

THERMOGRAVIMETRIC ANALYSIS OF POLYMERS WITH INDANIC STRUCTURE

L. H. Tagle and F. R. Diaz

ORGANIC CHEMISTRY DEPARTMENT, FACULTY OF CHEMISTRY, CATHOLIC UNIVERSITY OF CHILE, P.O. BOX 6177, SANTIAGO, CHILE

(Received October 8, 1991)

The thermal stability of polycarbonates, polythiocarbonates, and polyesters derived from a diphenol with an indanic structure, was studied and compared with the corresponding polymers derived from a diphenol with the same number of carbon atoms but no forming the indanic ring, showing that polymers with an indanic structure degrade at lower temperature due the rigidity of the indanic ring respect to those with an aliphatic structure. Also, the kinetic parameters of the thermal decomposition were determined by using the Arrhenius relationship and a computer program. In the considered range, all the polymers studied degraded in a single stage and the E values increase when the bulk of the side group increases and the rigidity decreases.

Keywords: indanic structure, kinetic parameters, polymers, TG

Introduction

Organic macromolecular systems, like all other substances, may undergo a number of transformations under the effect of heat treatment. These changes are of a chemical or physical character, but simultaneous occurrence of both types of transformations is frequent. However, in polymeric materials the most frequent manifestation of such transformations is the change of mass, which can be observed by dynamic thermogravimetry.

In recent years the applications of polyesters have expanded remarkably, not only as synthetic fibres but also as tyre, films, food containers and, more recently as reinforced thermoplastic material for injection moulding. During the manufacture and the processing of polyesters, they are subjected to high ranges of temperature. These conditions can result in degradation reactions which deteriorate the desired properties of the polymer during processing or in the practical use of the material. For this reason it is important to know the behaviour that

*John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest*

present polyesters and polymers in general, when are heated under controlled conditions, as in dynamic thermogravimetry.

In a previous paper [1], we described the synthesis of polyesters derived from terephthaloyl and adipoyl dichlorides with 1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-6-indanol has diphenol, using phase transfer conditions. Also we synthesized the polycarbonate and polythiocarbonate derived from the same diphenol. The yields and inherent viscosities obtained were low due principally to the rigidity of the diphenol.

On the other hand, we synthesized polymers from a diphenol with the same number of carbon atoms but forming an aliphatic chain bonded to the central atom between the aromatic rings, under the same conditions. However, in this case the yields and inherent viscosities obtained were higher than those obtained for the polymer from the diphenol with an indanic group, and the phase transfer process was more effective, due to the flexibility of the diphenol [1].

As a form to verify the thermal behaviour of the polymers with the rigid diphenol, and continuing our work in the thermal studies of polymers [2, 3], in this work we describe the thermal stability of polymers derived from 1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-6-indanol, which are compared with the thermal behaviour of those derived from the diphenol with the same number of carbon atoms but forming an aliphatic chain bonded to the central atom between the aromatic rings.

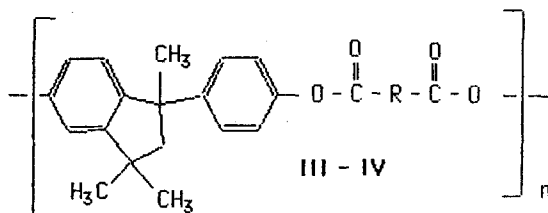
Experimental

The synthesis of 1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-6-indanol (**I**), 2,2-bis-(4-hydroxy-phenyl)-4-methyl-pentane (**II**), the corresponding polyesters with terephthaloyl dichloride (**III** and **V**) and adipoyl dichloride (**IV** and **VI**), the polycarbonates (**VII** and **IX**) and the polythiocarbonates (**VIII** and **X**), were described in previous papers [1, 4]. The polycarbonate from **II** and phosgene (**IX**) was synthesized under phase transfer conditions according to a procedure described previously [5].

Dynamic thermogravimetry analyses were carried out in a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (4–8 mg) were placed in the platinum sample holder and the thermal degradation measurements were carried out between 20° and 650°C at a heating rate of 20 deg·min⁻¹ under nitrogen flow.

