

## Solubility, curing and heat resistance of some ester-imide oligomers as a function of the nature and content of some comonomers

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### Abstract

Substitution of ethyl glycol by neopentylglycol in ester-imide oligomers increases solubility and decreases glass transition temperature, while increase of quantity of dimethylterephthalate has opposite effects. Oligomer containing neopentylglycol and the lower quantity of dimethylterephthalate, which dissolves even in mixtures of methyldipropylene glycol/xylene or toluene 1/1 by weight to obtain 40% or more concentrated solution, is the most convenient. Heat resistance, mechanical and electrical properties, and dielectric losses are optimum if oligomers are cured by heating for 4 h at 260°C. Curing consists in increase of molecular weight and transformation of oligomers in polymers by the elimination of water and diols. Thermal degradation of polymers involves three stages: elimination of unreacted comonomers and of a part of bound diols; elimination of the rest of diols, dimethylterephthalate and *tris*-(2-hydroxyethyl)isocyanurate; elimination of structures trimellitic anhydride – diaminodiphenylmethane containing aromatic and imidic rings. Neopentylglycol and large quantities of dimethylterephthalate reduce the heat resistance of polyester-imides.

**Keywords:** Curing of ester-imide oligomers; Electric insulators; Ester-imide oligomers; Polyester-imides; Thermal degradation of polyester-imides

### 1. Introduction

Intrinsic and oxidative heat resistance of aromatic rings and of heterocycles have been known for a long time but their introduction into polymeric structures was realized pretty late, through amide [1], imide [2], ester [3] or sulphone [4,5] groups. Unfortunately, structures conferring high heat resistance reduce solubility and increase glass transition or melting temperatures of polymers [6], making their processing more difficult. Heat resistance and easiness of processing are therefore opposite properties. This is why a

slight decrease of heat resistance in the favour of processing is generally accepted and polyester-imides [7] as well as polyamide-imides [8], with similar thermal stability, were synthesized.

Polyester-imides, electric insulators with high heat resistance, have the following advantages [9–11]: greater workability and solubility, flexibility, adhesion to different metals, resistance to solvents and environmental conditions, hardness, lower costs than polyamide-imides. Usually they are commercialized as cresol solutions, solvents known to be carcinogenic. This is why more soluble ester-imide oligomers were synthesized, substituting ethylene glycol by neopentylglycol. Its influence as well as the influence of the

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content of dimethylterephthalate on solubility of oligomers and on the heat resistance of the cured ones were studied in view of their use as electric insulators. Curing conditions and mechanism for oligomers and mechanism of thermal degradation of the cured ones were also studied.

## 2. Experimental

Four ester-imide oligomers, R<sub>1</sub>–R<sub>4</sub> were synthesized by melt copolycondensation of the following comonomers: *tris*-(2-hydroxyethyl)isocyanurate (THEIC), ethylene glycol (EG) or neopentylglycol (NPG) as hydroxylic components; trimellitic anhydride (TMA) and dimethylterephthalate (DMT) as carboxylic ones; diaminodiphenylmethane (DDM) as aminic component, using two different ratios of

DMT. Their composition and number average molecular weights,  $M_n$  are given in Table 1.

Ester-imide structure was confirmed by IR spectroscopy.

Diffraction X-ray patterns shown the lack of crystallinity.

Glass transition temperatures,  $T_g$ , were determined using a DSC V4 OB DuPont 2000 at a heating rate of 20 K min<sup>-1</sup> in nitrogen. Samples of 17–25 mg and temperatures ranging between 20 and 300°C were used.

The compounds given in Table 2 were used as solvents. The results for oligomer to solvent ratios 1/4 by weight are given in the same Table together with their global,  $\delta$ , and partial –  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$  – solubility parameters of solvents [12,13].

Curing of oligomers was realized by heating at 1, 4, and 6 h at 260°C. A curing mechanism was established by TG, DTA, DSC, IR, and gas chromatography.

