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MECHANISM OF THERMAL DEGRADATION OF POLY(VINYL ACETATE)

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The thermal degradation of poly(vinyl acetate) was investigated under dynamic atmosphere of helium up to 400° with a thermobalance. The volatile products were analyzed by a gas chromatograph.

Acetic acid proved to be the main component of the volatile products (90 to 95%). Kinetic measurements of numerous samples obtained showed that the rates and orders of the degradation were different for all the samples and depended on their internal structures (the polydispersity). This is contrary to data published by A. Servotte et al. [1] and agreed with N. Grassie [2, 3].

This dependence of the degradation on the internal structures of the samples is latter verified by a probabilistic approach.

In recent years, the degradation of a number of poly (vinyl) compounds has been studied. On the thermal degradation of poly (vinyl acetate), important works have been published by N. Grassie [2, 3] and A. Servotte et al. [1].

Existing techniques for studying the thermal degradation of polymeric materials are either very time consuming or very qualitative especially when the degradation reaction is complex.

A method that gives rapid, yet quantitative results for the parameters of thermal degradation of polymeric material is by thermobalance which combines DTA, TG and DTG. Moreover, the heating atmosphere can be controlled and changed quite easily.

There is no shortage of publications presenting DTA curves for a wide range of polymeric materials. This might possibly give the impression that the DTA curve, for a plastic is unique and characteristic i.e. is a "finger-print" which can serve for identification when compared with curves for known materials.

In fact, this is not so, the DTA curve itself, is not necessarily reproducible since the thermal degradation of polymeric material depends – beside many factors – on the internal structure of the sample used.

In this paper, poly (vinyl acetate) is degraded up to 400° in a thermobalance, under the inert dynamic atmosphere of helium. The heating temperature is programmed linearly at 10°/min.

The results, obtained by the analytical scheme concurrently developed for determining the kinetic parameters of thermal degradation, are compared, for different samples based on their differences in internal structure. The latter, are given by combining the gel permeation chromatography (GPC) to the analysis apparatus.

Experimental

Polymerization

Vinyl acetate monomer provided was distilled to remove trace of inhibitor. It was then emulsified at 40° using a semi-batch reactor with the redox reaction of tert butyl hydroperoxide and sodium bisulfite as source of initiators, pluronic, F-68 as emulsifier.

The polymer samples, in form of latex were withdrawned from the reactor as function of time of the reaction. After drying at room temperature and under vacuum, the percentage of conversion of samples were determined. Their number and weight average molecular weight were given by GPC (gel-permeation chromatography) using THF as solvent.

The degradation

Samples were heated up to 400° by a Mettler recording vacuum thermoanalyzer type 1, number 68, in the dynamic inert atmosphere of helium. The rate of heating was 10°/min. The sample holder was the 8 mm diameter and 20 mm height type, made of alumina.

Gas chromatography

The volatile products of degradation were passed through a chromatograph vapor fractometer model 154C single stage with thermal conductivity detection.

Determination of acetic acid evolved

The volatile products of degradation were condensed in liquid nitrogen. The amount of acetic acid evolved was measured quantitatively by acid-base titration with phenolphthalein as indicator. The standard NaOH solution of 0.03 N was back-titrated with a standard solution of acetic acid, the difference about 3% was due to the absorption of CO_2 gas in the air and the systematic errors.

Results and discussion

Volatile products of degradation

The polymer started to be degraded at about 250°. From 250 to 350°, acetic acid being the most abundant component. An acid-base titration of the degradation products showed a loss in weight of 70% (theoretical percentage of loss of