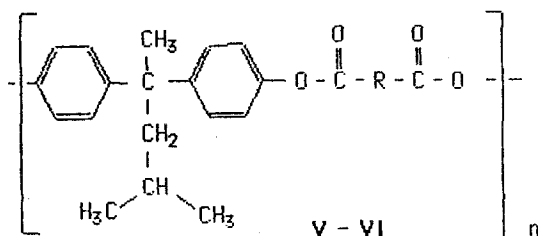
Results and discussion

The following polyesters, polycarbonates, and polythiocarbonates



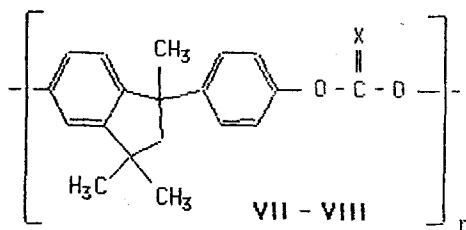
where III $R = p\text{-C}_6\text{H}_4\text{-}$

IV $R = \text{--}(\text{--CH}_2\text{--})_4\text{--}$



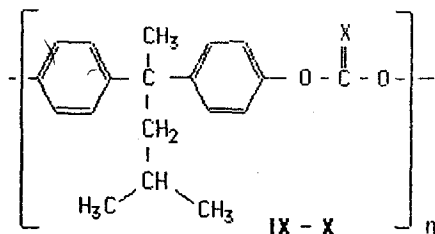
where V $R = p\text{-C}_6\text{H}_4\text{-}$

VI $R = \text{--}(\text{--CH}_2\text{--})_4\text{--}$



where VII $X = \text{O}$

VIII $X = \text{S}$



where IX $X = \text{O}$

X $X = \text{S}$

were analyzed by dynamic thermogravimetry.

Figures 1–4 show the thermogravimetric curves of the studied polymers, from which the thermal decomposition temperatures (TDT) were determined at 10% of weight loss. Table 1 shows the TDT values for these polymers.

When the synthesis of these polymers was described [1], we attributed the low values of yields and inherent viscosities obtained for polymers **III**, **IV**, **VII** and **VIII** to the rigid structure of the indanic diphenol **I**, being the phase transfer process of low efficiency.

In all cases, polymers derived from diphenol **I** with an indanic structure, degrade at lower temperature than those derived from diphenol **II**, which has the same number of carbon atoms, but forming an open chain bonded to the central atom between the aromatic rings. This behaviour can also be due to the high rigidity that presents the diphenol **I**. On the other hand, it has been described in the thermal stability of polythiocarbonates and polycarbonates [6, 7], when the bulk of the side chains is increased, the thermal stability is also increased, and the *t*-butyl group as side chain is a bulky one.

Polycarbonate **IX** was synthesized from monomer **II**, in order to compare with polycarbonate and polythiocarbonate synthesized from **I**. The data for polythiocarbonate **X** were taken from a previous paper [6]. As it can be seen in Table 1, these types of polymers also derived from the rigid monomer with an indanic structure have less thermal stability.

In the same sense, polyesters derived from an aromatic acid dichloride (**III** and **V**) are more stable than those derived from an aliphatic acid dichloride (**IV** and **VI**). This behaviour has been described for several kinds of polymers [8].

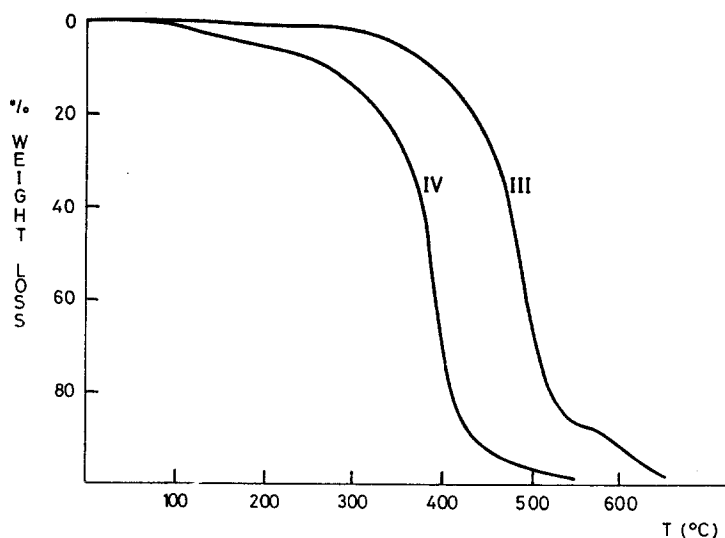


Fig. 1 Thermogravimetric curves of polyesters **III** and **IV**

In polycarbonates and polythiocarbonates, the difference between those derived from diphenol I respect to diphenol II, are higher because the influence of the diphenol is higher than in polyesters because in those polymers the acid dichlorides (phosgene or thiophosgene) are very small. It is probable that polycarbonates and polythiocarbonates, specially those derived from diphenol II, have higher molecular weights than the polyesters, due to the higher solubility that

