

CCA-1715

YU ISSN 0011-1643

UDC 547+541.64

Original Scientific Paper

Thermal Degradation of Poly(Dimethyl Itaconate)

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Received July 7, 1986

This article investigates the thermal degradation behaviour of poly(dimethyl itaconate), performed by TG and other degradation procedures, in order to establish the kinetics of the reaction and the probable mechanism of thermal degradation. From TG curves and from GC—MS observations, the occurrence of a deziping reaction, producing predominantly monomer, was observed, preceded by carbon-carbon bond scissions in the lateral substituents. The results are compared with those known from the literature for the structurally similar poly(methyl methacrylate).

INTRODUCTION

Increased attention has been paid in recent years to the investigation of polymers of itaconic acid esters, both from the fundamental and practical points of view. With properties similar to those of the structurally related poly(acrylates) and poly(methacrylates), interest in these polymers is justified also due to the fact that itaconic acid and also several other reactants for the monomer syntheses can be obtained by fermentation of agricultural wastes.¹ A review of the literature referring to the fundamental problems relating to the structure and properties in function of the composition and size of the two very similar lateral substituents in the monomer residue of the chain is presented elsewhere.² However, to the best of our knowledge, no attention has been so far devoted to problems of thermal degradation, in spite of its significance for practical applications.

The present investigation is an initial attempt in the field trying to establish the thermal degradation behaviour of the best known polymer of this group, poly(dimethyl itaconate) (PDMI), at the same time also the first member of the polymer homologous series of poly(di-*n*-alkyl itaconates). In the near future more attention will be paid also to poly(dicyclohexyl-) and poly(diphenyl itaconate), as parent polymers of polymer homologous series of itaconates with cyclohexyl- and phenyl ester substituents.

EXPERIMENTAL

PDMI represents a colourless brittle transparent film-forming product of high molar mass with T_g well above ambient temperature.³ The sample investigated was obtained by free radical polymerization of the monomer with α,α' -azobis(isobutyronitrile) initiator in bulk and purified by reprecipitation from benzene/methanol.⁴ Some of the experiments were performed with unfractionated polymer of $\overline{M}_v = 4.5 \times 10^5$ g/mol, calculated from intrinsic viscosity values in benzene.⁴ Several other experiments for establishing the effect of degradation on the molar mass

distribution (MMD) were performed with polymer fractions with molar masses ranging from 4 to 8×10^5 g/mol and $\overline{M}_w/\overline{M}_n = 1.5-2.0$ obtained by GPC on a Knauer instrument with computer data processing, calibrated with PMMA samples of very narrow distribution (Röhm, F. R. Germany) with acetone as an eluent. Nitrogen (Tehnogas, Yugoslavia) or argon (Linde, F. R. Germany) of highest purity were used as carrier gases in TGA and pyrolysis, after passing through appropriate filters to remove traces of moisture and oxygen.

Thermogravimetric measurements were performed on a Perkin-Elmer TGS-2 instrument with 5–7 mg samples of powdered polymer. The carrier gas flow was 15 ccm/min. Non-isothermal experiments with heating rates of 0.625, 2.5, 10, 20 and 40 °C/min were performed in the range of 30°–350 °C at 10 °C intervals by rapidly heating the sample to the desired temperature and maintaining it for a period of 60 minutes.

TG data were analyzed by several methods proposed in the literature for determining kinetic parameters, including the methods of Freeman-Carroll⁵ and Flynn-Wall⁶. However, the former method yielded great scattering of the results and, therefore, the latter was adopted as the most convenient for analyzing non-isothermal TG data. This proved to be a fast and simple method enabling the determination of thermal degradation activation energies on the basis of three or more TG runs performed at different heating rates. According to the definition, the conversion, C , is equal to the mass of the decomposed material, divided by the total loss of mass when the temperature (T) or time (t) tend to infinity. In differential form, the rate of decomposition can be expressed as:

$$\frac{dC}{dT} = \left(\frac{A}{\beta} \right) f(C) \exp \left(- \frac{E_a}{RT} \right) \quad (1)$$