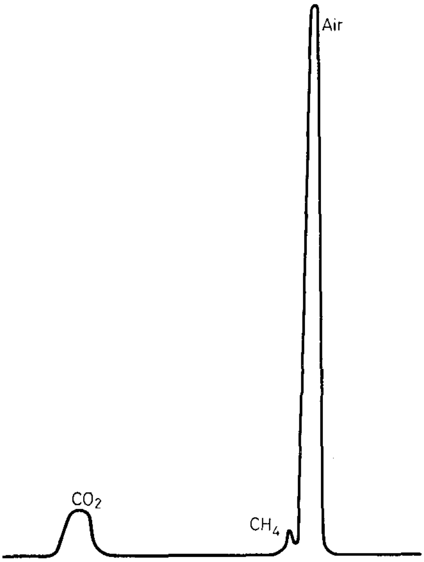

Fig. 1. Volatile products chromatogram at 350°

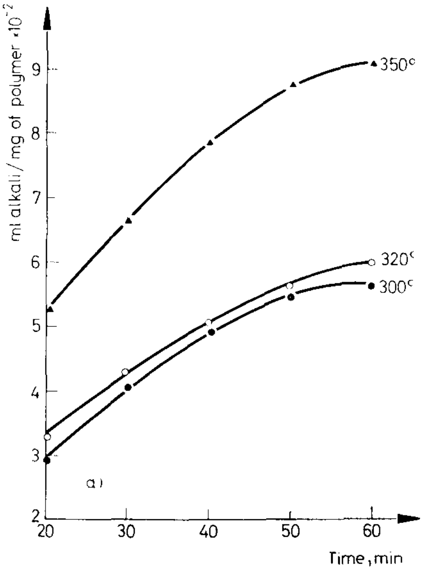

Fig. 2a. Effect of temperature on production of acetic acid

weight corresponding to complete deacetylation) indicating that 90 to 95% of these products are acetic acid. The results confirm those obtained by Grassie [2, 3]. From 350° to the end of the degradation (400°) the amount of acetic acid evolved decreases rapidly. A typical chromatogram of the volatile degradation products (beside acetic acid) in this range of temperature is given in Fig. 1. The first peak of the chromatogram is the air presents in the line, the second peak (very small one) is methane and the last one is CO_2.

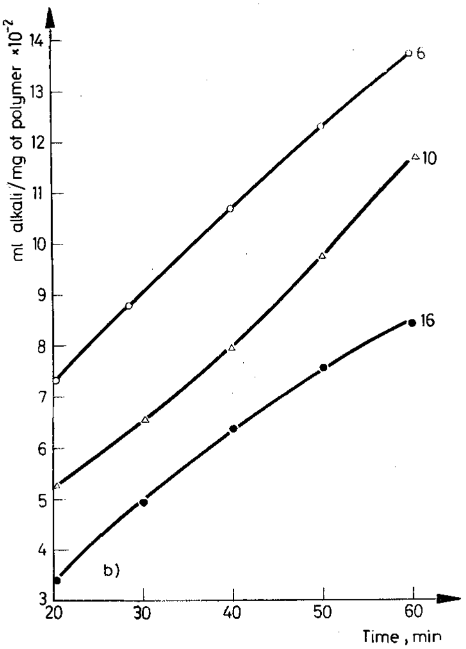

Fig. 2b. Effect of molecular weight on production of acetic acid. $\overline{M}_w 16 > \overline{M}_w 10 > \overline{M}_w 6$

Bamford and Dewar [4] have shown that acetic acid can be pyrolyzed in the temperature of the order of 500° to either ketene and water or methane and carbon dioxide. It is evident, however, from the series of the chromatograms reported that the amount of CO_2 and methane are very small compared with that of acetic acid.

Any decomposition of acetic acid taking place under that condition of temperature must therefore be negligibly small.

Therefore, in the range from 250° to 350°, the primary reaction of the degradation is the production of acetic acid.