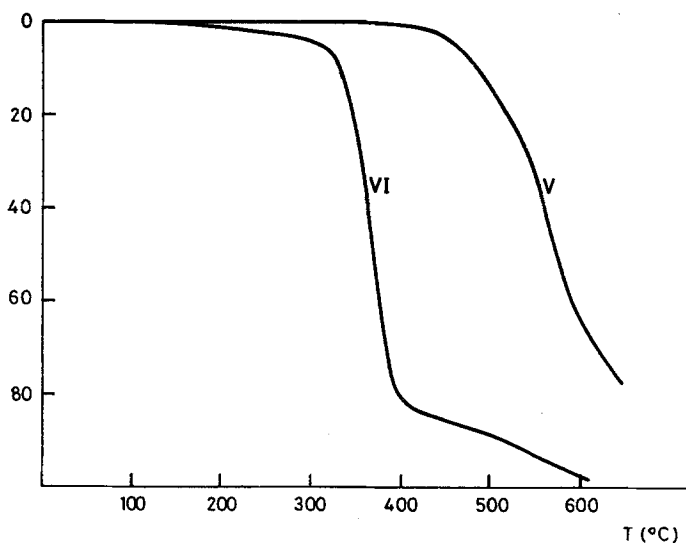


Fig. 2 Thermogravimetric curves of polyesters V and VI

Table 1 Thermal decomposition temperatures (TDT) for polymers III-X

Polymer	TDT / °C
III	388
IV	270
V	485
VI	333
VII	308
VIII	272
IX	440
X ^a	405

^a taken from Ref. [6]

presented during the polymerization step, which makes the phase transfer process more effective.

