of *m* values is determined through the variation of the enthalpy of the system.

RESULTS AND DISCUSSION

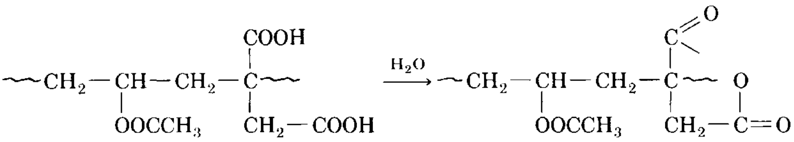
Thermogravimetric analysis, performed at a heating rate of 5°C/min, showed substantial changes in the mass of the analyzed samples at temperatures above 100–150°C (Fig. 1). The influence of the content of itaconic units in the copolymer on its thermal stability is more significant in the temperature range from 200 to 300°C [Figs. 2(a) and 2(b)] and is more clearly expressed in the case of copolymers with random distribution of itaconic units. The process of thermal degradation of polyvinylacetate (PVA) homopolymer and copolymer containing 8.5 mol % IA was studied. The experiments were run in the temperature range 20–1000°C at a heating rate of 40°C/min [Figs. 3(a) and 3(b)]. The processes of acetic acid splitting and of breaking of polyene structures alternate in a steplike pattern for the homopolymer, while for the copolymer they take place at the same time. On the DTG curve of the copolymer two more relatively small peaks were observed, which are in the low temperature range. The first one, having a maximum value at around 60°C, is due to the release of residual solvent. We presumed that the weight losses in the range 130–230°C could be attributed to inner dehydration



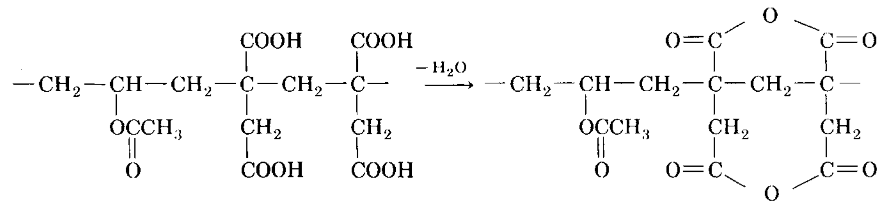
(b)

Fig. 2. (*Continued from the previous page.*)

according to the following Schemes:



Scheme 1



Scheme 2

The DSC curves for products, obtained by both methods of IA addition, with 4 and 8.5 mol % IA, show that the intensity of the heat effect in this

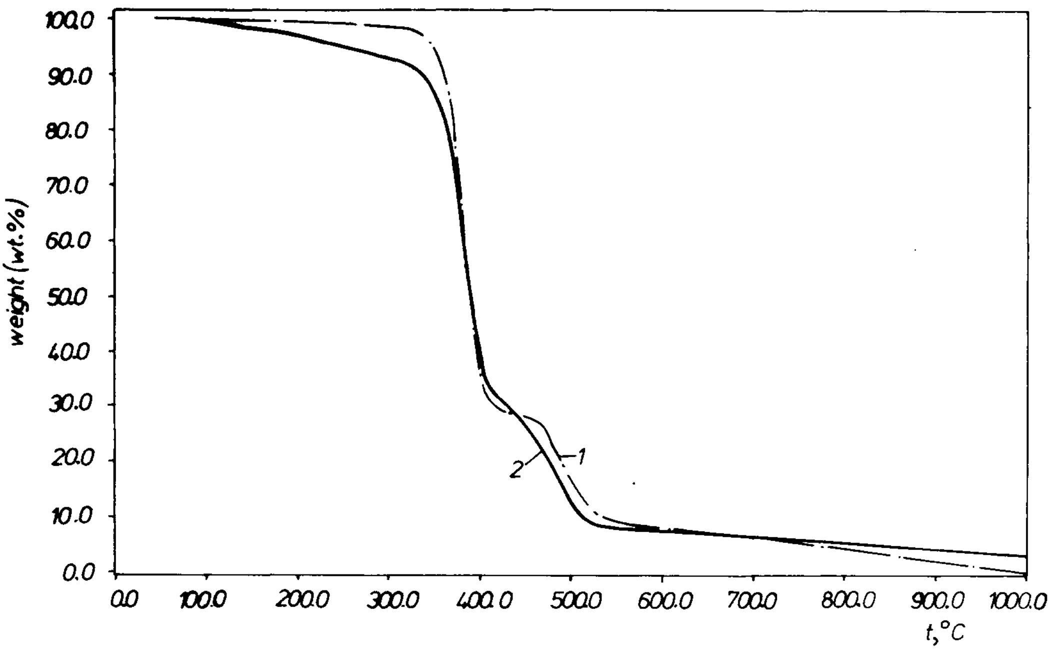


Fig. 3(a). Termogravimetric curves: (1) polyvinylacetate homopolymer; (2) VA–IA copolymer (8.5 mol % IA).