Figures 2a and 2b show the effect of average molecular weight of samples and temperature of degradation on the amount of acetic acid evolved. It is quite evi-

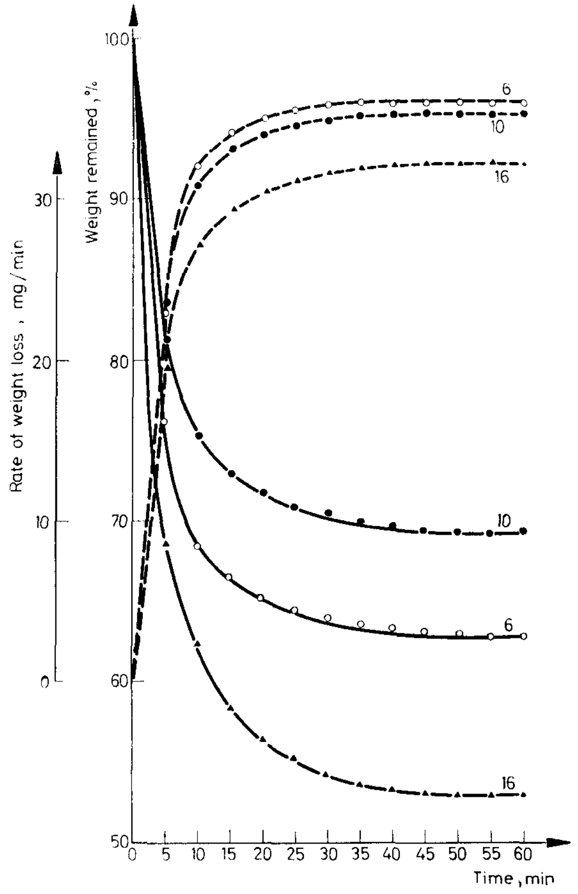

Fig. 3. Rate of weight loss vs. time. Temperature 320°

dent that with the same sample, the quantity of acetic acid evolved is higher at higher temperature of degradation (Fig. 2a), and samples of lower average molecular weight degraded more easily than samples of high molecular weight (Fig. 2b).

Analysis of the thermal curves

Figure 4 shows the typical thermogram of the degradation. At about 60°, the TG curve shows a gain in weight of the sample (point *a*) due to the adsorption of the helium carrier gas on the polymer. From 100° to 200°, the polymer is stable, the degradation only starts at about 250° where the weight of the sample starts to decrease rapidly, corresponding to the decomposition reaction which gave mostly acetic acid gas.

Under the DTA curve, the first endothermic peak (point *b*) corresponds to the process of adsorption as observed with the TG. The second (point *c*) and third (point *d*) endothermic peak correspond respectively to the decomposition of the low molecular weight fraction and the high molecular weight fraction of the sample. The areas under these two peaks are directly proportional to the heat of fusion and indicate the relative fraction of low and high molecular weight. The ratio of the peak areas should be of the same order as the polydispersity of the sample. This can be seen in Table 1. The effect of low and high molecular weight fractions on the polydispersities is discussed elsewhere.

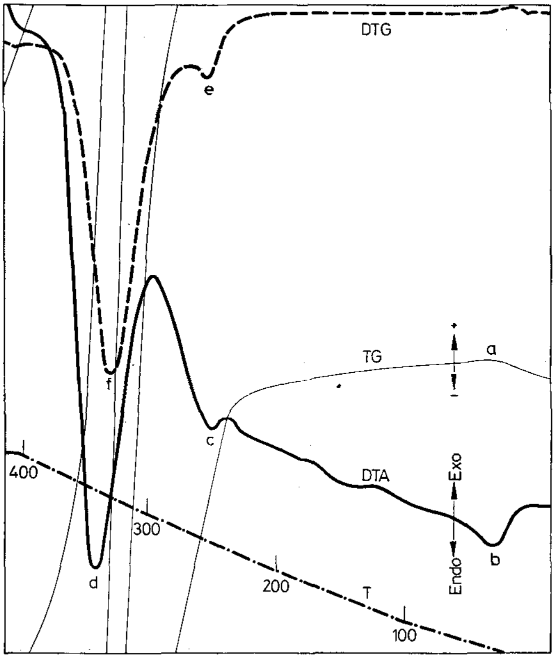

Fig. 4. Thermal curves of No. 10. Heating rate: 10°/min.; DTA sensitivity: 5 μV/inch; TG sensitivity: 1 mg/inch; DTG sensitivity: 1 mg/inch/min.

