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Thermal Stability of Poly(hexamethylene Oxide) Related to the Method of Synthesis

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ABSTRACT

Thermal degradation of poly(hexamethylene oxide) has been studied by thermogravimetry and gas-liquid chromatography (GLC). The method of polymerization clearly influences the thermal stability of PHMO, as it affects the nature of the endgroups of the polymer. Polymers ending in OH groups, prepared by polycondensation, have a lower thermal stability than those obtained by cationic ring-opening polymeriztion, and both are still lower in thermal stability than the polymers capped with methoxy groups. The main differences in the degradation products are that oxepane is formed only from polymers with OH endgroups and in this case two different mechanisms of degradation are proposed.

INTRODUCTION

In previous papers [1, 2] we reported some thermal and crystallization properties of poly(hexamethylene oxide) (PHMO). This kind of work requires repeated heating to melting of the sample. The absence of decomposition of the sample in successive heating cycles must be established before the thermodynamic study of thermal and crystallization properties can be undertaken.

Thermal degradation of PHMO has been previously analyzed by Blyumenfel'd [3], but the relationship of the influence of the polymerization method on thermal stability has not previously been reported. However, we have found some differences in the thermal stability of the sample depending on the method followed for its preparation, i. e., polycondensation of 1,6-hexanediol or ring-opening polymerization of oxepane; these differences were attributed to the nature of the endgroups.

This paper is concerned, first with some of the kinetic factors that, in both types of polymerization, control the nature of the endgroups in the polymer, and second with its thermal stability, which was studied by using thermogravimetric techniques and GLC analysis of the gaseous products formed in its decomposition.

EXPERIMENTAL

Reagents

Commercial 1,6-hexanediol was recrystallized from an acetone-petroleum ether mixture. Oxepane was treated with $SOCl_2$ and $FeCl_3$ and then distilled and stored in a vacuum line over sodium.

Methylene chloride was washed with sulfuric acid for several days, distilled, dried with CaH_2 in a vacuum line and stored in ampoules. Tetrahydrofuran and oxepane were dried with biphenyl-sodium in a vacuum line. The triethyloxonium hexachloroantimoniate salt was prepared as described by Meerwein [4].

Polymerization

The polymerization of 1,6-hexanediol was conducted in a three-necked flask with stirring under an N_2 atmosphere. The reactions were carried out at 175°C, with the use of H_2SO_4 or mixtures with $Et_2O{\cdot}BF_3$ as a catalyst. The progress of the reaction was follwed by measuring the $\overline{M}_n$ values at regular time intervals. The polymers were dissolved in THF, precipitated with methanol and finally lyophilized.

The ring-opening polymerization of oxepane was carried out in dried methylene chloride under high vacuum with $SbCl_6^-Et_3O^+$ as catalyst. The polymerization was killed with MeOH.

Synthesis of PHMO with Methylated Endgroups

Poly(hexamethylene oxide) with OH endgroups was synthesized by polycondensation with H_2SO_4 as catalyst. The methylation of this

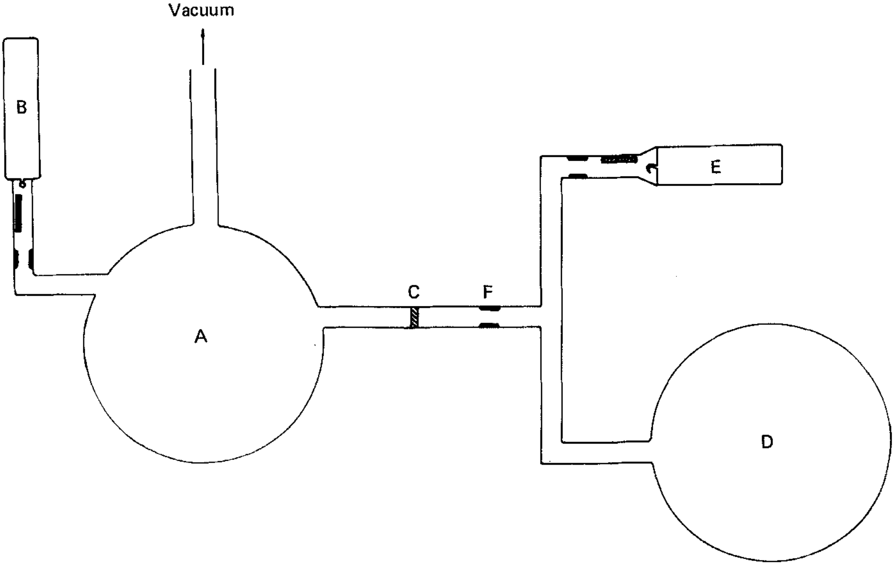


FIG. 1. Methylation apparatus.

sample was carried out in the glass apparatus described in Fig. 1. The procedure was as follows: a solution of sodium biphenyl in oxepane was prepared in vessel A and mixed with lyophilized, dried poly(hexamethylene oxide) with OH endgroups and introduced into ampoule B. The resultant very viscous solution was transferred through the glass filter C into vessel D, and this vessel was removed by sealing at the constriction F. After that, methyl iodide was added to the polymer solution. The viscosity of this solution immediately drops, due to the disappearance of the ONa endgroups.