where A is the pre-exponential factor, β the heating rate, E_a the activation energy, R the universal gas constant, T the absolute temperature and $f(C)$ a function of the conversion. If one assumes that A , $f(C)$ and E_a are independent of T and A and E_a independent of C , the following integral can be written:

$$F(C) = \int_0^C \frac{dC}{f(C)} = \int_{T_0}^T \exp(-E_a/RT) dT = \left(\frac{AE_a}{\beta RT} \right) \cdot p \left(\frac{E_a}{RT} \right) \quad (2)$$

where p is a function of E_a , introduced to simplify the calculation.⁶ Equation (2) can be obtained in a form suitable for linear plotting:

$$\log F(C) = \log \frac{AE_a}{RT} - \log \beta + \log \left[p \left(\frac{E_a}{RT} \right) \right] \quad (3)$$

Introducing the approximation proposed by Doyle⁷, for $E_a/RT > 20$:

$$\log p(E_a/RT) = -2.315 - 0.457 E_a/RT \quad (4)$$

into equation (3), and differentiating at constant conversion:

$$d \log \beta / d(1/T) = -(0.457/R) E_a \quad (5)$$

From thermograms obtained at several heating rates, the temperatures for any selected conversion can be obtained, and after introducing these values into the $\log \beta$ vs. $(1/T)$ plot, activation energies are obtained from equation (5). The procedure should be repeated for several values of conversion: the consistence of the E_a values obtained confirms the independence of E_a on T and C .

Isothermal TG data were analyzed by the standard differential method in its general and special form, based on the assumption of the first order of the reaction. This method yields rate constants at the reaction temperatures as well as the reaction order n . If one assumes that rate constants are temperature dependant according to the Arrhenius equation, then from TG runs at several temperatures the activation energy of the process can be determined. This is an alternative method for the determination of E_a , obtainable also from the Flynn-Wall method.

In order to investigate volatiles, amounts of 50–70 mg of polymer were degraded isothermally in a simple set-up containing polymer in a cylindrical

Pyrex tube, placed in a small furnace with precise temperature control. During the experiment the tube was flushed with a stream of argon, the heating time for obtaining the desired temperature was about 1 minute, experiments lasting from 2 to 30 minutes were performed in the range of 250 °C to 350 °C. The condensed volatiles were analyzed by a GC—MS combination, using a Varian GC Model 3700 + MS Model MAT 44 system with an OV-1 column with methyl silicon of 25 m length and 25 μ m film thickness. Other parameters of the system were the following: $T_{inj} = 245$ °C, $t_{fur} = 45$ °/3°/min/200 °C, $T_{sep} = 186$ °C. The polymer residue was acetone soluble and was also analyzed by GPC.

In order to achieve total thermal destruction of the polymer, pyrolysis of several grams of polymer was performed in a glass flask on a heated sand support, coupled with a condenser and flushed with a stream of nitrogen. At temperatures of about 450 °C, maintained for 30 minutes, the polymer degraded completely. The evolved vapours were condensed and analyzed on a Varian Aerograph Series 1400 with an OV-101(3⁰/o) glass column. The column temperature was programmed in the following way: 50°/10°/min/250 °C, $T_{det} = 280$ °C, $T_{inj} = 300$ °C. IR spectra of both the distillate and the tar-like polymer residue were taken on a Perkin-Elmer 457 instrument in film form.

RESULTS

The non-isothermal TG and DTG curves obtained at various heating rates are presented in Figure 1 and Figure 2. Simple smooth S thermogravi-

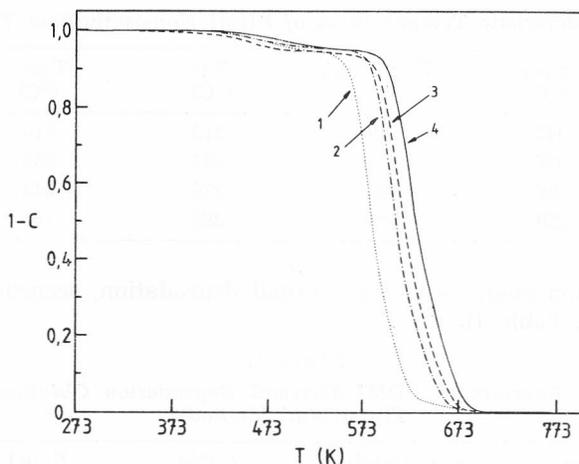


Figure 1. Non isothermal TG curves of PDMI, heating rates β : 1 = 2.5 °/min, 2 = 10 °/min, 3 = 20 °/min, 4 = 40 °/min.

metric curves were obtained with a single pronounced DTG peak most probably indicating the occurrence of a single degradation reaction.