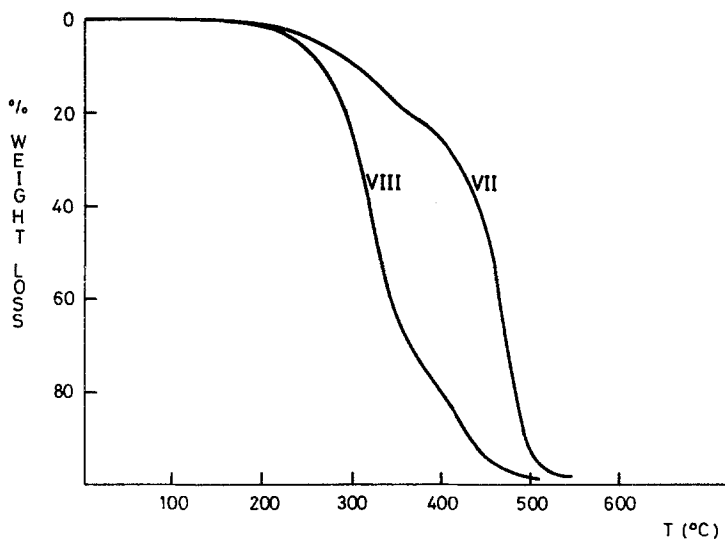


Fig. 3 Thermogravimetric curves of polycarbonate VII and polythiocarbonate VIII

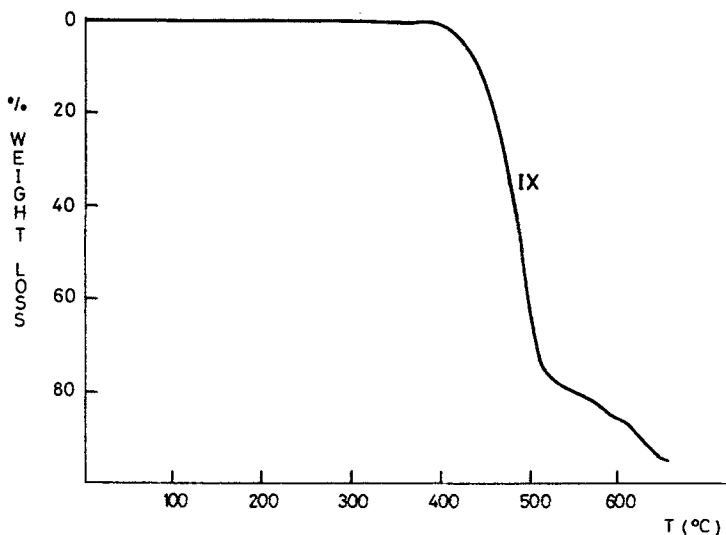


Fig. 4 Thermogravimetric curve of polycarbonate IX

In order to know the kinetic parameters associated with the degradation process, the thermogravimetric weight loss data were attributed to the kinetic equation:

$$-\frac{d\alpha}{dt} = k_n (1 - \alpha)^n \quad (1)$$

where α is a fraction of the sample weight reacted at time t , and k_n is the specific rate with a reaction order n . The reaction rates $d\alpha/dt$ were calculated using a differential technique with the heating rate (20 deg/min) incorporated directly into the temperature vs. sample weight fraction data, according to the method developed by Wen and Lin [9]. The specific rates were calculated from the Arrhenius relation:

$$k_n = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where E is the activation energy, A the preexponential factor, T the absolute temperature and R the gas constant. Equations (1) and (2) were combined and used in logarithmic form:

$$\beta = -\left(\frac{d\alpha}{dT}\right) = A (1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (3)$$

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from a linear least-squares fit of the data in a semi-logarithmic plot of β vs. $1/T$, which are shown Figs 5–8. The linearity of each plot was good (> .995) although some scatter was detected at the beginning and end of the decomposition which can be attributed to the difficulty to obtain accurate measurements at the beginning and the end of an experiment, as it is frequently encountered in kinetic measurements.

Table 2 shows the kinetic parameters E and A determined for all polymers, the temperature ranges and the reaction order n .

As it can be seen, the E values for the degradation process for polymers derived from diphenol **I**, are lower than those derived from diphenol **II**, showing the same tendency that as the values of TDT, when the bulk of the side group increases, and the rigidity decreases, the E values also increases.

All the polyesters and polycarbonate **VII** showed a kinetic order 0, and polythiocarbonates and polycarbonate **IX** a first kinetic order. A zero kinetic order means that $-d\alpha/dt$ is constant, which suggests when the mass of sample is increased, the rate of the mass loss is constant. It can occur of the concentration of volatile material in the surface of sample is constant, as in a simple evaporation [10]. A first kinetic order, implies that the rate of the mass loss depends on the concentration of volatile material.

It has been described that polythiocarbonates degrade according to a first order kinetic [6], but polycarbonates can degrade according to a zero kinetic order or to a first kinetic order, which depends on the molecular weight and the

polydispersity index [7], according to the mechanism proposed by Davis and Golden and Abbas [11, 12].