Polymer Characterization

The samples of lower molecular weight were fractionated in THF/ methanol at 40°C. To avoid an effect of crystallization on the liquid-phase distribution equilibria, the higher molecular weight was fractionated at 60°C in isopropanol/ethylene glycol. The number-average molecular weight $\overline{M}_n$ was measured in a Hitachi Perkin-Elmer 115 vapor pressure osmometer in carbon tetrachloride at 25°C or in a Mechrolab membrane osmometer in THF at 25°C.

Thermogravimetric Analysis

The thermal stability of the samples was studied by using a Dupont Model 950 thermobalance in a nitrogen atmosphere. The samples were heated at 100°C for 24 hr prior to thermogravimetric analysis. The gaseous products formed were collected in a cold trap and analyzed by GLC.

RESULTS AND DISCUSSION

Polycondensation

The synthesis of poly(hexamethylene oxide) by polycondensation has been reported by Lal and Trick [5], who used as catalyst mixtures of sulfuric acid and $Et_2O{\cdot}BF_3$ and the reported molecular weights were relatively low. Later work by Hobin [6] claims that no advantages are derived from the addition of $Et_2O{\cdot}BF_3$ to the sulfuric acid in the synthesis of model polyether oligomers. Moreover some theoretical objections to the use of $Et_2O{\cdot}BF_3$ have been remarked. In order to check this point and due to the interest in getting high molecular weights of PHMO we tested both catalyst systems.

The experimental conditions of the preformed experiment are given in Fig. 2. The catalyst concentrations were small, and the temperature was not very high (175°C); the resulting inconvenience was that in order to obtain high conversions very long times of polymerization were necessary.

The three experiments described in Fig. 2 have in common that, in the first stages of the reaction, besides water, about 3 g of the cyclic monomer are recovered. This amount represents 10% of the initial diol content, and it must be produced by some intramolecular condensation. It appears quite clear from Fig. 2 that the presence of $Et_2O{\cdot}BF_3$ decreases the initial rate of polycondensation compared with the rate with sulfuric acid only and strongly limits the final conversion. The IR spectra of the final polyoxide obtained in presence of $Et_2O{\cdot}BF_3$ shows a weak absorption at 905 cm^{-1} that can be attributed to C–H out-of-plane bending corresponding to the $R{-}CH{=}CH_2$ group. This absorption is not present in the polymer synthesized with H_2SO_4 alone.

When only sulfuric acid is used as catalyst in the polycondensation of 1,6-hexanediol, the degree of polymerization increases linearly with time in the first 100 hr. At longer times, the experimental points describe a curve in such a way that at 700 hr only $\overline{M}_n = 6900$ has been reached. Such curvature can be explained by considering that, as the conversion increases, the relation between the sulfuric acid and hydroxyl groups rises also, and the possibility of some ether cleavage is favored. Moreover, due to the low polycondensation rate, long heating times are necessary and some charring of the product cannot be avoided. By increasing the amount of sulfuric acid moderately, the polycondensation rate increases in the first steps, as it is expected

