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A KINETIC STUDY OF THE THERMAL DEGRADATION OF POLY(DIHEXYL ITACONATE)

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ABSTRACT

The kinetics of thermal degradation of poly(dihexyl itaconate) (PDHI), in the absence of oxygen, were determined on the basis of non-isothermal and isothermal TG data. Two PDHI samples of different weight average molar masses were used in the study. Two distinct DTG peaks were registered in the investigated range of 30° - 600°C. Uniform values of the thermal degradation activation energy, E_a, (118 kJ/mol) were obtained from non-isothermal data using the Flynn-Wall method for both samples up to mass losses of 60 - 70 %. The E_a's at higher mass losses averaged about 150 kJ/mol. Corresponding E_a values were obtained from isothermal TG data analysed by classical kinetics. There seemed to be no influence of sample molar mass on the value of E_a.

INTRODUCTION

Interest in polymeric derivatives of itaconic acid has recently been revived as these materials can be applied as resists in lithography /1/. In this age of limited resources, itaconic acid itself is an attractive raw material as it can be synthesised from non-petrochemical sources by fermentation processes /2/.

No extensive work has been performed on the thermal stability of this class of compounds /3/. A more detailed investigation of the thermal degradation of poly(dialkyl itaconates) was initiated by studying the thermal degradation of poly(dimethyl itaconate) (PDMI) /4/. The major PDMI thermal decomposition mechanism was found to be depolymerisation.

The next step was to then examine how the thermal degradation mechanism of poly(dialkyl itaconates) would be affected by increasing the substituent in the side chain and, thus, poly(dihexyl itaconate) was chosen.

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EXPERIMENTAL

Poly(dihexyl itaconate) was obtained by bulk polymerisation of di-n-hexyl itaconate at 50°C with AIBN as initiator /5/. The polymer was purified by multiple precipitation from benzene solution using methanol. PDHI is a clear, tacky solid at room temperature. Two polymer samples, obtained by varying the initiator concentration, with weight average molar masses of 2.6 x 10^5 g/mol (sample 1) and 7.0 x 10^5 g/mol (sample 2) were used in the study.

Thermogravimetric measurements were performed using a Perkin Elmer TGS-2 instrument with purified nitrogen as the carrier gas (flowrate 15 cm^3/min). Heating rates of 2.5, 10, 20 and 40°C/min were applied in non-isothermal experiments in the temperature interval 30° - 600°C. DTG measurements were performed in the same interval at a heating rate of 0.625°C/min. Isothermal experiments were done in the range 230° - 310°C (10° intervals). The sample masses ranged from 6-8 mg.

RESULTS AND DISCUSSION

Non-isothermal measurements (Fig. 1) yielded the following characteristic temperatures.

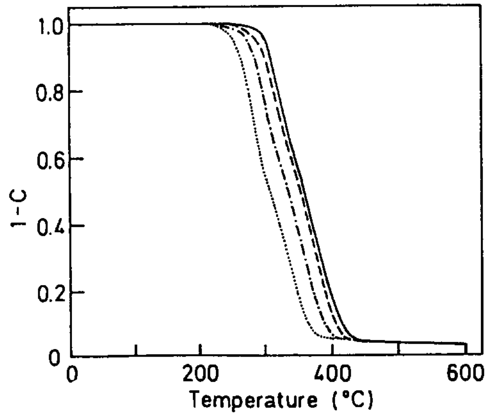

Fig. 1. Non-isothermal TG curves of PDHI (sample 1), heating rates β : 2.5 (· · · · · ·), 10 (- · - · -), 20 (- - - -) and 40 °C / min (———).

The temperatures of 5% mass loss, $T_{0.05}$, at a heating rate of 2.5°C/min were 233.5° and 253.0°C for samples 1 and 2, respectively.

However, this difference in temperature diminished with conversion yielding at $T_{0.50}$ 312.5°C and 306.5°C, respectively, for samples 1 and 2. $T_{0.90}$ was 372.5°C (sample 1) and 364.5°C (sample 2). At 600°C both samples attained approximately 95% mass loss.

Two distinct maxima were registered in DTG analysis (Fig. 2). For sample 1 they were found to be at 262.5°C and 318.0°C, while sample 2 yielded 266.3°C and 320.0°C, respectively.