A slight shoulder at conversions of about 70% would not develop into a separate DTG peak even at a minimum heating rate of 0.625 °C/min. Before attaining 250 °C a mass loss of several % was noted in all experiments. Upon this small initial decrease, rapid sample deterioration took place, the polymer completely disappearing at approx. 420 °C.

The characteristic process temperatures, the DTG maxima, the first low and flat and the second sharp and pronounced, as well as the temperatures of 5, 50 and 95% mass loss are presented in Table I.

The results of isothermal TG experiments are shown in Figure 3.

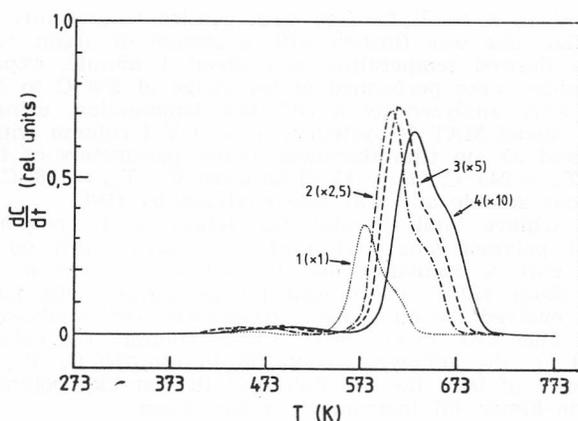


Figure 2. Non-isothermal DTG curves of PDMI (magnification factor in parentheses), heating rates β : 1 = 2.5 °/min, 2 = 10 °/min, 3 = 20 °/min, 4 = 40 °/min.

TABLE I
Characteristic Temperatures of PDMI Non-isothermal TGA

dT/dt (°C/min)	$T_{DTG \max 1}$ (°C)	$T_{DTG \max 2}$ (°C)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{95\%}$ (°C)
2.5	185	306	215	310	352
10	195	333	234	335	382
20	203	339	276	343	391
40	230	359	280	355	403

The activation energies of the thermal degradation, according to equation (2) are given in Table II.

TABLE II
Activation Energies of PDMI Thermal Degradation Obtained by the Flynn-Wall Method

C (%)	E_a (kJ/mol)	C (%)	E_a (kJ/mol)
10	131	60	136
20	144	70	127
30	141	80	130
40	130	90	133
50	140		
average $E_a = 135$ kJ/mol			

The data obtained indicate that below 280 °C there was no considerable polymer mass loss, i. e. it did not exceed 15% after a 60 minute exposure at 280 °C. Rapid mass loss commenced at 300 °C and higher temperatures, i. e. more than 50% mass loss was observed after 15 minute exposures. The kinetic parameters of PDMI degradation are presented in Table III.

A characteristic chromatogram of condensible volatiles from isothermal degradation runs is shown in Figure 4. As evidenced from GC and MS

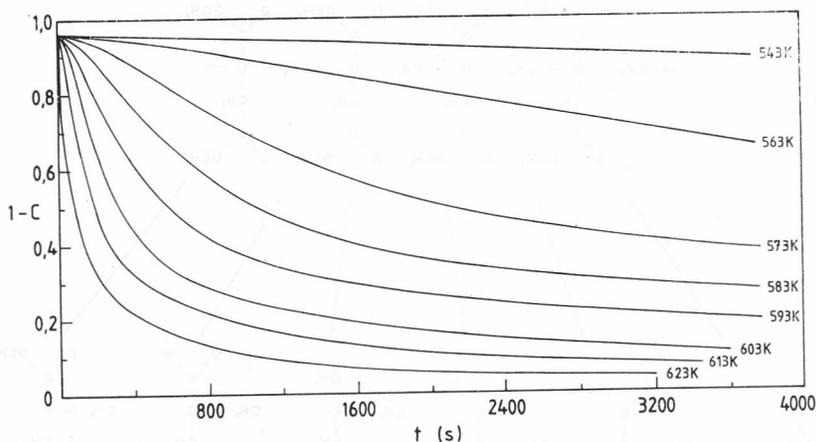


Figure 3. Isothermal degradation curves of PDMI.

