THERMAL BEHAVIOUR OF SOME MORE SOLUBLE ESTER-IMIDE OLIGOMERS

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Thermal behaviour of four ester-imide oligomers, two containing ethylene glycol and two neopentyl glycol as dihydroxy comonomers and two different amounts of dimethyl-terephthalate emphasises the effect of the nature of glycol and amount of dimethyl-terephthalate on their thermal stability. DSC, TG, DTG and DTA data show that neopentyl glycol has as effect the decreasing of relative weight losses of oligomers compared with the corresponding ones containing ethylene glycol both when low and high amounts of DMT were used, when relative weight losses up to about 0.73 (temperature up to about 400°C) are considered. An increased amount of DMT decreases weight losses when ethylene glycol was used at temperatures ranging between 230 and 250-260°C and increases them between about 330 and 420°C. With neopentyl glycol as dihydroxy comonomer, an increased amount of DMT increases relative weight losses at temperature ranging between 230 and 420°C.

Introduction

Two ester-imide oligomers soluble in more solvents and mixtures of solvents compared with the commercial ones containing ethylene glycol as dihydroxy comonomer were obtained synthesizing the oligomers using a branched dihydroxy comonomer – neopentylglycol. The corresponding oligomers containing ethylene glycol were also prepared for comparison purposes. Thus, four ester-imide oligomers, R_1-R_4, were obtained by the melt copolycondensation of the following comonomers: tris(2-hydroxyethyl)-isocianurate (THEIC), ethylene glycol (EG) or neopentylglycol (NPG) as hydroxyl components; dimethyl-terephthalate (DMT) and trimellitic anhydride (TMA) as carboxyl ones; diaminodiphenylmetane (DDM) as amine comonomer. Their preparation was described in an earlier paper [1].

R_1 and R_2 contain EG and two different amounts of DMT, while R_3 and R_4 contain NPG and the same amount of DMT (R_2 and R_4 contain high amount). Some of their characteristics: composition, confirmation of ester-imide structure by IR, solubility in different solvents, global and partial solubility parameters and glass transition temperatures determined by DSC were also discussed [1, 2].

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Some ester-imide oligomers may become H thermal class insulators after their curing by heating or catalytically [3 ÷ 6]. Hence, their thermal behaviour is very important for understanding the reactions that produce their thermal curing. Thermal behaviour of oligomers R_1-R_4 within the temperature range 20-420°C, studied by DSC, TG, DTG and DTA, is presented into the present paper in order to throw a light on the mechanism of their curing by heating.

Experimental part

DSC curves in nitrogen were recorded using a DSC V4 DuPont instrument. The sample weights were 17-25 mg, heating rate 20 K min^{-1} and temperature range 40-300°C.

TG, DTD and DTA curves were obtained in air, using a type C 1989-MOM Budapest instrument as well as a DuPont 2000 one. The sample weights were 30-40 mg, heating rate 10 K min^{-}1 and temperature 20-400°C. GLG for identification of EG was performed using a Carlo Erba FRACTOVAP model D Chromatograph, equipped with FID. Carbowax 20M was used as stationary phase and Chromosorb as support.

Result and discussion

DSC curves of the four oligomers were registered between 40 and 320°C (curing temperature is under 300°C) are presented in Figure 1.