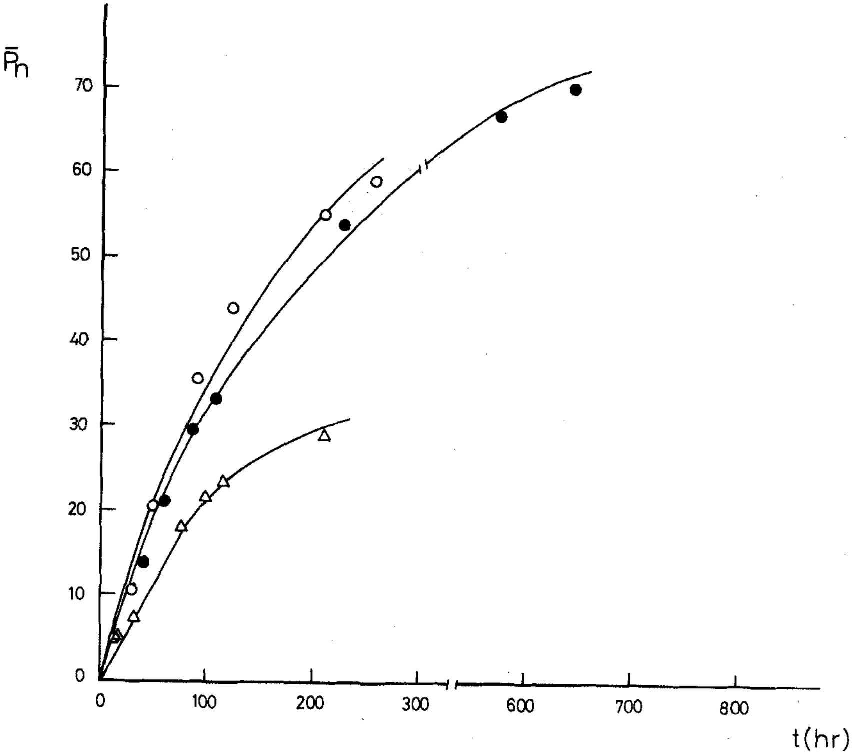


FIG. 2. Polycondensation of 1,6-hexanediol at 175°C: (○) [1,6-Hex.] = 9.7 M, [H_2SO_4] = 2.75×10^{-2} M; (●) [1,6-Hex.] = 9.7 M, [H_2SO_4] = 8.1×10^{-3} M; (△) [1,6-Hex.] = 9.7 M, [H_2SO_4] = 2.75×10^{-2} M; [Et_2OF_3B] = 7.9×10^{-2} M.

for a process of pseudo-second order, following Eq. (1), but the same *final conversion is obtained.* As is shown in Fig. 2, the curvature of the conversion curve is more pronounced at higher catalyst concentrations than under more dilute conditions. So by this method, it is *a very difficult task to obtain polyoxide of more than* $\overline{M}_n = 7000$.

$$1/(1 - p) = \overline{P}_n = k[H^+]t = k't \qquad (1)$$

However, fractionation of this material allows one to isolate fractions which represent the 15% of the starting material with molecular weight up to 25,000.

Ring-Opening Polymerization

When the proper experimental conditions are used, the cationic polymerization of some heterocycles, for example tetrahydrofuran (THF), occurs with the characteristic of a living polymerization, that is, without appreciable transfer or termination reactions [7]. In this way, high molecular weights of the corresponding polyoxide can be reached without any serious difficulties. The polymerization became less ideal in going from an almost flat molecule like THF to oxepane (OX), which has a puckered conformation.

The kinetics of the cationic ring opening polymerization of OX was first studied by Saegusa [8] and recently by Penczek [9]. The published data show that with oxonium salts the initiation, although slow, is faster than the propagation and a termination reaction also is present [8, 10], although with a counterion of low nucleophilicity and at low conversion termination can be absent [9]. These facts are corroborated in experiments depicted in Fig. 3, in which the polymerization of oxepane in Cl_2CH_2 has been initiated by $Et_3O^+SbCl_6^-$. The progress of the polymerization, was followed by dilatometry, and the concentration of living ends measured by the method of Saegusa [11]. As can be seen in Fig. 3, linear plots of $\ln[(M)_0/(M)_t]$ vs. $\int [P^*]dt$ were obtained up to high conversions.

Although a kinetic study of the polymerization of oxepane was not the aim of this work, from the plot in Fig. 3 a k_p value of 2.5×10^{-5} liter/mole-sec at -5°C was obtained. This value is higher than the value reported by Saegusa [8] and it is close to the Penczek data (after recalculation for -5°C, $k_p = 4 \times 10^{-5}$ liter/mole-sec) [9]. The excellent concordance indicates the optimal of the experimental conditions. Minor discrepancies in the values can be attributed to differences in concentration of oxepane and to the influence of the polarity of the medium on the value of the rate constants, as was clearly pointed out by Penczek [9].

A few samples of OX were polymerized to relatively high conversion, and the $\overline{M}_n$ of the isolated polymer was measured (Table 1). From the above kinetic considerations the expected $\overline{M}_n$ should be equal to yield times $100[M]_0/[C]_0$, where the symbols have the usual meaning. But it was found that the experimental $\overline{M}_n$ was always lower than the theoretical value. It seems that as the monomer to initiator ratio increases those differences increase too, although this last assertion needs more experimental data for confirmation. Therefore, from the values of Table 1 it may be concluded that a chain-transfer reaction is present in this polymerization. The mechanism of this transfer reaction could be transfer from the growing ion to the monomer or can be assumed that the termination reaction is an anion-cation reaction, in which the growing ion-pair collapses to give