TABLE III

Kinetic Parameters of PDMI Thermal Degradation Obtained from Isothermal TGA

Temp (°C)	Assumption of 1st order		Differential method
	$k \times 10^4$ (s ⁻¹)	$k \times 10^4$ (s ⁻¹)	n
300	2.9	5.1	2.1
310	5.0	10.8	2.5
320	7.1	30.3	2.9
330	10.4	36.3	2.3
340	13.8	33.5	1.9
350	17.2	45.2	1.9
E_a (kJ/mol)	105	124	

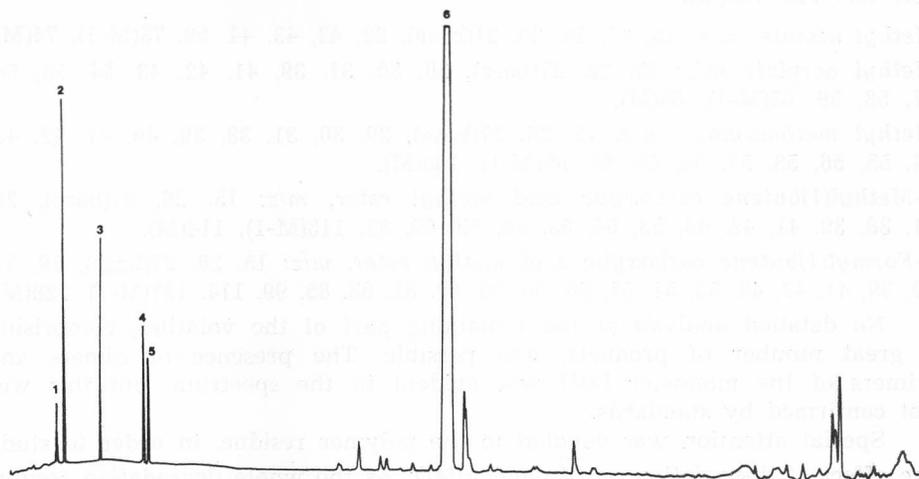


Figure 4. Gas chromatogram of condensable volatiles of PDMI thermal degradation, peaks 1 = Methyl acetate, 2 = Methyl acrylate, 3 = Methyl methacrylate, 4 = (2) Methyl(1)butene carboxylic acid methyl ester, 5 = (2)Formyl(1)butene carboxylic acid methyl ester, 6 = Dimethyl itaconate.

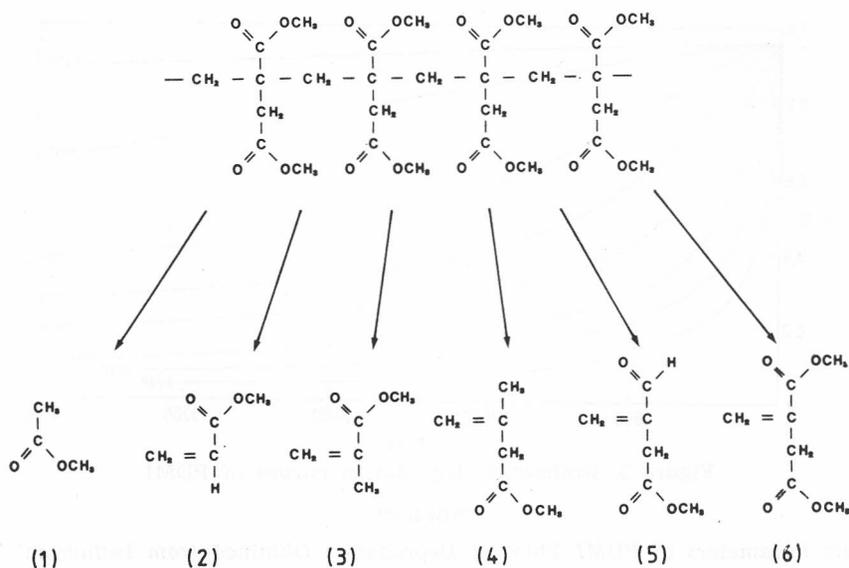


Figure 5. Condensable volatiles of PDMI thermal degradation.