Table 1

Composition of ester-imide oligomers given as ratios of molar concentrations of functional groups of comonomers

Oligomer	Comonomer	OH/COOH	COOH/NH <sub>2</sub>	NH <sub>2</sub> /anhydr.	$M_n$
R <sub>1</sub>	THEIC, EG, DMT, TMA, DDM	2.10	2.49	1.00	1230
R <sub>2</sub>	THEIC, EG, DMT, TMA, DDM	1.61	3.23	1.00	119
R <sub>3</sub>	THEIC, NPG, DMT, TMA, DDM	2.10	2.49	1.00	1350
R <sub>4</sub>	THEIC, NPG, DMT, TMA, DDM	1.61	3.23	1.00	1130

Table 2

Solvents, their global and partial solubility parameters and oligomer solubility

Solvent	Solubility parameters/(MPa) <sup>1/2</sup>				Oligomer solubility			
	$\delta$	$\delta_d$	$\delta_p$	$\delta_h$	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
Tetrahydrofuran	19.4	16.8	5.7	8.0	+	+	+	+
Dichloromethane	19.8	18.2	6.3	6.1	+	+	+	+
Acetone	20.0	15.5	10.4	7.0	–	–	+	–
1,2-Dichloroethane	20.0	18.8	5.3	4.1	+	–	+	+
Cyclohexanone	20.2	17.8	8.4	5.1	+	+	+	+
Morpholine	21.5	18.8	4.9	9.2	+	+	+	+
Pyridine	21.7	19.0	8.8	5.9	+	+	+	+
Methyldiethyleneglicol	21.9	16.2	7.8	12.7	–	–	–	–
<i>m</i> -Cresol	22.7	18.0	5.1	12.9	+	+	+	+
Dimethylformamide	22.9	17.0	13.3	9.2	+	+	+	+
<i>N</i> -Methylpyrrolidone	22.9	18.0	12.3	7.2	+	+	+	+
Dimethylenetriamine	25.8	16.8	13.3	14.3	+	+	+	+
$\gamma$ -Butyrolactone	26.0	19.0	16.6	6.5	+	+	+	+
Dimethylsulphoxide	28.4	18.4	16.4	10.2	+	+	+	+

– –: No interaction;

+–: Swelling; and

+: Complete dissolution.

Thermal stability of the cured resins was evaluated from TG curves obtained with a Derivatograph type C, 1989 – MOM Budapest, at a heating rate of  $10 \text{ K min}^{-1}$  in air, using samples of 30–40 mg and temperatures between 25 and  $1000^\circ\text{C}$ .

### 3. Results

IR spectra of oligomers  $R_1$ – $R_4$  present absorption bands characteristic to hydroxylated ester-imide oligomers [14–20].

Table 3  
Global and partial solubility parameters and the radius of interaction spheres for the four oligomers

Oligomer	Solubility parameters/(MPa) <sup>1/2</sup>				Radius of interaction sphere (MPa) <sup>1/2</sup>
	$\delta$	$\delta_d$	$\delta_p$	$\delta_h$	
$R_1$	22.1	18.2	9.6	8.2	7.6
$R_2$	22.3	18.0	10.0	8.6	7.2
$R_3$	21.9	17.8	9.6	8.4	7.6
$R_4$	22.1	18.0	9.6	8.2	7.6