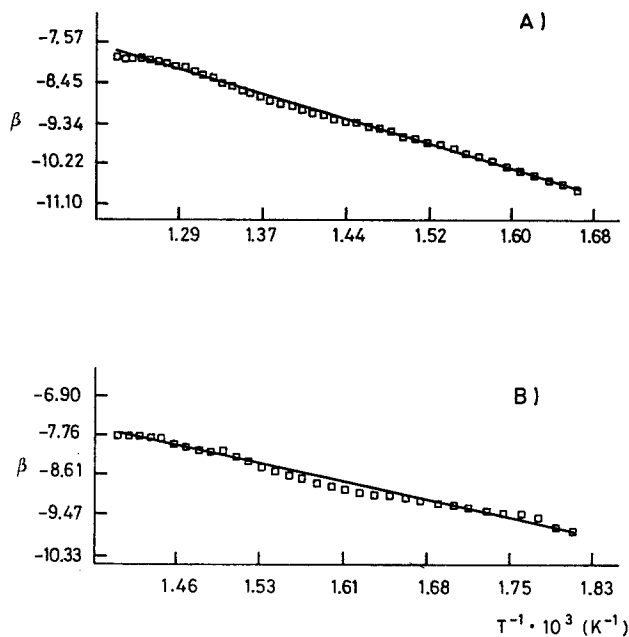


Fig. 5 Arrhenius plot for the degradation of A: polyester III; B: polyester IV

Table 2 Kinetic parameters of the thermal decomposition of polymers III-X

Polymer	Range / °C	<i>n</i>	<i>E</i> / kcal·mol ⁻¹	<i>A</i> / sec ⁻¹
III	330 – 540	0	14.7	4.20
IV	280 – 440	0	10.3	7.01·10 ⁻¹
V	450 – 610	0	21.5	9.39·10 ¹
VI	310 – 400	0	26.3	2.36·10 ⁵
VII	250 – 510	0	8.7	9.72·10 ⁻²
VIII	230 – 430	1	20.3	1.13·10 ⁴
IX	400 – 560	1	54.1	1.89·10 ¹²
X ^a	390 – 500	1	60.9	2.77·10 ¹⁶

^a taken from Ref. [6]

As it has been pointed out that the intramolecular ester exchange is the mainly responsible mechanism for the primary steps of thermal decomposition of

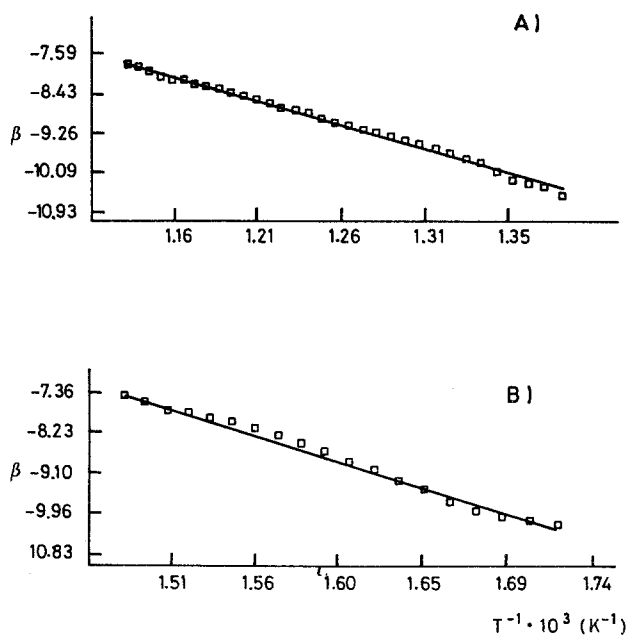


Fig. 6 Arrhenius plot for the degradation of A: polyester V; B: polyester VI

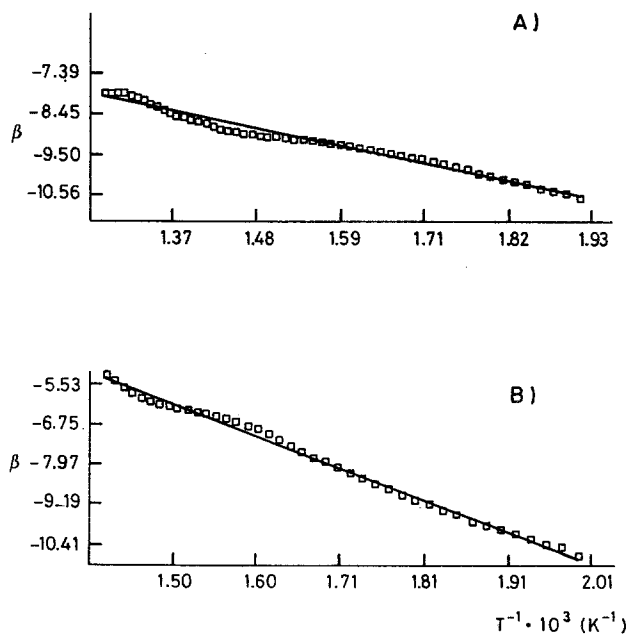


Fig. 7 Arrhenius plot for the degradation of A: polycarbonate VII; B: polythiocarbonate VIII

polyesters from aliphatic dicarboxylic acids and diphenols, and in totally aromatic polyesters [8], and therefore a series of cyclic oligomers are produced, which are probably volatilized according to a zero kinetic order.