The DTG curve, which measures the rate of weight loss of the sample in mg/min, passes through the first maximum (point *e*) 2.1 mg/min and the second maximum (point *f*) 9.1 mg/min corresponding to the fusion peaks of low and high molecular weight fraction of the sample.

Also presented in the thermal curve is the temperature one which increases linearly at 10°/min.

Table 1
Molecular weight vs. DTA peaks

No of sample	$\overline{M}_n$	$\overline{M}_w$	Poly-dispersity	Ratio of peak areas	Temperature at 1st DTA peak	Temperature at 2nd DTA peak
1	56,529	191,509	3.40	3.77	261	327
2	32,742	201,616	6.16	4.03	263	327
5	30,677	192,189	6.26	5.12	267	327
6	28,900	160,894	5.75	—	252	331
8	37,198	218,478	5.87	4.38	262	327
9	31,579	189,304	5.99	8.53	264	321
10	16,717	231,888	13.90	10.72	252	342
12	73,954	254,054	3.43	2.35	267	328
16	49,259	281,049	5.70	6.97	250	341
A	310,288	612, 500	1.97			325
B	243,109	638,152	2.62		283	323
C	464,460	1,473,520	3.17		330	470

In Table 1, due to the lowest polydispersity of sample *A*, only one peak (point *C* in Fig. 5) at 325° under DTA curve is observed. With sample *C*, there is a shift in the temperatures of the peaks, probably due to the highly cross linking resulting from the irradiation.

A: Poly(vinyl acetate) sample obtained by irradiation under γ ray within 16 hours.
B: Poly(vinyl acetate) sample obtained by irradiation under γ ray within 240 hours.
C: Poly(vinyl acetate) sample obtained by irradiation under γ ray within 72 hours.
* The radiation was of the order of 7 Roentgen/min.

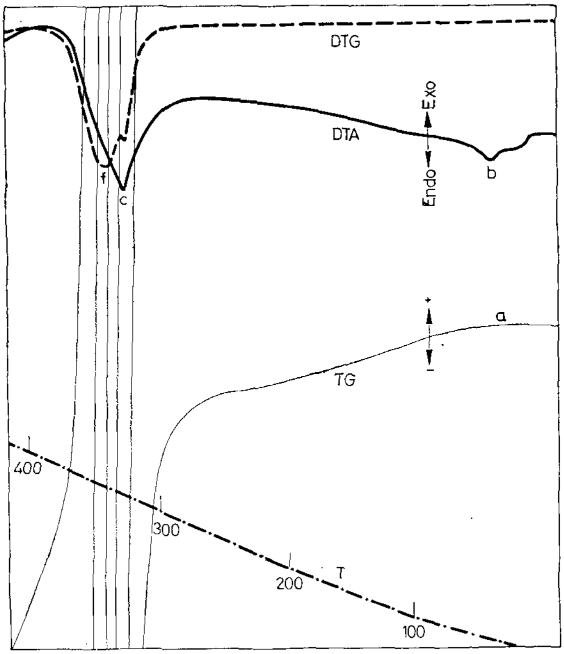

Fig. 5. Thermal curves of No. A. Heating rate: 10°/min.; DTA sensitivity: 5 μV/inch; TG sensitivity: 1 mg/inch; DTG sensitivity: 1 mg/inch/min.

Kinetic

A simplified scheme for depicting weight loss suffered by the polymers during thermal degradation was described elsewhere [6]. Table 2 is calculated from the thermal curves of polymer samples with trial value of *n* (*n* is the order of the degradation) from 0 to 5.0 with step of 0.5. These trials were made by using Fortran IV, systems 360 computer until the best straight line obtained. The slopes of these lines (Fig. 6) determined by the method of least squares with 95% confidence interval by using student *t* test, were served to calculate the activation energies of the degradation.