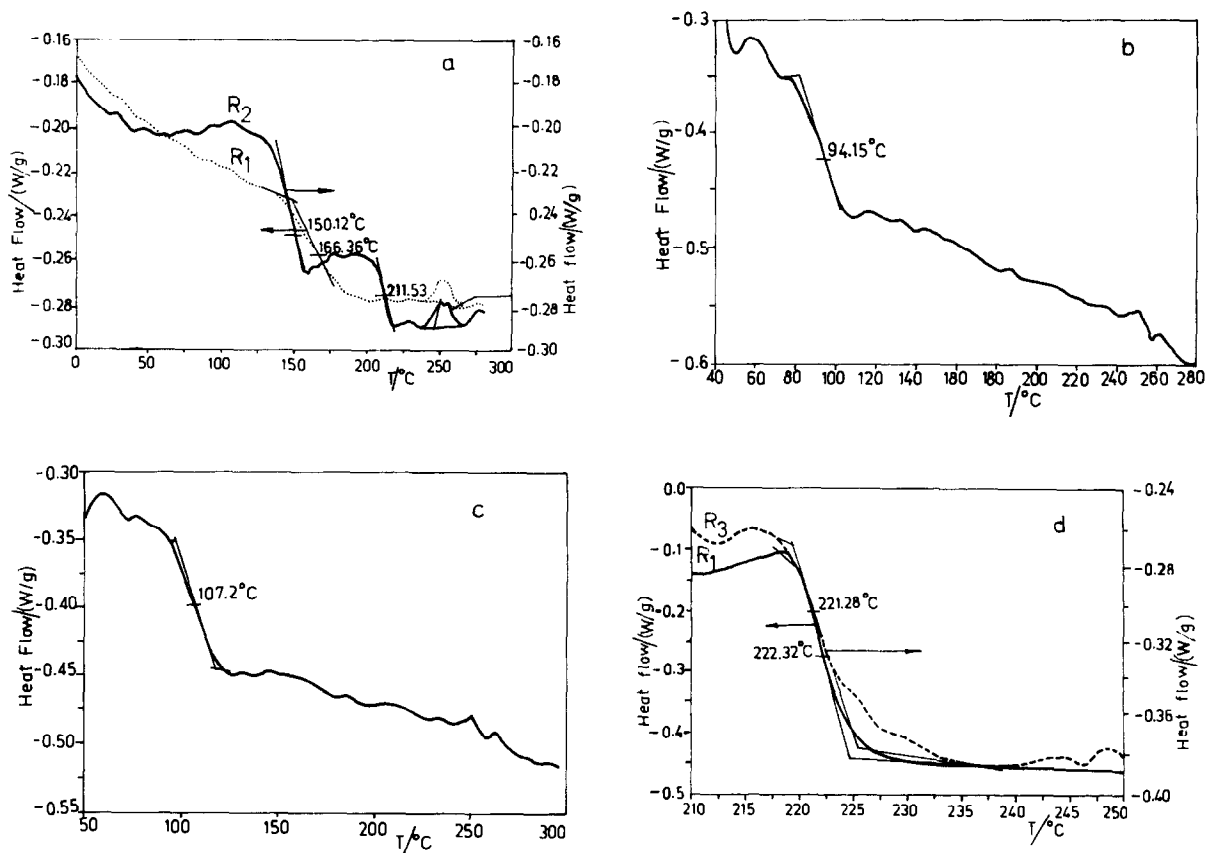


Fig. 1. DSC curves of uncured  $R_1$ – $R_4$  and cured  $R_1$  and  $R_3$  oligomers: (a) – uncured  $R_1$  and  $R_2$ ; (b) – uncured  $R_3$ ; (c) – uncured  $R_4$ ; (d) – cured  $R_1$  and  $R_3$ .

Table 4

Glass transition temperatures of oligomers R<sub>1</sub>–R<sub>4</sub> and of polymers obtained by curing of R<sub>1</sub> and R<sub>3</sub>

Compound	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
Oligomer $T_g/^\circ\text{C}$	166.4	150.1; 211.5	94.2	107.2
Polymer $T_g/^\circ\text{C}$	222.3	–	221.3	–

X-ray diffraction patterns show that all oligomers are in glassy state.

The global and partial solubility parameters of oligomers and the corresponding radii of interaction spheres obtained from solubility data by Hansen's [12] method are given in Table 3. The highest value of  $\delta$  and the lowest interaction radius were obtained for oligomer R<sub>2</sub>; R<sub>3</sub> has the lowest  $\delta$ .

Glass transition temperatures of the four oligomers and of the corresponding cured ones, obtained from DSC curves, are given in Fig. 1(a)–(d) and Table 4. When NPG was used a drastic decrease of  $T_g$  was observed: R<sub>3</sub> compared with R<sub>1</sub> and R<sub>4</sub> with R<sub>2</sub>. Increase of DMT content increases  $T_g$  both when EG and NPG were used: R<sub>2</sub> compared with R<sub>1</sub> and R<sub>4</sub> with R<sub>3</sub>.