range increases with the increase of the amount of IA and has endothermic character [Fig. 4(a)]. The IR spectra of samples, treated up to 130 and 190°C and of untreated ones, obtained in the presence of 8.5 mol %, agree with our assumption that cyclodehydration takes place (Fig. 5). The spectra for both methods are identical. On the spectrum of the sample, treated at 130°C, bands with peaks at 1780 and 1862 cm^{-1} are only slightly noticeable, while for that treated at 190°C they are clearly expressed. The existence of these bands is assigned to oscillations of carbonyl groups in the cyclic anhydrate. In the 2500–2800 cm^{-1} range, the band, corresponding to absorption of —OH from the carboxyl group, gradually disappears. This confirms the proceeding of cyclodehydration, accompanied by the formation of five-member, and six- and eight-member cyclic anhydrous structures according to Scheme 1, and Scheme 2, respectively.

Based on the DSC curves of the samples, obtained by both methods and using IA in an amount from 2 to 8.5 mol %, the kinetic parameters of the cyclodehydration process were calculated. The results are summarized in Table I.

The different energies of activation, obtained for the two methods of IA addition, confirm the difference in the structures of the corresponding products. It is very likely that the building up of a number of itaconic units next to one another leads to the formation not only of five-member anhydrous rings but also of six- and eight-member cycles as a result of the dehydration. Due to the relatively low concentration of the latter, no splitting of the characteristic bands is observed on the IR spectra. After being treated at 220°C, the samples retain their white color and are soluble in methanol, which evinces the proceeding mainly of intramolecular cyclodehydration. The absence of bands

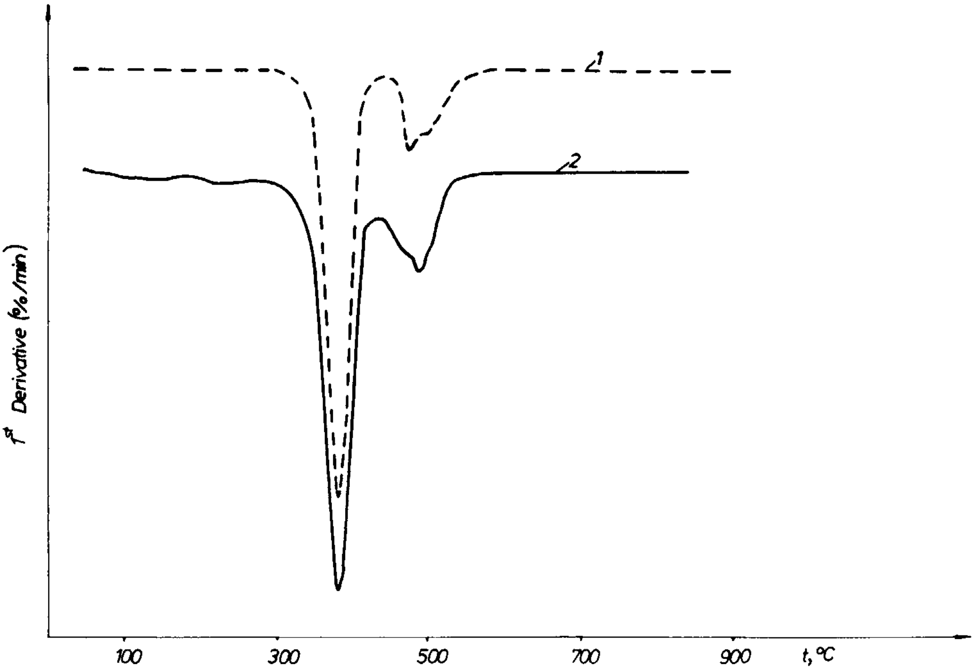
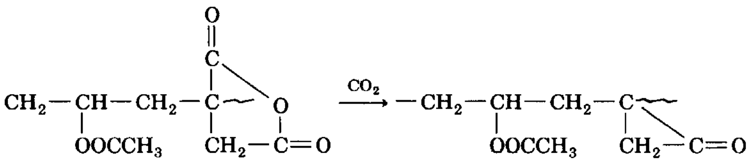