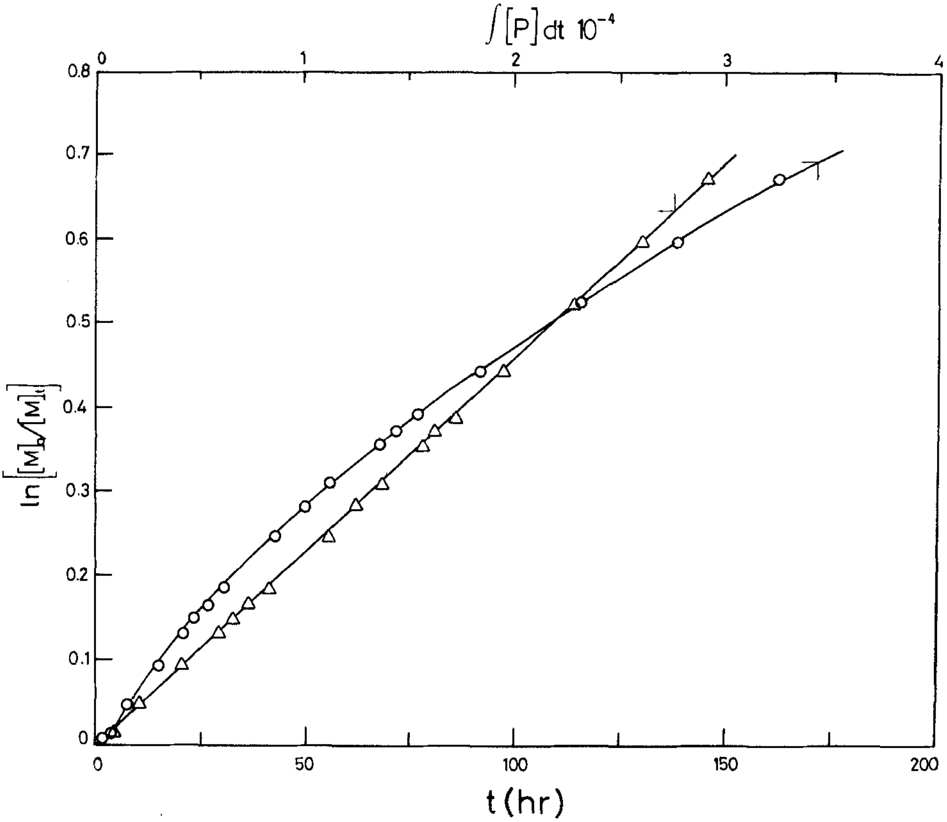


FIG. 3. Polymerization of oxepane in CH_2Cl_2 initiated by $(CH_2H_5)O_3^+\ SbCl_6^-$; T ≈ -5°C.

TABLE 1. Oxepane Polymerization in Cl_2CH_2 at 0°C

	Run I	Run II	Run III
$[M]_0/[C]_0$	248	195	94
Yield (%)	47	30	36
$\overline{DP}_{exptl}$	87	50	31
$\overline{DP}_{n,theor}$[a]	117	59	34

[a] $\overline{DP}_{n,theor}$ = yield $[M]_0/[C]_0$; catalyst, $Et_3O^+SbCl_6^-$.

one chain ending in C - Cl; simultaneously, $SbCl_5$ is formed. This $SbCl_5$, at least in part, could initiate a new chain. However, we cannot firmly assert this mechanism, because it is not known if $SbCl_5$ is able to initiate the polymerization of OX, although other pentahalides like PF_5 [10] that are more acid than $SbCl_5$, polymerize oxepane. Attack of $SbCl_5$ on an oxygen of the formed polymer to give chain scission is another explanation for the $\overline{M}_n$ data; this kind of degradation is well known in polyacetals.

But whatever the correct interpretation may be, after killing with methanol, the samples depicted in Table 1 are not totally methoxy group-ended. The importance of this fact, concerning the thermal stability of this polymer, will be discussed in the next section.

Thermal Stability

The thermal stability of the polymers depends greatly on the nature of the endgroups of the chain. This is especially important in those polymers in which the degradation takes place by a chain end-initiated unzipping mechanism which produces monomer as degradation product.

A well known example of this behavior in polyethers is the first member of this series, poly(methylene oxide). In this polymer, the thermal stability depends, in an important way, on the nature of the endgroups. Concerning our polyether, PHMO there is only a single previous work [3] in which the thermal degradation has been studied. Among the products isolated the cyclic monomer oxepane was not formed, and it was concluded that the mechanism of degradation proceeds only by a radical mechanism starting by a C–C scission, this bond being in α position to the ether bond.

Differences in the thermal stability of samples with the same molecular weight, $\overline{M}_n = 3000$, obtained apparently by the same way (polycondensation from 1,6-hexanediol), are clearly seen in Fig. 4. But in one case, H_2SO_4 alone was used as catalyst in the synthesis, and in the other synthesis $H_2SO_4/Et_2O{\cdot}BF_3$ was used. As it has been pointed out before, the main structural differences between both samples corresponds to the endgroups: for the first sample, these are OH and for the last, vinyl were founded by I. R. It seems that the lower thermal stability is associated with the sample OH ended.