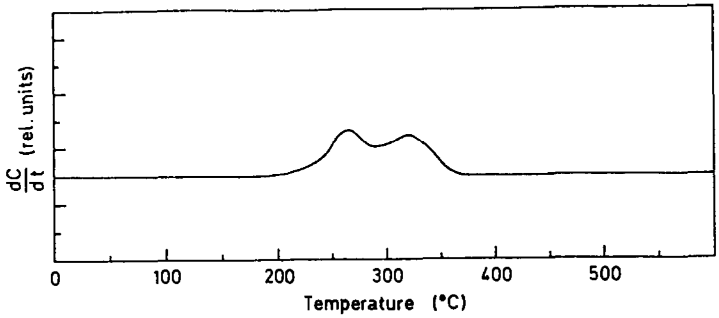

Fig. 2. Non-isothermal DTG curve of PDHI (sample 1), heating rate $\beta = 0.625$ °C / min

As the Freeman-Carroll technique /6/ proved to be unsuitable for this polymer system, the Flynn-Wall method /7,8/ was applied for determining the thermal degradation activation energy, E_a, from non-isothermal data. Although, in the case of both samples, a slight change in the slope of the TG curves was registered at 50% mass loss (also confirmed by peak separation in DTG), uniform values of E_a were obtained for both samples up to mass losses of 60-70%. The average E_a in that interval was 118 kJ/mol for sample 1 and 112 kJ/mol for sample 2. The activation energies at higher mass losses averaged about 153 kJ/mol for sample 1 and 136 kJ/mol for sample 2, the data scatter being considerably higher in this mass loss range.

Isothermal TG data (Fig. 3) were analysed by classical kinetics assuming that polymer decomposition followed the reaction:

$$sS(s) = bB(g) + cC(s) \qquad (1)$$

where S denotes the initial polymer, B the volatile degradation products and C the residue upon degradation.

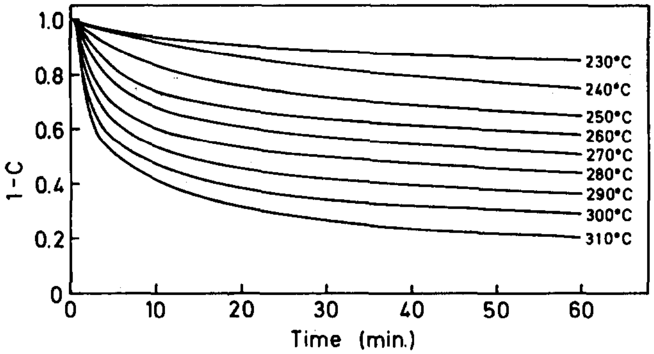

Fig. 3. Isothermal TG curves of PDHI (sample 1)

The rate of disappearance of polymer, r_s is then:

$$r_s = -dS/dt = k \cdot S^n \qquad (2)$$

The rate constant, k, is assumed to be Arrhenius dependent:

$$k = A \exp(-E_a / RT) \qquad (3)$$

This method enables determination of the rate constants k, activation energy E_a, apparent reaction order n and pre-exponential factor A. It is assumed that $dS/dt \approx \Delta S / \Delta t$. The relative amount of polymer S at time t is defined via the conversion, expressed by mass loss C, as 1-C. Equation 2 can then be tranformed to the following form:

$$\ln r_s = \ln \frac{\Delta(1 - C_t)}{\Delta t} = \ln k + n \cdot \ln \frac{(1 - C_t)_{av}}{1 - C_o} \qquad (4)$$

where. $\Delta(1-C_t) = (1 - C_t)_{i+1} - (1 - C_t)_i$
$\Delta t = t_{i+1} - t_i$
$(1-C_t)_{av} = [(1 - C_t)_{i+1} - (1 - C_t)_i] / 2$ and
$(1-C_o)$ is the amount of polymer at $t = 0$ /9/.

As the sample is never instantaneously exposed to the desired temperature in isothermal measurements, sample mass loss can occur in this transition time yielding a C_0 greater than 0.

From the linear dependence, defined by equation 4, one can calculate the apparent reaction order from the slope and the rate constant from the intercept. E_a and A can then be easily be calculated via the Arrhenius equation.

An activation energy of 116 kJ/mol was obtained for the first process in sample 1 with a pre-exponential factor of 8×10^8 s^{-1}. The apparent reaction orders decreased with increasing temperature in the interval 250° to 310° C from about 10 to about 4 indicating a considerable temperature influence on individual degradation reactions. In the case of sample 1 the agreement between the values of E_a obtained by non-isothermal and isothermal TG data was very good.

An activation energy of 133 kJ/mol was obtained for the first process in sample 2., $A \approx 8 \times 10^{10}$ s^{-1}. The apparent reaction orders followed the same trend as the n's of sample 1. The scatter of data in this series of experiments was much greater than in the sample 1 series (where it was quite low). That would explain the discrepancy with the E_a obtained by the Flynn-Wall method.

CONCLUSIONS

From the results obtained it may be concluded that polymer molar mass does not, in the particular range investigated, significantly affect the value of thermal degradation activation energy. As expected, the influence of polymer molar mass is reflected in the temperature at which mass loss begins.

It is, of course, not possible to postulate a thermal degradation mechanism only on the basis of kinetics. However, it may be stated that there are two phases in PDHI decomposition, the first one commencing between 150° and 220° C, depending on the sample molar mass, and the second starting slightly below 300° C. Nothing can be said with certainty about the nature of these phases, i.e. their complexity, without detailed product analysis.

Due to the more complex structure of PDHI, it is expected that the fraction of depolymerisation will be lower as there are more scission possibilities. Further work on the elucidation of the PDHI degradation mechanism is in progress.

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