spectra, the major product of thermal degradation is the monomer — dimethyl itaconate (DMI), present in amounts of about 70%. Other identified components, comprising a total of about 10% of the mixture, include methyl acetate, methyl acrylate, methyl methacrylate, (2)methyl(1)butene carboxylic acid methyl ester and (2)formyl(1)butene carboxylic acid methyl ester (Figure 5). The mass spectra of the identified components are given below:⁸ *Dimethyl itaconate*, m/z : 15, 27(base), 29, 31, 38, 39, 40, 41, 42, 43, 45, 53, 54, 55, 56, 58, 59, 68, 69, 70, 71, 82, 83, 87, 98, 99, 113, 115, 125, 126, 127, 128, 129, 130, 143, 158(M).

Methyl acetate, m/z : 15, 27, 29, 30, 31(base), 32, 42, 43, 44, 59, 73(M-1), 74(M).

Methyl acrylate m/z : 15, 26, 27(base), 29, 30, 31, 39, 41, 42, 43, 54, 55, 56, 57, 58, 59, 85(M-1), 86(M).

Methyl methacrylate, m/z : 15, 26, 27(base), 29, 30, 31, 38, 39, 40, 41, 42, 43, 54, 55, 56, 58, 59, 68, 69, 85, 99(M-1), 100(M).

2-Methyl(1)butene carboxylic acid methyl ester, m/z : 15, 26, 27(base), 29, 31, 38, 39, 41, 42, 43, 53, 54, 55, 58, 59, 69, 82, 113(M-1), 114(M).

2-Formyl(1)butene carboxylic acid methyl ester, m/z : 15, 26, 27(base), 29, 31, 38, 39, 41, 42, 43, 53, 54, 55, 56, 58, 59, 69, 82, 83, 85, 99, 114, 127(M-1), 128(M).

No detailed analysis of the remaining part of the volatiles, comprising a great number of products, was possible. The presence of dimers and trimers of the monomer DMI was evident in the spectrum, but this was not confirmed by standards.

Special attention was devoted to the polymer residue, in order to study the effect of degradation on \bar{M}_w and MMD. As the whole degradation residue was acetone soluble, it was concluded that no crosslinking leading to gel-formation took place. In this respect, GPC results presented in Figure 6 indicate that the initial PDMI sample with a uniform MMD upon degradation

produced three distinct fractions, a high molar mass fraction, a major fraction with M_w close but always slightly lower than the original molar mass of the sample, and a third low M_w fraction. M_w of the major fraction decreased proportionally with increasing temperatures of degradation and duration of the exposure, as presented in Table IV and Figure 7.

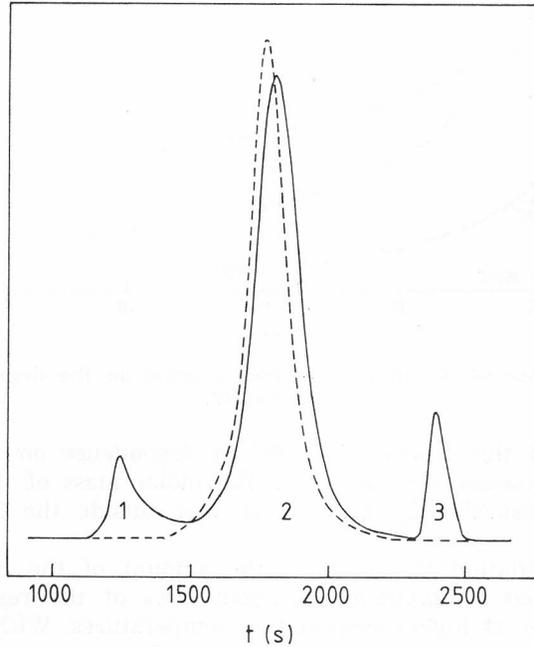


Figure 6. Typical GPC of degraded polymer residue with three distinct fractions, 1 = high M_w -fraction, 2 = major medium M_w -fraction with M_w close to that of the original sample, 3 = low M_w -fraction; dotted line — original polymer sample.