In spite of this, it has been described for complex reactions as those that occur in thermal degradation of condensation polymers, the kinetic order and E values have a limited significance, due principally to the fact that the physical state of the sample is far from ideal and may change during the reaction. It is necessary to consider that the degradation process, specially in polyesters, can be composed of several stages that can not be separated in clear ranges of temperature [13]. So, assumptions about the reaction order and constancy of the activation energy over a particular temperature range may therefore be questionable. Moreover, the kinetic treatment of thermal degradation assume that the residual weight of the sample may be handled as if it was a concentration, which is of doubtful validity [14].

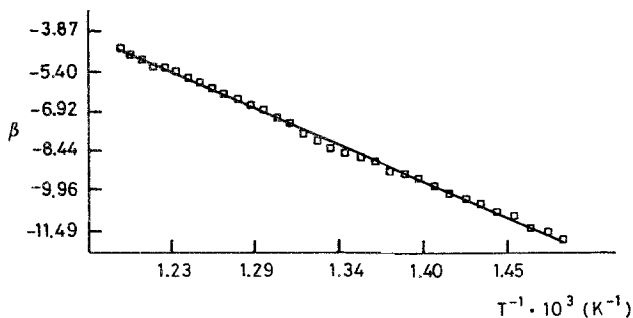


Fig. 8 Arrhenius plot for the degradation of polycarbonate IX

Despite, thermal degradation is a good tool to analyze the influence of the structures of the diphenol and the diacid in the thermal stability of these polymers, and to determine the temperature range in which they can be used, and the kinetic parameters associated with the total degradation process.

* * *

The authors acknowledge the financial support of this work by 'Fondo Nacional de Investigación Científica' (FONDECYT), through grant 763/90.

References

- 1 L. H. Tagle, F. R. Diaz and L. Jimenez, *Polym. Bull.*, 28 (1992) 645.
- 2 L. H. Tagle, F. R. Diaz and M. A. Vargas, *Thermochim. Acta*, 191 (1991) 201.
- 3 L. H. Tagle, F. R. Diaz and C. Margozzini, *J. Thermal Anal.*, 36 (1990) 2521.
- 4 L. H. Tagle, F. R. Diaz and P. Riveros, *Polymer J.*, 18 (1985) 501.

- 5 L. H. Tagle and F. R. Diaz, *Eur. Polym. J.*, 23 (1987) 109.
- 6 L. H. Tagle, F. R. Diaz and L. Rivera, *Thermochim. Acta*, 118 (1987) 111.
- 7 L. H. Tagle and F. R. Diaz, *Thermochim. Acta*, 144 (1989) 283.
- 8 G. Montaudo and C. Puglisi, *Development in Polymer Degradation*, Ed. N. Grassie, Vol. 7, Elsevier Applied Science, London 1987, p. 35.
- 9 W. Y. Wen and J. W. Lin, *J. Appl. Polym. Sci.*, 22 (1978) 2285.
- 10 G. G. Cameron and A. Rudin, *J. Polym. Sci., Polym. Phys. Ed.*, 19 (1981) 179.
- 11 A. Davis and J. H. Golden, *Makromol. Chem.*, 110 (1967) 180.
- 12 K. B. Abbas, *Polymer*, 21 (1980) 936.
- 13 J. R. MacCallum, *British Polym. J.*, 11 (1979) 120.
- 14 I. C. McNeill, *Comprehensive Polymer Science*, Ed. G. Allen, Vol. 6, Pergamon, London 1989, p. 456.

Zusammenfassung — Die Stabilität gegen Wärme von Polycarbonaten, Polythiocarbonaten und Polyestern gewinnen aus einem Diphenol mit einer Indan Struktur wird studiert und verglichen mit denjenigen von analogen Polymeren gewinnen aus einem Diphenol mit der gleichen Nummer von Kohlenstoffatomen ohne Bildung von einem Indanring. Diese Versuche zeigen, daß die Polymere mit einer Indanstruktur bei tiefer Temperatur als diejenige mit einer aliphatischen Struktur degradieren auf Grund der Strenge des Indanringes. Die kinetischen Parameter der Zersetzung gegen Wärme der Polymeren wurden durch die Arrhenius Gleichung und ein Computerprogramm in dem angesehenden Bereich bestimmt. Alle Polymere durch einen Schritt zerfallen. Die *E*-Werte zunehmen, wenn die Größe der Seitengruppe zunimmt und die Strenge abnimmt.