In order to have a better insight into the influence of endgroups on the degradation rate of PHMO we have obtained a series of thermogravimetric curves of three polymer samples, fractionated and of the same $\overline{M}_n = 10{,}000$: A-1, synthesized with H_2SO_4 from 1,6-hexanediol; A-2, synthesized with $Et_3O^+ SbCl_6^-$ from oxepane and killed with methanol; and sample A-3, in which the endgroups were carefully methylated as is described in the experimental part. As seen in Fig. 5, the thermal stability of the three samples decreases in the order: A-3 $>$ A-2 $>$ A-1.

The differences in the thermal stability of these three samples are

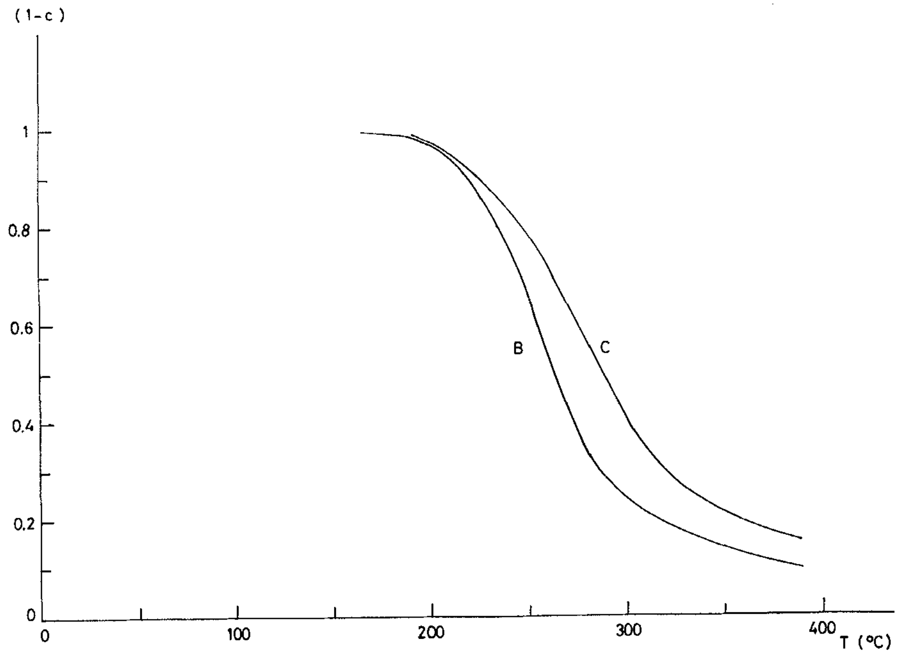


FIG. 4. Thermal decomposition of POX ($\overline{M}_n$ = 3000) synthesized (B) with H_2SO_4 and (C) with $H_2SO_4/Et_2O{\cdot}BF_3$.

very pronounced and they cannot be attributed to molecular weight differences, because the $\overline{M}_n$ is almost the same. The presence of weak points, especially of peroxide groups, is precluded by previous thermal treatment which the samples underwent at 100°C in vacuo. The discrepancies must be attributed to differences in the degradation mechanism. In the collected products of the degradation of sample A-1, after analysis by gas chromatography, similar products to those reported by Blyumenfel'd [3] were found, but in addition a significant amount (~15%) of oxepane was identified; on the other hand, cyclic monomer was not found in the methylated polymer or in the sample prepared by cationic polymerization.

The effect which the variation of the heating rate produces in the shape of the differential curves is shown in Fig. 6. Decreasing the rate of heating in sample A-1 leads to a thermogram in which two peaks are obtained on the differential curve, but this does not occur in the other two samples. This behavior was predicted for two independent first-order reactions with different activation energies [12]. These facts, together with the finding that the formation of oxepane is