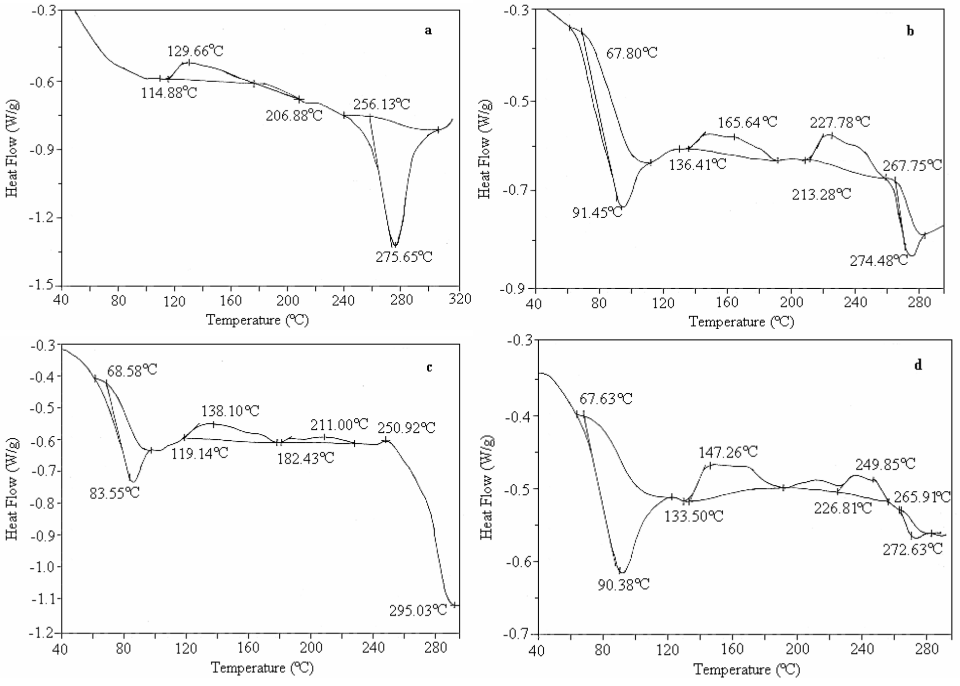

Fig. 1: *DSC curves in nitrogen for: a – R_1; b – R_2; c – R_3; d – R4*

They show that, increasing the temperature, an endothermic process at temperatures ranging between about 60 and 110°C, followed by two more or less delimited and obvious exothermic ones ranging between about 115 and 250°C and a pretty sharp endothermic process between about 250 and 320°C can be observed.

The endothermic process appearing at low temperatures can be assigned to the elimination of water included at the end of syntheses, during the oligomers' solidification.

The exothermic processes could be due to the cyclization of the remaining amic acids, which did not formed imide rings at the end of the reaction, i.e. to their imidization by cyclization, as well as to the esterification reactions. But the ester-imide oligomers have small amounts of carboxyl groups, as acidity indices – having values between 180 and 210 mg KOH/g – show, and the last reactions are produced in small amounts.

The last endothermic process can be assigned to the elimination of glycols – EG in the case of R_1 and R_2 and NPG for R_3 and R_4 – that produces the increasing of chain length and hence has as effect the increase of molecular weights. EG and NPG were identified by the analysis of condensation products: the first one by gas-liquid chromatography and the second one by determination of the melting point.

TG curves of the four oligomers normalized to unity are presented superposed in Figure 2, to facilitate the comparison of their heating behaviour.

The TG curves emphasise different weight losses for the four oligomers within the temperature range 200-420^{0}C. Thus, oligomers containing NPG have lower relative weight losses compared with the corresponding ones containing EG both when low and high amounts of DMT were used when relative weight losses up to about 0.73 are considered. R_3 has also lower relative weight losses compared with R_1 within the entire mentioned temperature range, while R_4 has higher weight losses compared with R_2 only into the temperature range 320-420^{0}C. NPG reduce hence weight losses only when low amount of DMT were used.

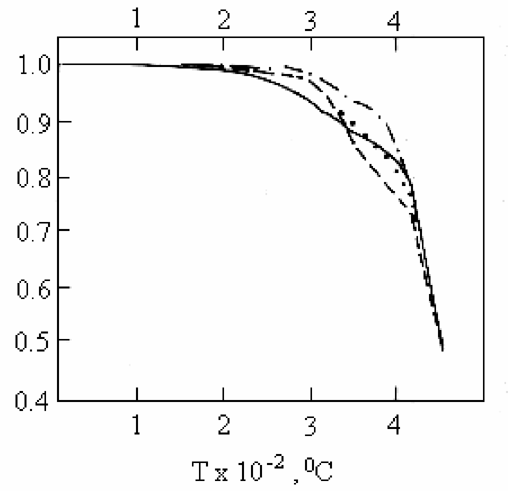

Fig. 2: *Superposed TG curves of the four oligomers normalized to unity:*— - R_1; — — - R_2; —·— - R_3; ···· - R_4

Regarding the effect of DMT, an increased amount of DMT decreases weight losses when EG is used at temperatures ranging between 230 and 250-260^{0}C and increases them between about 330 and 420^{0}C. With NPG as dihydroxy alcohol, an increased amount of DMT increases relative weight losses between 230 and 420^{0}C. These results are contrary to theoretical expectation: an increased number of aromatic rings into the main chain increases the heat resistance. This can be explained by the higher number of ester groups, which are more sensitive to thermal degradation, into the main chain of these oligomers, due to a higher amount of DMT.