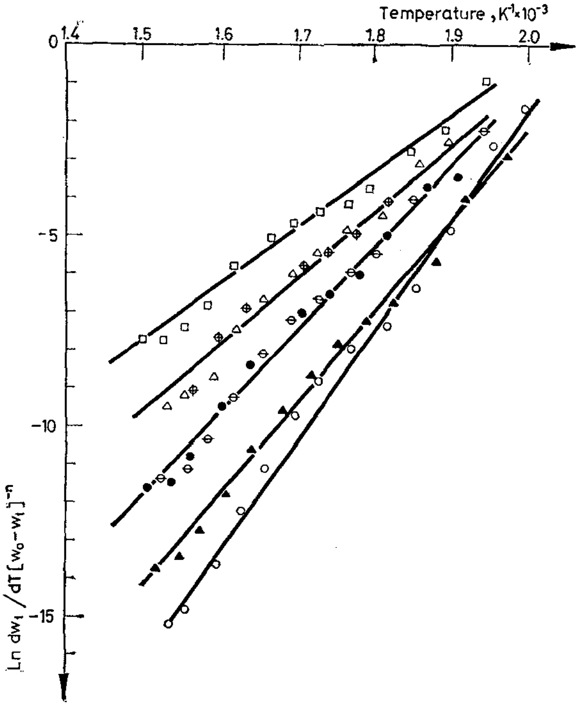

Fig. 6. Linear plot of rate vs. reciprocal of temperature. No. ○ 15; ● 2; ⊖ 5; ⊕ 8; △ 12; ▲ 10; □ 9

From Table 2, it was observed that the orders of degradation varies from 1.5 to 3 for samples having the weight average molecular weight from 189, 304 to 281, 049, the activation energies for both initiation and propagation steps varied from 30 to 50 Kcal/mole with uncertainty from 3 to 10 Kcal/mole.

One notable exception is sample no 10 where the order of degradation is 3.0 and the activation energy is 47.8 Kcal/mole. This is relatively high for its weight average molecular weight of 231,888. This anomaly is due to the high polydispersity of the order of 13.9 of the sample. The polydispersity being the ratio of $\bar{M}_w$ over $\bar{M}_n$, the $\bar{M}_w$ is particularly sensitive to the presence of high molecular weight chains and thus the activation energy for the degradation is comparatively high.

Grassie [2, 3] recorded for the total energy of activation 53.6 Kcal/mole with polymers having $\bar{M}_n$ going from 125,000 to 640,000.

Table 2

Effect of molecular weight on the order of degradation

Number of sample	$\bar{M}_n$	$\bar{M}_w$	Polydispersity	Order of degradation	Activation energy Kcal/mole
9	31,579	189,304	5.99	1.5	29.84
5	30,677	192,189	6.26	2.0	29.31
12	73,954	254,054	3.43	2.0	40.73
2	32,742	201,616	6.16	2.5	42.06
8	37,198	218,478	5.87	2.5	47.31
10	16,717	231,888	13.90	3.0	47.83
15	49,259	281,049	5.70	3.0	50.81
A	310,288	612,500	1.97	3.0	80.71
B	243,109	638,152	2.62	2.5	74.25
C	464,460	1,473,520	3.17	3.5	90.57

The high values of order of degradation and activation energy for samples resulted from irradiation probably due to the highly cross-linking of the polymer and hence many chain branching.

A probability approach

A probabilistic method has been previously described [5] for the treating of the kinetics of polymer degradation via elimination, based upon the example of poly (vinyl chloride) thermal degradation.

The main features of the model developed to characterize this process are the following:

a) The degradation is a special kind of chain reaction (zip reaction), the initiating step of which is the random unimolecular splitting off of HCl (its rate constant being α).

b) The chain propagation is carried out in the series of allyl-activated unimolecular step (the rate constant of which is β). The activation takes place only in the monomeric unit adjacent to the decomposed one in the direction determined by the head to tail linkage.

c) The chain termination takes place by a reaction step which interrupts the propagation of activation, i.e., a reaction step takes place the product of which has no activating effect on the neighboring monomeric unit (it is determined by a probablity factor δ, characteristic of the occurence of this kind of decomposition step).