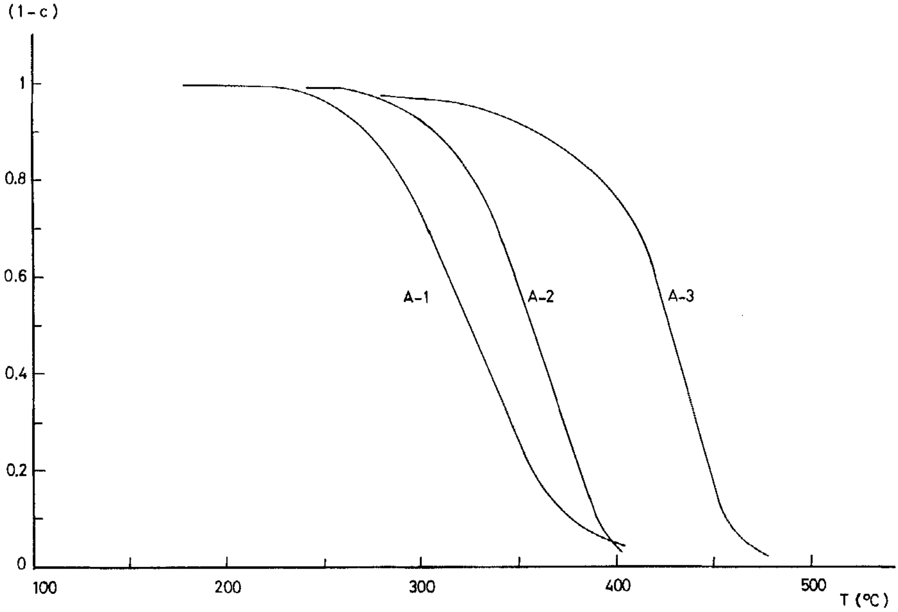
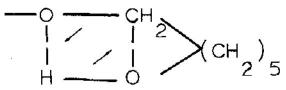


FIG. 5. Thermal decomposition of POX ($\overline{M}_n$ = 10,000).

only associated with the presence of OH-ended chains allows one to conclude that two simultaneous degradation mechanisms are operative in this polymer: one probably a radical-chain mechanism, in which the initiation of the chain process takes place with C–C bond scission in the α position relative to the ether bond [3], and another, in which the OH endgroups participate, resulting in the formation of monomer oxepane. This last process is not a free-radical mechanism because the formation of oxepane is not produced either in the methylated samples nor in the cationic polymers. The oxepane may be produced by a molecular [13] or an ionic mechanism. In the first case, four bonds are mainly involved and the electrostatic effect of the hydrogen bond on the last ether unit would facilitate the necessary electron movement in this transition state.



Keeping in mind the relatively not very high value of the ceiling temperature [14] for the equilibrium oxepane $\rightleftharpoons$ poly(hexamethylene oxide), the formation of monomer by an ionic mechanism is highly