TG curves of oligomers R<sub>1</sub> and R<sub>3</sub>, normalized to unity, heated for 1, 4, and 6 h at 260°C are given in Fig. 2(a, b). They show minimum weight losses, for both oligomers, for a heating time of 4 h. These were considered the optimum curing conditions.

TG curves of the oligomers as well as those of the cured ones for 4 h at 260°C are presented in Fig. 3(a)–(d): curing produces an increase of heat resistance within the temperature range 250–350°C.

Superposed IR spectra of oligomers before and after curing, given in Fig. 4, show an attenuation of 3400 and 1070 cm<sup>-1</sup> bands specific for hydroxyl groups, of 2960 and 2880 cm<sup>-1</sup> ones specific for methylene groups and those of 2980 cm<sup>-1</sup> corresponding to methyl groups.

DSC curves in nitrogen emphasize three distinct stages for the curing process: 60–110, 150–200, and 210–260°C. TG, DTG, and DTA curves in air, shown in Fig. 5(a)–(d), give weight losses ranging between 4.80 and 10.32% within the temperature range 150–325°C.

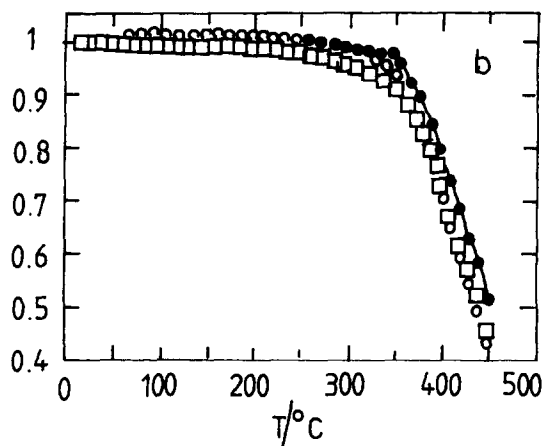
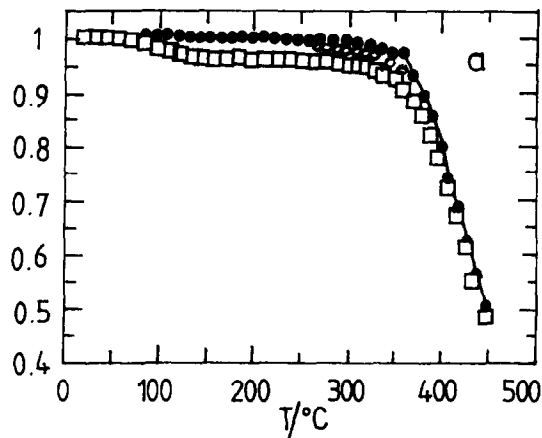


Fig. 2. TG curves of oligomers cured at 260°C normalized to unity: (a) – R<sub>1</sub>; (b) – R<sub>3</sub>; ○ – 1 h; • – 4 h; □ – 6 h.

DSC curves of the cured R<sub>1</sub> and R<sub>3</sub> show that  $T_g$  increases from 166 and 94°C, respectively, to about 220°C.

TG and DTG curves of the cured R<sub>1</sub> and R<sub>3</sub> oligomers reveal that their degradation occurs approximately within the same temperature range (Fig. 6). Degradation steps, kinetic parameters of degradation reactions determined by the differential method, and kinetic functions,  $f(\alpha)$ , which give the best correlation with experimental data are given in Table 5.