Assuming the polymer molecule is large enough for the effect of branching points and chain ends on monomeric units to be neglected. Then, there is no distinguishable monomeric unit in the polymer chain, and the polymer can be handled as a closed infinite chain. In this case, the probability of decomposition of an arbitrary monomeric unit at a time t, is equal to the value of conversion at the given time, irrespective of the position of the selected monomeric unit.

According to the above assumptions and based on the probabilistic approach, Kelen et al. [4] developed the following formula for a k long sequence of polyene, consisting of k conjugate double bonds:

$$C_k = \zeta\delta^2 e^{-2\alpha t}(1 - \delta e^{-\alpha t})^{k-1} \tag{1}$$

$$\zeta = \frac{1 - e^{-\alpha t}}{1 - (1 - \delta)e^{-\alpha t}} \tag{2}$$

where: t: time of the reaction (min)

C_k: concentration of the polyene

ζ: the conversion of the eliminating process

α: rate constant of initiation

β: rate constant of propagation

$\sum\limits_{k=1}^{\infty} C_k = \zeta x$

x: probability of polyene forming

Limiting conditions:

$$\left.\begin{array}{l} \text{a) } x = 1,\ 0 \le \delta \le 1 \\ \text{b) } \delta = 1,\ 0 \le x \le \infty \end{array}\right\} \text{ represents a single 1st order reaction}$$

c) $\delta = 0$ auto catalysis or auto-inhibition

If $\beta \gg \alpha (x \simeq \infty)$ a monomeric unit under activation decomposes instantly. In (1), the time dependence of the conversion can be linearized so that:

$$C_k = \alpha \cdot \delta(1 - \delta)^{k-1} t \tag{3}$$

Fig. 3 depicts the comparison of the experimentally determined polyene concentrations (by quantitative determination of acetic acid evolved) and of the calculated values vased on the probabilistic approach. For this figure

$$\alpha = 1.38 \times 10^{-4}\ \text{min}^{-1} \tag{4}$$

From the above table, the probability of the termination step is highest for the high molecular weight sample which resulted in the higher rate of degradation of the low molecular weight sample.

Table 3

Influence of the length of polyene sequence *k* on the termination step

Sample	$\overline{M}_n$	$\overline{M}_w$	δ	k
6	28,900	160,894	0.16	2.05
10	16,717	231,888	0.40	1.65
16	49,259	281,049	0.40	1.71

The good agreement obtained in Fig. 7 verifies the correctness of the assumptions made.

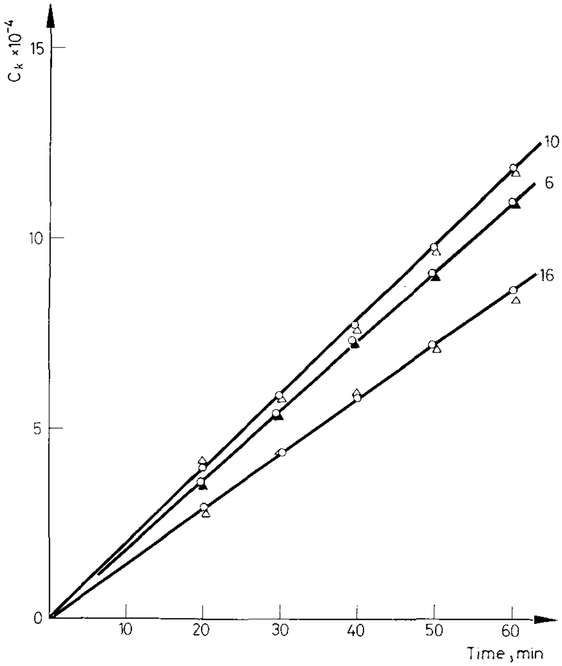

Fig. 7. Polyene concentration vs. time. Temperature: 320°. △ ▲ Experimental data ○ Calculated