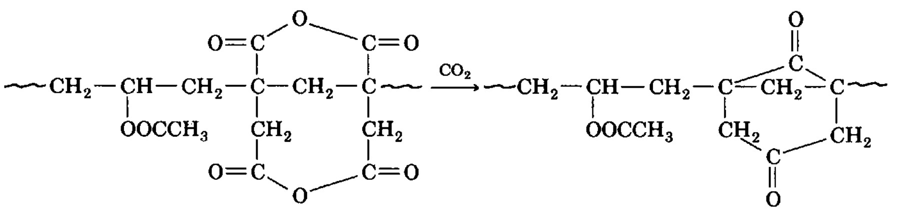
Fig. 3(b). DTG curves: (1) polyvinylacetate homopolymer; (2) VA–IA copolymer (8.5 mol % IA).

characteristic for keto groups shows that in this temperature range no decarboxylation by the cycloanhydrous structures takes place.[4]

In the 240–290°C range intensive endo effects are observed, which are due to the splitting of acetic acid from the macrochains [Fig. 4(b)]. A slight decrease of the initial degradation temperature in comparison to the corresponding homopolymer products as well as broadening of the endo peak are observed. This is assigned to the overlapping of the two processes—decarboxylation of cycloanhydrous structures and splitting of acetic acid and formation of double bonds in the main chain. The decarboxylation proceeds according to Scheme 3 for continuous IA addition and according to Schemes 3 and 4 for single IA addition at the beginning of the process.