Correlation of weight compositions given by the recipes with weight losses given by TG curves for PEI

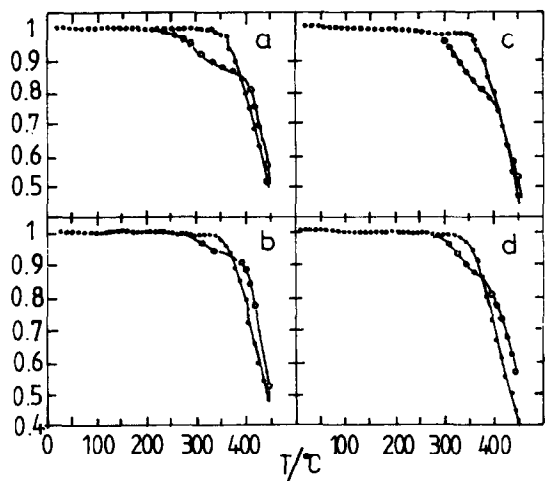


Fig. 3. TG curves normalized to unity for: (a) – R<sub>1</sub>; (b) – R<sub>2</sub>; (c) – R<sub>3</sub>; (d) – R<sub>4</sub>; ○ – uncured; • – cured 4 h at 260 °C.

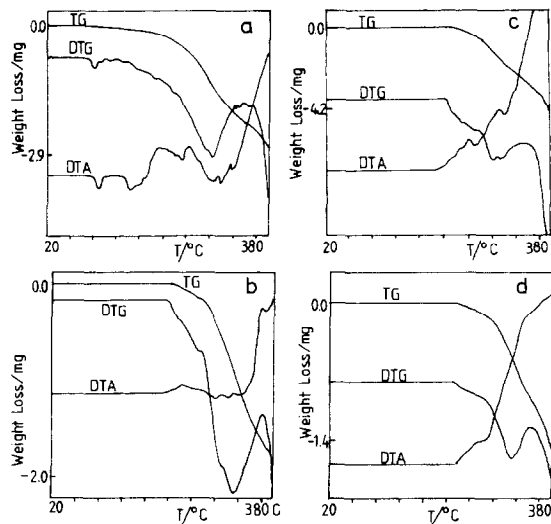


Fig. 5. TG, DTG and DTA curves in air for oligomers: (a) – R<sub>1</sub>; (b) – R<sub>2</sub>; (c) – R<sub>3</sub>; (d) – R<sub>4</sub>.

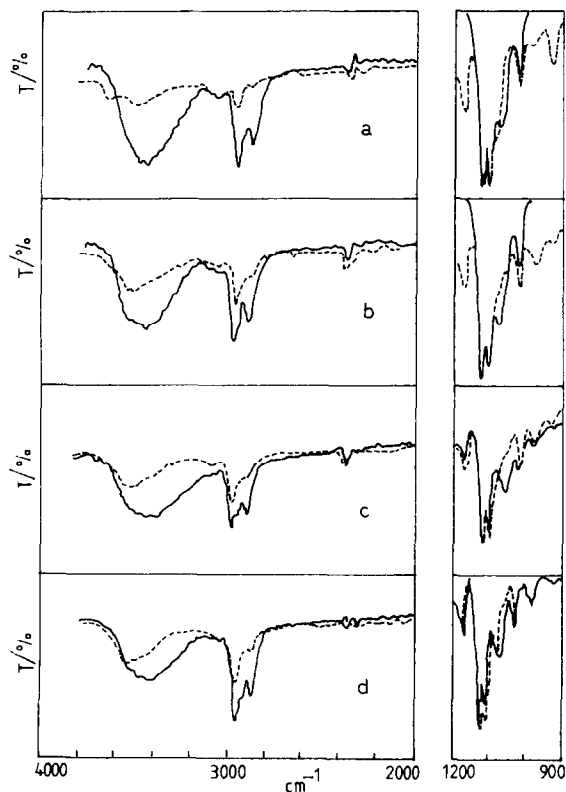


Fig. 4. Superposed IR spectra: (a) – R<sub>1</sub>; (b) – R<sub>2</sub>; (c) – R<sub>3</sub>; (d) – R<sub>4</sub>; - - - - uncured; — — — — cured.