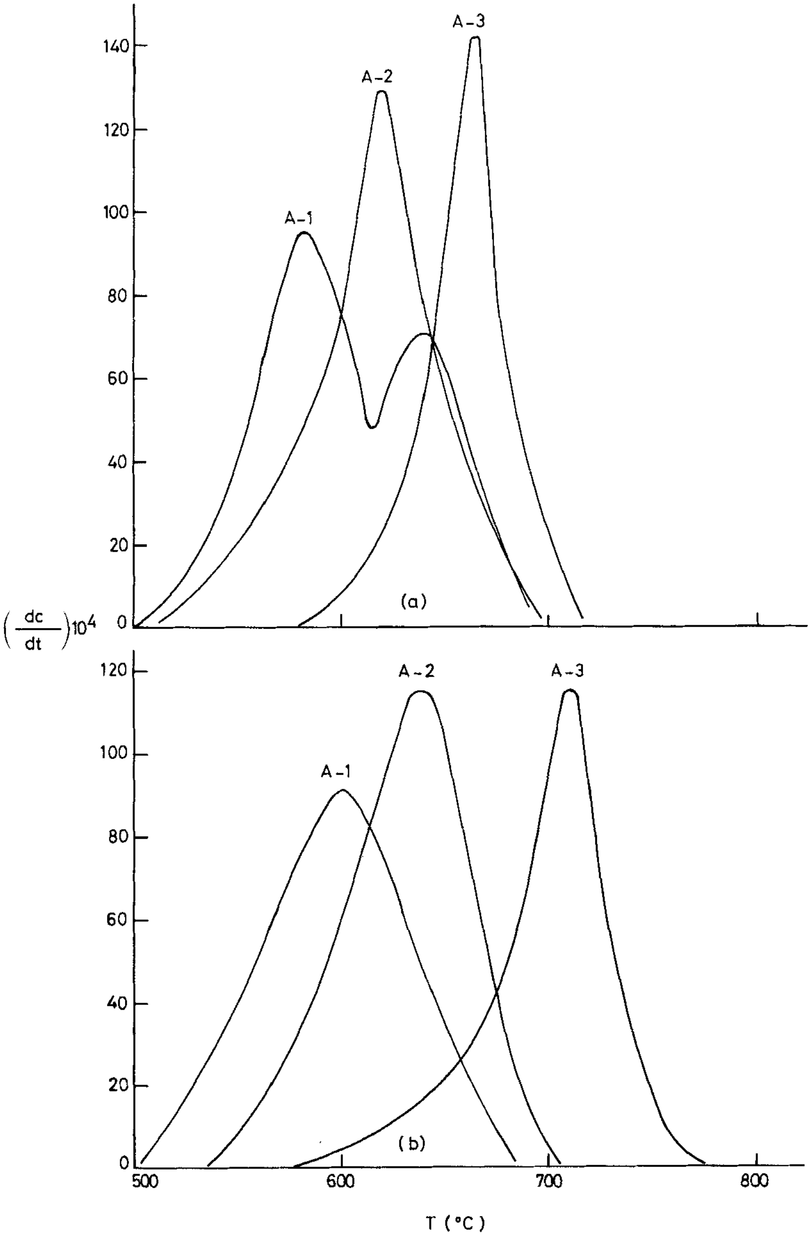


FIG. 6. Effect of rate of heating on the thermogravimetric rate against temperature.

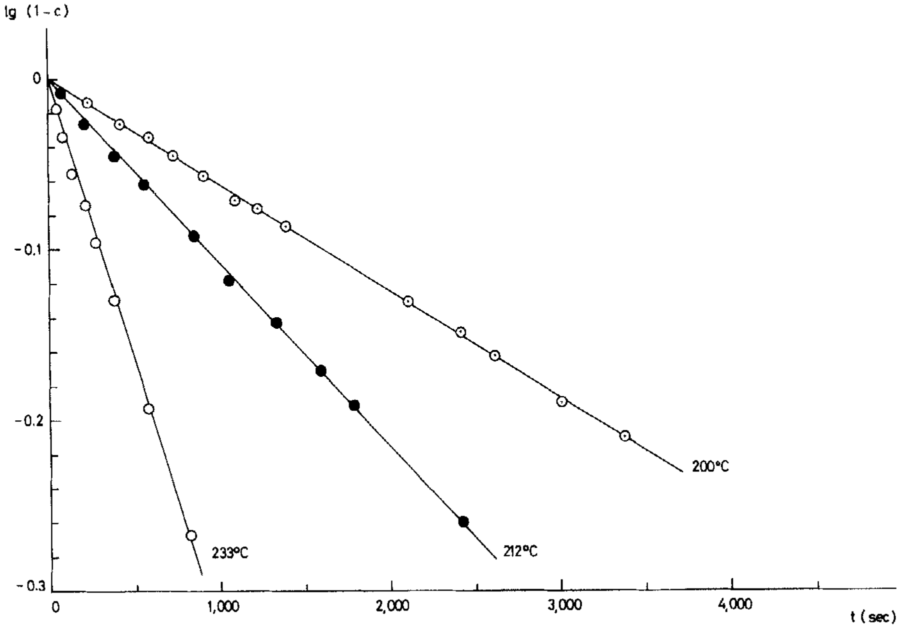


FIG. 7. Isothermal degradation of sample A-1.

probable if any impurity gives by solvation the necessary energy to transform the covalent O–H bond to an ionic bond.

On the other hand, the activation energy for the degradation must reflect the differences in the chain endgroups, especially, in the early stages of the process, below 20% degradation. Figure 7 shows the weight loss (%) against time for the isothermal degradation of sample A-1. The data are represented linearly, indicating a first-order reaction. From the slope of these lines the degradation rate constants and the values of the activation energy were obtained for the three samples; the apparent activation energies were 27, 25, and 37 kcal/mole for samples A-1, A-2, and A-3, respectively. In the nonisothermal experiments, the Coats-Refern method has been used [14]. For a first-order reaction it has been shown that:

$$\log\left(-\log\frac{1-c}{T^2}\right) = \log\frac{AR}{aE_a}\left(1-\frac{2RT}{E_a}\right) - \frac{E_a}{2.3RT}$$

The usual plot $\log[-\log(1-c)/T^2]$ vs. $1/T$ is linear (Fig. 8), and from the slopes, the activation energy was calculated. These values