TABLE IV

Dependence of the Molar Mass of the Major PDMI Residue Fraction on Temperature and Time of Degradation, $\bar{M}_w = 6.0 \times 10^5$ g/mol

Temp. (°C)	Time (min)	$\bar{M}_w \times 10^{-5}$ (g/mol)	Temp. (°C)	Time (min)	$\bar{M}_w \times 10^{-5}$ (g/mol)
250	5	3.9	300	2	4.1
	15	2.1		5	1.5
	30	1.4		10	0.6
				15	0.3
280	2	5.7	320	2	3.7
	5	4.1		5	1.3
	15	1.2	350	2	2.4
	30	0.5		3.5	0.4
			5	0.2	

The low molar mass fraction was not detected in all polymer residues. The amount of this fraction never exceeded 10% of the residue. No trend

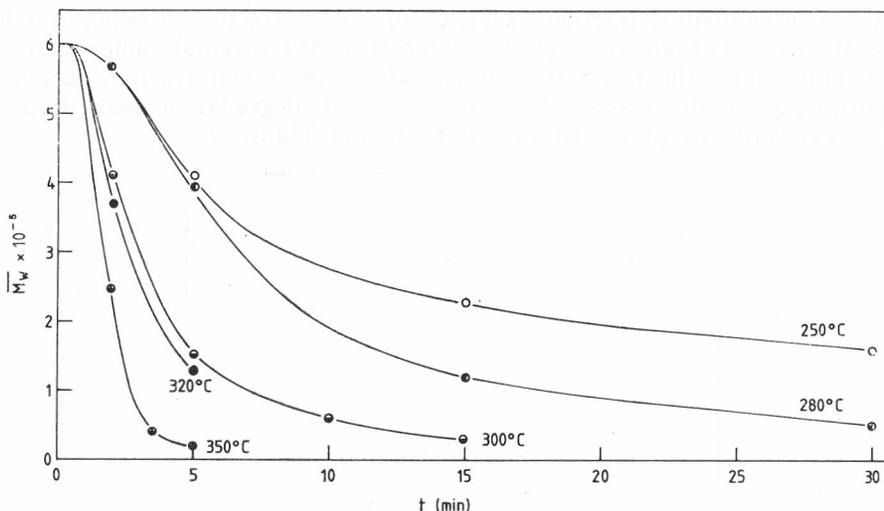


Figure 7. Dependence of M_w of the polymer residue on the degradation time and temperature.

in the position of this fraction in GPC in dependence on temperature and duration of degradation was observed. The molar mass of this fraction was, however, not measurable by GPC as it was outside the lower bounds of the instrument.

At any degradation temperature, the amount of the high molar mass fraction approached a maximum of about 20% of the residue. This limit was reached faster at higher degradation temperatures. With prolonged time of degradation, the maximum slowly decreased.

The condensed volatiles upon pyrolysis, according to GPC, contained mainly monomer DMI (~60%), methyl acrylate (~5%) and various oligomers (more than 20%). These results are in agreement with those obtained by isothermal degradation of the sample. The pyrolysis residue, of a tar-like appearance, was readily soluble in solvents such as toluene, chloroform, carbon tetrachloride and acetone. The IR spectrum of the crude tar yielded aliphatic, ester, carbonyl and vinylidene bands, without any indication of aromatization during the process.

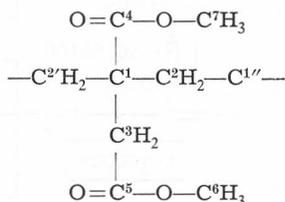
DISCUSSION

From the results obtained we attempted to draw conclusions regarding the nature of the thermal degradation process, its possible mechanism and the stability of PDMI in relation to poly(methyl acrylate) and poly(methyl methacrylate).