From this approach, it is observed that there is a similarity between the mechanism of the degradation of poly(vinyl chloride) and poly(vinyl acetate). In both cases, the initiation step is a polyene formation process prior to the evolution ol acids (acetic acid in case of poly(vinyl acetate) and HCl in case of poly(vinyf chloride)). The propagation is a chain reaction which proceeds without the presence of free radicals. The chain termination will occur at either the end of the polymer chain or some non-uniformity in the chain which prevent the polyenes formation. These non uniformities would be randomly distributed so that if termination did take place, chains would be terminate from the beginning of the reaction and one would expect a stationary state to be set up reasonably quickly. In the experiment of N. Grassie [2, 3] even after 300 minutes of degradation, the stationary was not attained. On the contrary, we found the stationary state (Fig. 3) after heating at 10°/min in 1 hour. The appearance of this state in our experiments is to be in accordance with the values of δ, the probability factor of chain termination.

Furthermore, the fact that the kinetic parameters as orders, rates and activation energies of the degradation reaction are functions of the internal structure of the samples proved the parallel between the probabilistic and kinetic approach.

Conclusions

The thermal degradation of poly (vinyl acetate) from 250° to 350° in the dynamic atmosphere of helium gave mostly acetic acid. Above 350°, beside acetic acid, small quantity of methane and CO_2 were found and were believed to be the products of pyrolysis of acetic acid.

Kinetically, the orders and activation energies of the degradation varied from 1.5 to 3.0 and from 30 to 51 Kcal/mole respectively for sample of $\overline{M}_n$ from 30,000 to 50,000 with the polydispersity from 6 to 14. The kinetic parameters are functions of the internal structures of samples (poly dispersities).

This is contrary to data of A. Servotte et al. [1] who found that the rates of degradation were identical for all the samples and independent of the molecular weight. Except that a stationary state which corresponds to the complete deacetylation of the sample was found in our experiments after one hour of heating, our results are in accordance with those of N. Grassie [2, 3].

The probabilistic approach of Kelen et al. [5] although designed for the thermal degradation of poly (vinyl chloride) also is applicable for poly (vinyl acetate).

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Résumé — A l'aide d'une thermobalance, on a étudié la dégradation de l'acétate de polyvinyle en milieu dynamique d'Helium et ce jusqu'à 400°.

Les produits volatils obtenus furent analysés à l'aide d'un chromatographe. Il s'est avéré que le produit principal (soit 90 à 95%) de la dégradation est de l'acide acétique.

Des mesures cinétiques ont démontré que le taux et l'ordre de la dégradation sont différents pour les échantillons étudiés et dépendent de la polydispersité.

Ceci est en accord avec les résultats de Grassie [2, 3] mais à l'encontre des résultats obtenus par Servotte et al. [1].

Cette dépendance de la dégradation sur la polydispersité est vérifiée par l'approche probabilistique.

Zusammenfassung — Mit Hilfe einer Thermowaage wurde die Zersetzung von Polyvinylacetat im dynamischen Medium von Helium bis zu 400° untersucht. Die erhaltenen flüchtigen Produkte wurden in einem Chromatographen analysiert, wobei sich Essigsäure als Hauptprodukt (90 bis 95%) der Zersetzung erwies.

Die kinetischen Messungen zeigten, daß der Grad und die Ordnung der Zersetzung für die untersuchten Proben verschieden sind und von der Polydispersität bedingt werden.

Dies stimmt mit den Ergebnissen von Grassie [2, 3] überein, widerspricht aber denen von Servotte et al. [1].

Diese Abhängigkeit der Zersetzung von der Polydispersität wird durch eine Wahrscheinlichkeits-Annäherung bestätigt.

Резюме — Была исследована термическая деградация поливинилацетата при температуре до 400° в динамической атмосфере гелия с помощью термобаланса. Летучие продукты были проанализированы газ-хроматографически. Показано, что главной компонентой (от 90 до 95%) летучих продуктов является уксусная кислота. Кинетические измерения многочисленных образцов показали, что скорость и порядок деградации различны для всех образцов и зависят от их внутренней структуры (полидисперсности). Это противоположно данным, опубликованным А. Сервотте и сотр., но согласуется с данными Н. Грасси. Эта зависимость деградации от внутренней структуры образцов была подтверждена позже с помощью вероятностного приближения.