TG, DTG, and DTA curves in air – reproduced in Figures 3a-d – indicate weight losses within the temperature range 150-350^{0}C, accompanied by slight exothermic effects. The above temperature range is almost similar with that resulted from the DSC curves. These weight losses, reported to the corresponding initial weights, range between 4.80 and 10.32%.

Theoretical weight losses, calculated considering the molecular weight of oligomers, the ratio of di- to trifunctional oligomers and the stoichiometry of reactions [1], range between 4.80 and 8.64%. They are very close to the experimentally determined ones.

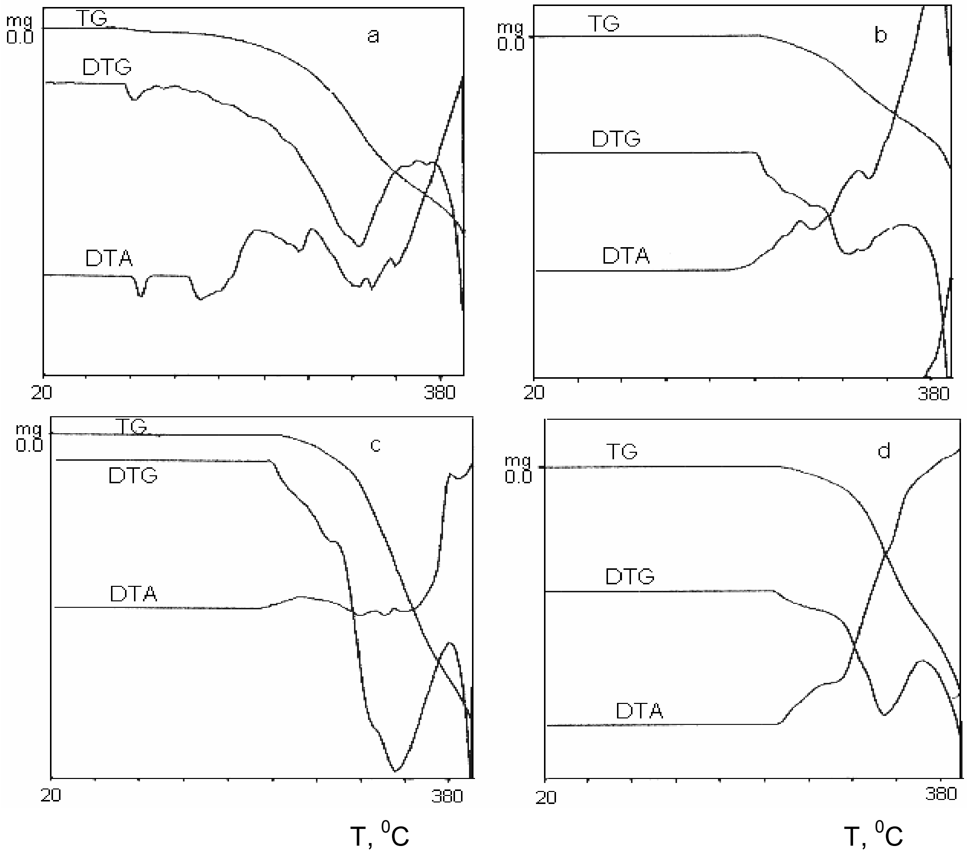

Fig. 3: *TG, DTG, and DTA curves in air for oligomers: a - R_1; b – R_2; c – R_3; d – R_4*

Kinetic parameters of the reactions taking place within the above temperature range were calculated from TG data using the differential method and the equation of reaction rate adapted to non-isothermal conditions [7]:

$$\beta(d\alpha/dT) = A \exp(-E_a)/RT)\, f(\alpha) \qquad (1)$$

where β is the linear heating rate, K s^{-1}; α - weight loss fraction; A – frequency factor, s^{-1}; E_a – activation energy, J mol^{-1}; T – temperature, K, and $f(\alpha)$ – kinetic function.