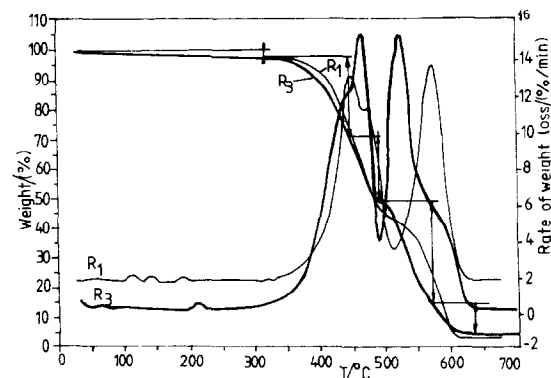


Fig. 6. TG and DTG curves of R<sub>1</sub> and R<sub>3</sub> cured for 4 h at 260 °C.

R<sub>1</sub> and R<sub>3</sub> within the temperature range 20–700 °C is given in Table 6.

The effect of NPG on heat resistance of cured oligomers is given in Fig. 7 and that of the content of DMT in Fig. 8: both NPG and DMT slightly decrease the heat resistance, so R<sub>4</sub> has the lowest heat resistance.

#### 4. Discussion

It is known that branching reduces the cohesion energy and increases polymer solubility. Substitution

Table 5

Degradation steps, kinetic parameters of degradation reactions and kinetic functions  $f(\alpha)$  which give the best correlation with experimental data

Oligomer	Degradation step	$n$	$A/s^{-1}$	$E/kJ\ mol^{-1}$	Temperature range/ $^{\circ}C$	Kinetic function/ $f(\alpha)$
R <sub>1</sub>	I	0.35	$2.0 \times 10^{-9}$	0.09	20–322	$\alpha^n$
	II+III	3.00	$1.3 \times 10^{-6}$	122.54	322–507	$(1-\alpha)^n$
	IV	2.80	$5.1 \times 10^{16}$	289.41	507–630	$(1-\alpha)^n$
R <sub>3</sub>	I	-1	$2.8 \times 10^{-7}$	3.85	40–320	$\alpha^n$
	II+III	3.00	$1.9 \times 10^6$	123.37	320–488	$(1-\alpha)^n$
	IV+V	3.00	$7.1 \times 10^{12}$	221.62	488–630	$(1-\alpha)^n$

Table 6

Correlation of weight compositions given by the recipes with weight losses given by TG curves for polymers resulted by curing of R<sub>1</sub> and R<sub>3</sub> within the temperature range 20–700 $^{\circ}C$

Oligomer	Monomers	Weight composition/% (recipe)	Weight losses/% (TG)	Relative deviation/%	Degradation steps
R <sub>1</sub>	EG+THEIC+DMT	59.92	57.11	4.5	I+II+III
	ATM+DDM	40.07	39.87	0.5	IV
R <sub>3</sub>	NPG+THEIC+DMT	63.12	50.86	19.4	I+II+III
	ATM+DDM	36.87	44.47	20.0	IV+V

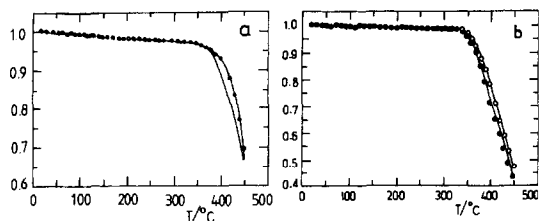


Fig. 7. TG curves of polyester-imides: (a)  $\circ$  – R<sub>1</sub>; – R<sub>3</sub>; (b)  $\circ$  – R<sub>2</sub>; – R<sub>4</sub>.

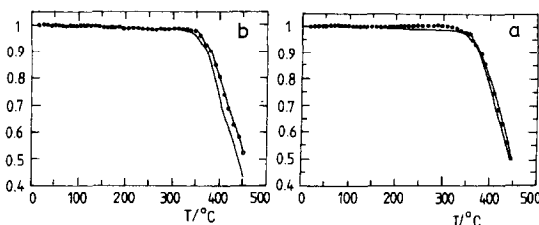


Fig. 8. Influence of quantity of DMT on heat resistance of polyester-imides: (a)  $\bullet$  – R<sub>1</sub>; – R<sub>2</sub>; (b)  $\bullet$  – R<sub>3</sub>; – R<sub>4</sub>.