From the shape of the TG and DTG curves, and from the analysis of volatiles of isothermal degradation, indicating the occurrence of one major reaction only, it was concluded that the basic reaction of thermal degradation of PDMI was that of depolymerization, i. e. the so called »de-zipping reaction«. However, only 70% of monomer is obtained by thermal degradation, inferior to the amount obtained from thermal degradation of PMMA,⁹ but closer to the value of 85% reported for poly(methacrylonitrile).¹⁰ Evidently,

the thermal degradation of PDMI should at least formally be similar to PMMA and poly(methacrylonitrile), but obviously from the standpoint of mechanism it should be quite different from PMA, where no monomer is evolved at all.¹¹ In this respect, the shoulder observed in DTG curves (Figure 2) indicates the presence of another reaction within the depolymerisation process.

In order to propose an acceptable mechanism, attention should be first focussed on bond strengths between atoms in the monomer unit; for the purpose of this discussion the carbon atoms in the monomer units sequence $M' - M - M''$ are numbered in the following manner:



From bond strengths published in the literature¹¹ C—C bonds 1—2, 1—3, 1—4, 1—2' and 3—5 are of the order of 335 kJ/mol and C—O bonds in ether bridges 331 kJ/mol. In terms of bond dissociation energies one would expect the existence of equal probability for random scission of any of these bonds in the described system. If, however, the effect of carbonyls on lowering the dissociation energies of bonds in β -positions relative to carbonyl is considered, then in our case $\text{C}^4=\text{O}$ would lower slightly the dissociation energies of bonds 2'—1, 1—2 and 1—3, spreading its effect on all three bonds equally, though $\text{C}^5=\text{O}$ would influence only bond 1—3, which is consequently under the combined influence of both carbonyls. Assuming that thermal degradation would be initiated by rupture of the weakest bond in the system, in addition to other weak loci probably present in the polymer at chain ends or from other defects in the structure, in our opinion bond 1—3 is the weakest bond in the system subject to random scission at elevated temperatures.

Upon the rupturing of this bond, the radical separated from the polymer would form methyl acetate, found in measurable amounts in the chromatogram (Figure 4), by hydrogen abstraction anywhere from the system. The lateral macroradical at C^1 , C^* , thus formed in the reaction, would undergo scission, i. e. rupture of the bond 2'—1'', forming a double bond $\text{C}^{2'}=\text{C}^1$ at one chain end and a macroradical at $\text{C}^{1'}$ at the end of the other polymer molecule portion. Both of these portions, the macroradical and the polymer molecule with unsaturation at the end and now inherent allyl hydrogens at C^2 can depolymerize subsequently in a chain reaction producing predominantly monomer DMI. This concept, in good agreement with experimental evidence, including information of a reaction order above 1 (Table III), is schematically presented in Figure 8.

By similar reasoning, assuming also a slight possibility of cleavage of bond 3—5, and of all the C—O ether bonds in the ester groups, prior to the depolymerization of the main chain, the occurrence of other components

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IZVOD

Termička degradacija poli(dimetil-itakonata)

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Proučena je termička degradacija poli(dimetil-itakonata) primenom izotermne i neizotermne termogravimetrije i drugim metodama. Utvrđene su karakteristične temperature početka i kraja degradacije. Primenom metode Flynnna i Walla te Freemana i Carrola određena je energija aktivacije i red reakcije razgradnje. Na osnovu analize isparljivih sastojaka degradacije kombinacijom GC—MS utvrđeno je prisustvo 70% (mas.) monomera u isparljivim proizvodima. Predložen je mehanizam iniciranja degradacije koji se sastoji u kidanju slabe veze u bočnoj grupi monomernog ostatka, posle čega nastupa cepanje glavnog niza i lančano odvijanje reakcije depolimerizacije. Poređeno je ponašanje poli(dimetil-itakonata) sa poli(metil-akrilatom) i poli(metil-metakrilatom) i nađeno je da poli(dimetil-itakonata) termički degradira slično poli(metil-metakrilatu), ali da su reakcije pri degradaciji raznovrsnije, zbog složenije strukture dimetil-itakonata.