Scheme 3



Scheme 4

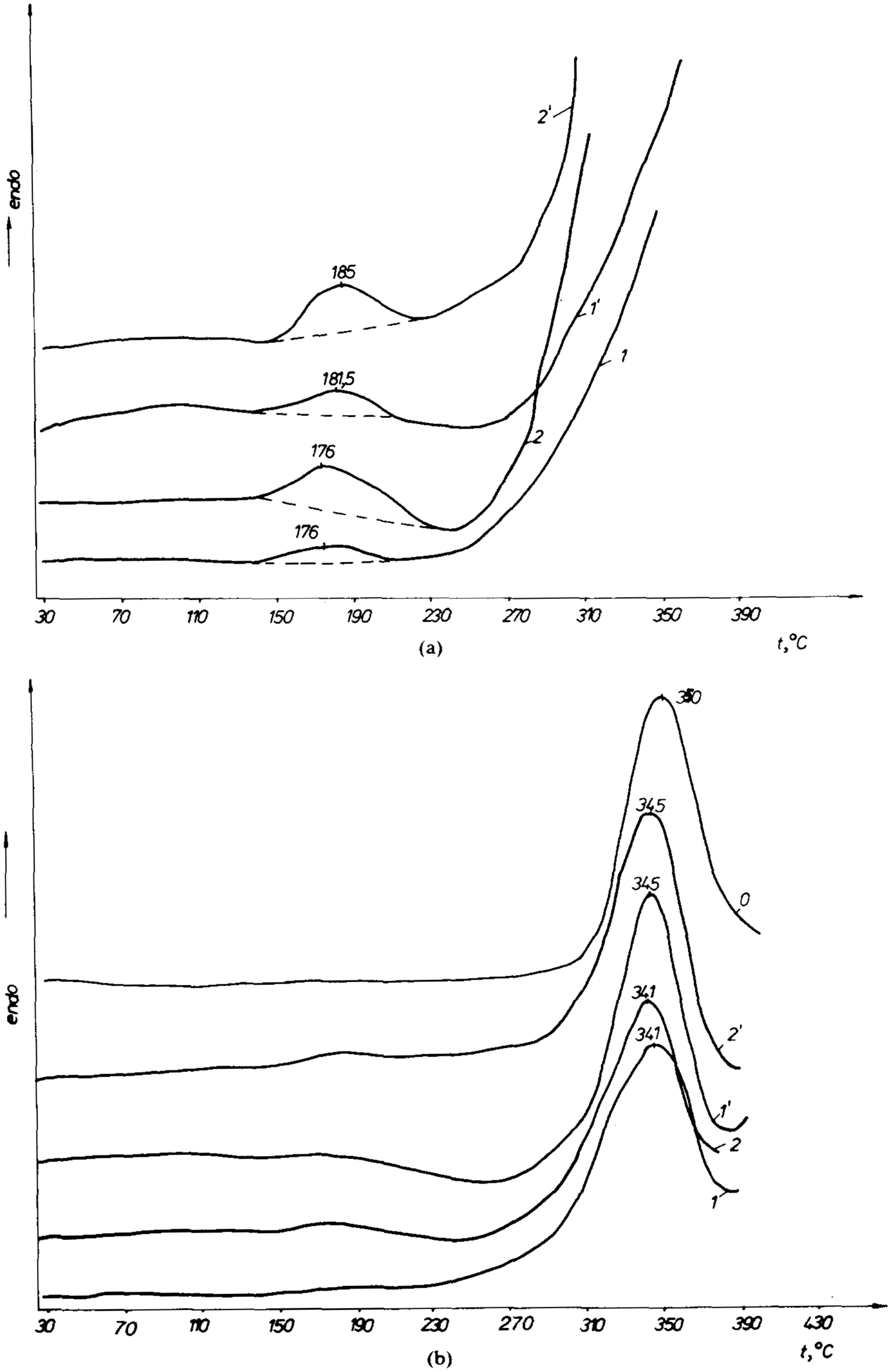


Fig. 4. DSC curves for copolymer products: (0) without IA; (1, 2) continuous addition of 4 and 8.5 mol % IA, resp.; (1', 2') single addition of 4 and 8.5 mol % IA, resp.; scanning rate = 10°C/min. Temperature range (°C): (a) 30–310; (b) 30–390.

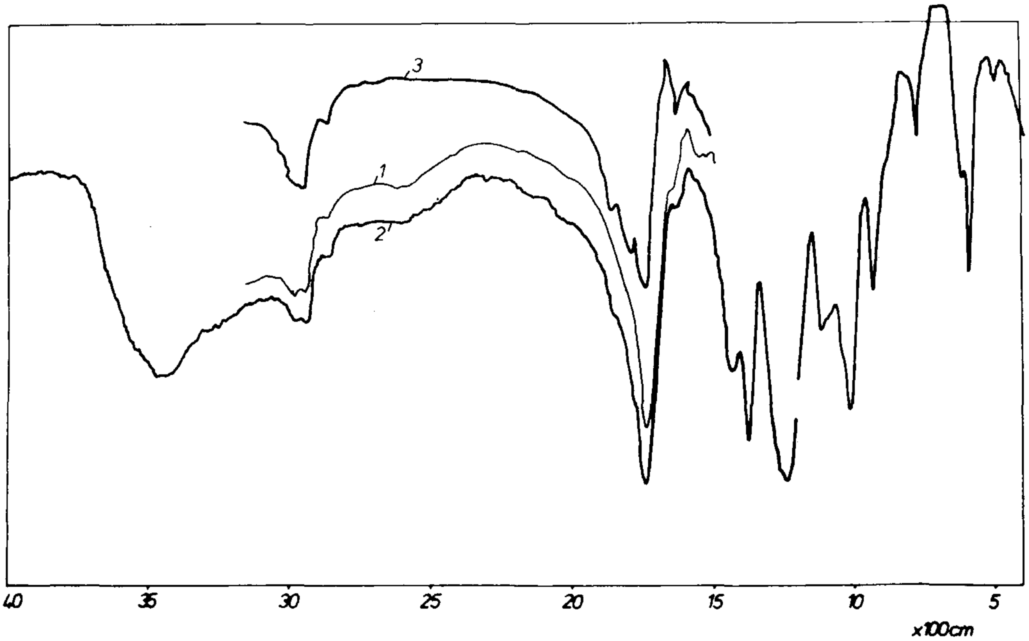


Fig. 5. IR spectra of copolymers (8.5 mol % IA): (1) untreated sample; (2) treated up to 130°C; (3) treated up to 190°C.

TABLE I
Kinetic Parameters of Dehydration Process

Method of IA addition	K_0 (L/s)	E_a (kJ/mol)	n
Single	27	109–128	1.04–1.40
Continuous	21	85	1.04–1.50

The total energy of activation of the processes, taking place in the temperature range of 240–380°C, was calculated and found to be 170–180 kJ/mol and the order of the reaction, 1.0–1.2.

The results obtained in our study show that the inclusion of itaconic units in the polymer chain for the amounts studied does not significantly interfere with the thermal stability of the product at temperatures in the range 100–150°C, especially for concentrations up to 2–3 mol %. The usual performance temperatures of vinyl acetate and vinyl alcohol polymers are much lower.

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