of EG with NPG in the oligomers R<sub>1</sub> and R<sub>2</sub> increases the solubility of the corresponding oligomers R<sub>3</sub> and R<sub>4</sub>, respectively, as shown by Table 2. Thus: R<sub>3</sub> is

soluble in 1,2-dichloroethane while R<sub>1</sub> swells with that solvent; R<sub>3</sub> swells with acetone and methyldiethylene glycol and R<sub>1</sub> does not interact with these solvents; R<sub>4</sub>, which contains larger quantity of DMT than R<sub>3</sub> does and equal to that contained by R<sub>2</sub>, swells with 1,2-dichloroethane while R<sub>2</sub> does not interact with it; R<sub>2</sub> has the lowest solubility and capacity of swelling. R<sub>3</sub> is also soluble in mixtures of methyldipropylene glycol and xylene or toluene 1/1 by weight at concentrations of 40% and higher. With usual concentrations ranging between 40 and 48%, such mixtures of solvents can be used for R<sub>3</sub> commercialization.

Table 3 shows the lowest  $\delta$  value obtained from solubility data by Hansen's method [12] for R<sub>3</sub>; R<sub>1</sub> and R<sub>4</sub> have equal values, so R<sub>1</sub> contains less DMT but R<sub>4</sub> contains NPG; the highest value of  $\delta$  and the lowest value of interaction radius,  $R$ , were obtained – as expected – for R<sub>2</sub>, which contains EG and a larger quantity of DMT.

Oligomers containing NPG have lower glass transition temperatures compared to those containing EG and the same quantity of DMT (Fig. 1 and Table 4). The greatest decrease – about 70 $^{\circ}C$  – is observed for the oligomers containing the lowest quantity of DMT.

At the same time  $R_2$  presents two  $T_g$ , which suggests the presence of some sequences with specific  $T_g$ , larger quantities of DMT favouring the appearance of some DMT–EG sequences.

Curing conditions for oligomers deposited on electric conductors are imposed by the varnishing machine: 550°C and speeds of wire ranging between 18 and 30 m min<sup>-1</sup> for an oven length of 2 m. When applied on metallic plates three curing regimes were used: 1, 4, and 6 h at 20°C.

TG Curves of the cured  $R_1$  and  $R_3$  – Fig. 2(a,b) – present minimum weight losses due to the thermal degradation for a curing time of 4 h and this was considered the optimum curing time. Mechanical and electrical characteristics as well as dielectric losses of the cured films support this conclusion.

The curing mechanism was established by TG, IR, DTA, DSC, and gas chromatography.

Superposed TG curves of oligomers  $R_1$ – $R_4$  before and after curing, presented in Fig. 3, show an increase of heat resistance after curing within the temperature range 250–350 °C. This can be assigned to the increase of chain lengths, supposition supported by the increasing of  $T_g$  produced by curing: from 166°C for  $R_1$  and 94°C for  $R_3$  to about 220°C for both of them as can be seen in Fig. 1(a)–(d) and Table 4.

Reactions responsible for the increase of chain lengths and transformation of oligomers into polymers (PEI) were emphasized by IR, DTA, DSC, and gas chromatography.

Superposed IR spectra of cured and uncured  $R_1$ – $R_4$  within the range 4000–1000 cm<sup>-1</sup>, presented in Fig. 4(a)–(d), reveal attenuation of the following absorption bands: 3400 and 1070 cm<sup>-1</sup> specific for hydroxyl groups, 2960 and 2880 cm<sup>-1</sup> characteristic for methyl groups. This suggests that curing is produced by the elimination of compounds containing the above groups.

Analysing the condensation products the following compounds were identified: EG by gas chromatography for  $R_1$  and NPG for  $R_3$  by crystallization and melting point determination. Correlating these data with those found in the literature [21] it can be concluded that the curing process occurs by the elimination of water and of EG or NPG.

DSC curves in nitrogen point out the following stages for the curing process: 60–110°C – endothermic process – removal of included water; 150–200°C –

exothermic process – imidization of remaining amic acids with elimination of water; 210–270°C – exothermic process – increasing of chain lengths by elimination of EG or NPG.