The tested $f(\alpha)$ functions that give the best correlation with equation (1) are summarized in Table 1 together with their rate-controlling processes [7].

Table 1. Tested kinetic functions

Kinetic function	n	m	Rate controlling process
α^n	0.1–3.0	-	Nucleation (n<1) or growth of germs (n>1)
$(1 - \alpha)[-\ln(1 - \alpha)]^n$	0.1–3.0	-	Growth of germs
$\alpha^n(1 - \alpha)^m$	0.1–3.0	0.1–3.0	Nucleation or growth of germs in final stage
$(1 - \alpha)^{1/3}[(1 - \alpha)^{-1/3} – 1]^{-1}$	-	-	Three-dimensional diffusion (Jander)
α^{-1}	-	-	Uni-dimensional diffusion
$[(1 - \alpha)^{-1/3} – 1]^{-1}$	-	-	Three-dimensional diffusion (Gindsling-Brounstein)
$[- \ln(1 - \alpha)]^{-1}$	-	-	Three-dimensional diffusion
$(1 - \alpha)^n$	0.1–3.0	-	Chemical reaction (Friedman)

Kinetic parameters of degradation reactions of ester-imide oligomers were calculated from TG data using equation (1). The temperature ranges on which the parameters were obtained, the weight losses determined from TG curves and the calculated values are presented in Table 2.

Table 2. Temperature ranges, kinetic parameters, experimental and calculated weight losses

Oligomer	Temperature range, °C	Frequency factor, s^{-1}	Activation energy, kJ mol^{-1}	Reaction order	Weight losses, %	
					TG	Calculated
R_1	150-275	1.129	40.86	5	4.79	4.80
R_2	240-340	0.414	39.21	5	6.35	4.90
R_3	200-345	3888.020	79.02	5	10.32	7.20
R_4	225-330	499.450	70.73	5	7.09	8.64

The data in Table 2 show the best correlation between the determined and calculated weight losses for oligomer R_1 and the poorest for oligomer R_3. This can be explained by the fact that NPG presents more breaking possibilities compared with EG, and elimination occurs over a larger temperature range.

The existence of the compensation effect proves the similitude of the degradation reactions of the four oligomers.

The reaction orders higher than unity can be explained by the distribution of molecular weights and the simultaneous breaking of molecules that results in similar compounds.

Calculated weight losses correspond to molecular weight increases of about 40 times, i. e. by heating the oligomers were transformed into the corresponding polymers.

Conclusions

1. Oligomers containing NPG have higher heat resistance compared with the corresponding ones containing EG both when low and high amounts of DMT were used when relative weight losses up to about 0.73 are considered.

2. An increased amount of DMT decreases weight losses when EG is used as dihydroxy comonomer at temperatures ranging between 230 and 250-260^{0}C and increases them between about 330 and 420^{0}C.

3. When NPG is used as dihydroxy comonomer, an increased amount of DMT increases relative weight losses between 230 and 420^{0}C.

4. Oligomer R_3, containing NPG and small amount of DMT and having the best solubility, has the highest heat resistance within the entire studied temperature range.

REFERENCES

1. M. Leca and T. Staicu, *Rev Roumaine Chim*. **47**, (2002) 117.

2. M. Leca, T. Staicu, M. Micutz, *Revista de Chimie* (Bucuresti), in press.

3. Bessonov M. I., Katon M. M., Kundryavtsev V. V., Lains L. A., "**Polyimides, Thermally Stable Polymers**", Plenum Press, New York, 1987.

4. Wilson D., Stenzenberger H. D., Hergenrather P. M., "**Polyimides**" Chapman and Hall, New York, 1990.

5. Sroog C. E., Progr. Polymer Sci., **16** (1991) 561.

6. M. Leca, O. Segarceanu, C. Calina, *Thermochimica Acta* **269/270**, (1995) 245.

7. Segal E., Fatu D., "**Introduction to Non-isothermal Kinetics**", Editura Academiei, Bucharest, **1983** (in Romanian).