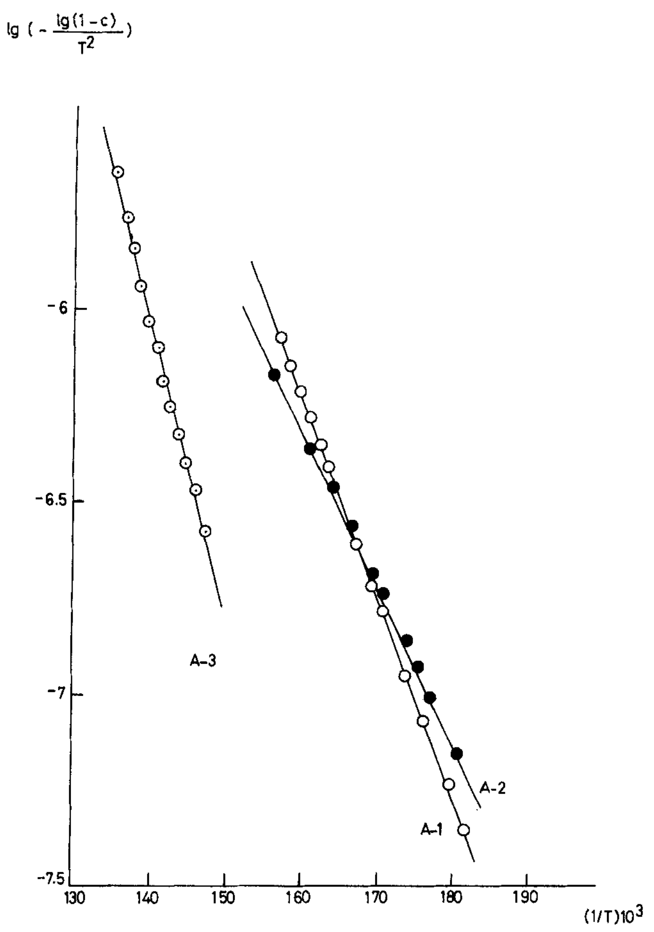


FIG. 8. Coats-Refern plot for samples A-1, A-2, and A-3.

are 26, 24, and 38 kcal/mole for A-1, A-2, and A-3, respectively, and they agree quite well with the values obtained from isothermal experiments. There is no explanation for the low value of the activation energy of the cationic sample because as, it was discussed before, the exact nature of its endgroups is not well known. In the GLC analysis of the degradation products of this sample, two unidentified minor peaks appear that are not found in the other two samples, showing a slightly different mode of degradation.

The analysis of the influence of molecular weight on the thermal stability of PHMO has been carried out on fractions with molecular weights ranging from 3,500 to 35,000, obtained from the polymer

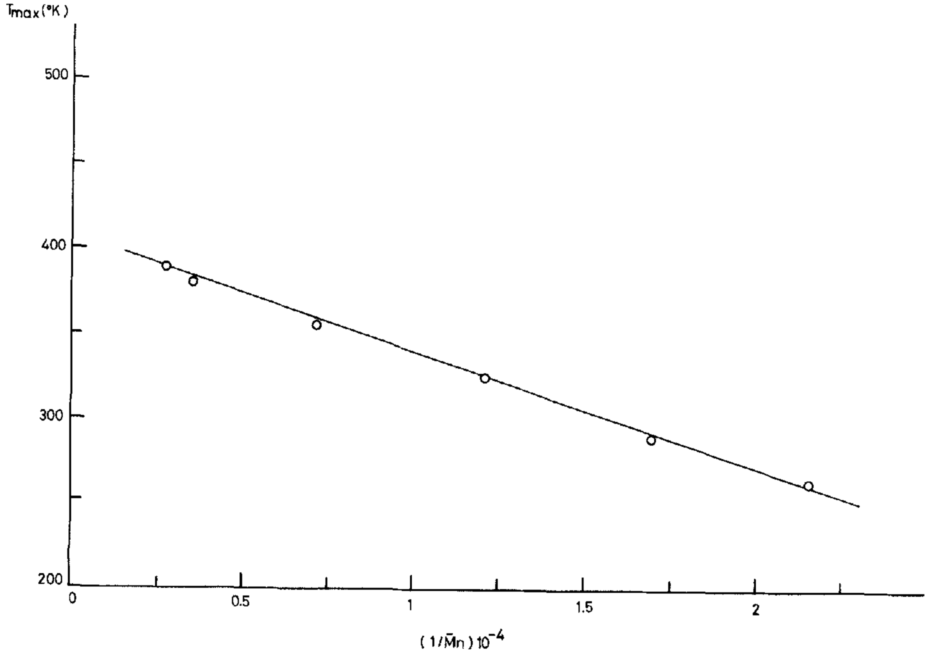


FIG. 9. Temperature at the maximum decomposition rate against reciprocal initial number-average molecular weight.

prepared by polycondensation with H_2SO_4. As expected for a mechanism in which the endgroups participate, there is strong dependence on the rate of degradation with molecular weight. The temperature at the maximum rate of decomposition has a clear dependence on the initial molecular weight, as is shown in Fig. 9. An increment in molecular weight of 10,000 represents an increase of 50°C on $T_{max.\ rate}$ in the molecular weight range which has been examined.

In summary, the preceding results allow to conclude that the thermal degradation of PHMO may occur simultaneously by depolymerization and by random chain scission, the former being present when the endgroups are OH; if these groups are capped, the thermal stability of the polymer increases, the cyclic monomer is not formed, and only products from a random chain scission are produced.

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