TG, DTG, and DTA curves in air – Fig. 5 – indicate weight losses during the curing process ranging between 4.80 and 10.32% reported to the corresponding initial weights and a slight exothermic process within the temperature range 150–350°C. Considering the molecular weights of oligomers, the ratio of difunctional to trifunctional oligomers, and the stoichiometry of reactions, the computed weight losses produced by the curing range between 4.80 and 8.64% and correspond to molecular weight increases of about 40 times.

Reactions responsible for thermal degradation of PEI obtained as a result of  $R_1$  and  $R_3$  curing take place within almost the same temperature range as TG and DTG curves in Fig. 6 show, which proves that they are very similar.

Kinetic parameters and conversion functions,  $f(\alpha)$ , giving the best correlations with experimental data are presented in Table 5. The tested kinetic functions are given in a previous paper [22]. Reaction orders higher than 1 are explained by the distribution of molecular weights and by the simultaneous breaking of molecules, which results in similar compounds. The existence of compensation effect proves once more the similitude of curing mechanisms of the four oligomers. This is also supported by DSC data which show the same sequence of thermal effects.

Correlating weight losses given by TG curves, weight composition from the recipes and the obtained kinetic parameters, the mechanism resumed in Table 6 can be suggested for thermal degradation of PEI obtained by curing of oligomers  $R_1$  and  $R_3$ :

- state I, controlled by diffusion elimination of unreacted comonomers and, eventually, of a part of bound EG or NPG;
- stages II+III – elimination of EG or NPG, DMT, and THEIC;
- stages IV or IV+V, respectively – elimination of TMA–DDM structures containing aromatic and imidic rings.

The relative deviations of weight losses from Table 6 point out a better correlation for  $R_1$  and a worse one for  $R_3$  due to NPG which presents more

breaking possibilities and elimination occurs over a larger temperature range.

Polyester-imides containing NPG have lower heat resistance than those containing EG, both when lower and higher quantities of DMT were used as shown in the TG curves in air normalized to unity from Fig. 7(a,b). The effect is more pregnant in nitrogen. This demonstrates the lability of C–C bonds in NPG which favours thermal degradation.

It is well known that the increase of proportion of aromatic rings into chains results in an increase of heat resistance. Contrary to expectations, an increase of DMT content reduces the heat resistance of polyester-imides, as Fig. 8(a,b) reveals. This is also demonstrated by DSC curves and is explained by the increased content of ester bonds into chains which favours thermal degradation.

## 5. Conclusions

1. Ester-imide structure of the four oligomers obtained by melt copolycondensation of THEIC, EG or NPG, TMA, DMT and DDM was proved by IR spectroscopy.
  2. Substitution of EG by NPG increases solubility and decreases  $T_g$  due to the branched structure of oligomers.
  3. Increase of DTM content reduces solubility and increases  $T_g$  due to the increased number of aromatic rings in the oligomeric chains.
  4. Optimum heat resistance, mechanical and electrical properties and dielectric losses were found for oligomers heated 4 h at 60°C.
  5. IR spectra demonstrate that curing implies elimination of hydroxyl, methylene, and methyl groups and gas chromatography and melting point, respectively, show that EG or NPG is eliminated.
  6. High reaction orders shown by the kinetic parameters are explained by the distribution of molecular weights and the simultaneous breaking of molecules. Compensation effect proves the similitude of curing mechanisms of the four oligomers.
- This is also supported by DSC data which show the same sequence of thermal effects.
7. Non-isothermal thermogravimetry emphasizes the following stages for the thermal degradation processes of polyester-imides resulted by curing of oligomers  $R_1$ – $R_4$ : I – elimination of the unreacted comonomers and of a part of EG or NPG; II+III – elimination of EG or NPG, DMT and THEIC; IV or IV+V – elimination of structures ATM–DDM containing aromatic and imidic rings.
  8. NPG as well as large quantities of DMT reduce the heat resistance of polyester-imides.

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