Phase Transfer Catalysis in Polycondensation Processes (XIX): Thermal Behaviour of Some Polyesters Containing Oxetanic Rings in the Main Chain with Potential NLO Properties

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ABSTRACT

The synthesis of a set of polyesters by phase transfer polycondensation of a mixture based on potassium isophthalate and various dyes and 3,3-bis (chloromethyl)oxetane is reported. All obtained structures were characterized by ^{1}H NMR spectroscopy and thermogravimetric analysis. The thermal behaviour of the synthesized samples with that of a physical mixture (homopolymer and dye) are comparatively discussed. The thermal stability is generally good, their decompositions do not occur at temperatures beyond 220 °C, while the pure dye degradation process starts at about 100 °C . So, it is shown that the presence of dye decreases the thermal stability of the physical mixtures, while the degradation of chemically modified polymers is found to be non-dependent. In the case of chemical structure, however, the dye insertion promotes the obtainment of non-linear optical (NLO) thermosets by opening of oxetanic rings in the presence of diamines. Therefore, such compounds might be used as precursors for coloured NLO networks.

Key Words: phase transfer catalysis, polyesters, thermal stability, polycondensation, oxetanic cycle

INTRODUCTION

In a series of previous papers, the possible obtainment of some polyethers and polyesters based on 3,3-bis(chloromethyl)oxetane (BCMO) and various bis-phenols or diacids, by the application of phase transfer catalysis as a working method, was discussed [1–4].

It is worth noting that some of them present liquid crystalline (LC) properties [2, 4].

The presence of an oxetanic ring in the main chain indicates some advantages. Thus, at a temperature of 160 °C, the oxetanic ring may be opened under the action of an amine, which permits the chain's

modification [5]. When diamines are employed, cross-linking materials, possessing non-linear optical (NLO) properties, may be achieved [6].

For the obtainment of coloured NLO materials, it is necessary to add the dye to the macromolecular chain.

The paper discusses thermal characterization of some polyesters based on 3,3–bis(chloromethyl)oxetane and isophthalic acid, whose chemical structures are modified with various dyes, for the establishment of the most convenient temperature domains for subsequent cross-linking processes. As the cross-linking processes were demonstrated to occur at a temperature higher than 160 °C, we are interested to find out if the thermalstability of the modified polyester structure is influenced by the dye presence on the macromolecular chain. On the other hand, the performed studies allowed us to demonstrate that the dye molecules were chemically connected to the polymer chain.

The chemical structure of the studied polyesters attracted them as precursors for NLO materials. Therefore, we are not interested in obtaining of higher molecular weights.

EXPERIMENTAL

Polymer Synthesis
The homopolyesters were synthesized by phase transfer polycondensation reaction of BCMO with potassium isophthalate, using tetrabutylammonium hydrogen sulphate (TBAHS) as phase transfer catalyst. In a typical run, 3 mmol (0.465 g) BCMO and 3 mmol (0.726 g) potassium isophthalate were dissolved in 15 mL DMF under stirring. Then,

0.5 mmol (0.169g) TBAHS was added and the reaction mixture was stirred for 5 h at 85 °C. The resulted product was precipitated in water, washed repeatedly with water and methanol, in order to remove the unreacted reagents and, finally, dried under vacuum (40 °C).

Chemically modified polyester structures were also synthesized by phase transfer polycondensation using BCMO and a mixture (1/363, w/w) of potassium isophthalate and different dyes as reagents, in the presence of TBAHS, as phase transfer catalyst, and a small amount of sodium hydroxide. Sudan Grun (SGu), Sudan Gelb (SGe), Evans Blue (EB) and Floresceine (Fl) were used as dyes.

The polycondensation reactions were performed in the same way as homopolyester synthesis.

Polymer Characterization
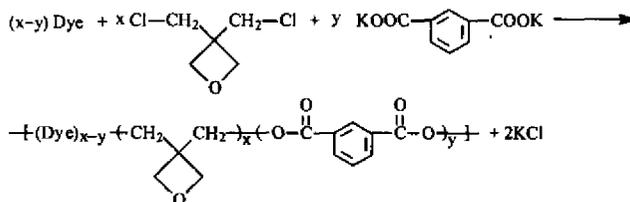The ^{1}H NMR spectra (60 MHz) were recorded on a JEOL spectrometer from DMSO-d6 solutions at 80 °C using TMS as an internal standard.

Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analyses (DTA) were performed under dynamic conditions on a MOM - Budapest apparatus, in air, at a heating rate of 13.7 °C/min. Samples of 50 mg in weight and platinum crucibles were used. Al_2O_3 was used as a reference material.
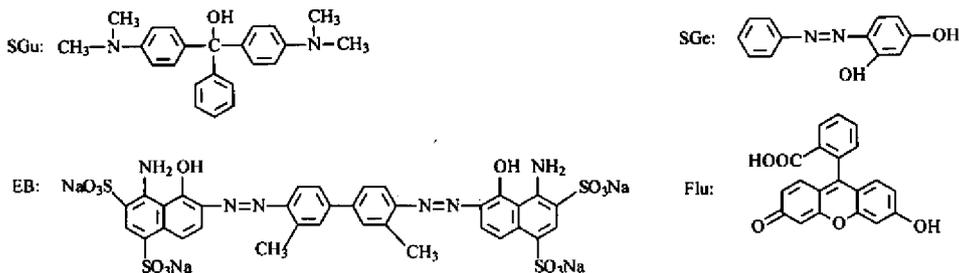
The kinetic treatment data were performed by differential and integral methods [7–9].
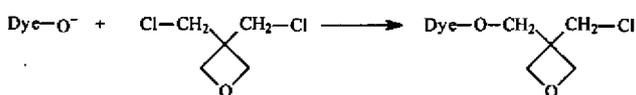
RESULTS AND DISCUSSION

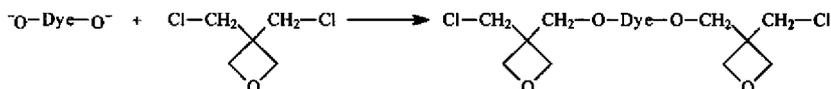The polymers were synthesized according to the reaction shown in Scheme I.

Scheme I

SGu: CH_3—N ... SGe: ...

EB: ...

Flu: ...

Scheme II

Dye—O⁻ + Cl—CH₂ CH₂—Cl ⟶ Dye—O—CH₂ CH₂—Cl

Scheme III

⁻O—Dye—O⁻ + Cl—CH₂ CH₂—Cl ⟶ Cl—CH₂ CH₂—O—Dye—O—CH₂ CH₂—Cl

Scheme IV

Dyes chemical structures are presented as in Scheme II.

The key code and the number average molecular weight of the analyzed samples are presented in Table 1.

We assume that, at the beginning, the hydroxylic groups of the dye molecules (as anions) react with BCMO. This supposition is based on the results

Table 1. The key code and the number average molecular weight of the analyzed sample.

Dye type	key code		$\overline{M}_n$
	Physical mixtures	Modified polyesters	
–	–	PES (unmodified)	2976
SGe	PES + SGe	PESSGe	1770
SGu	PES + SGu	PESSGu	1528
EB	PES + EB	PESEB	1920
Flu	PES + Flu	PESFlu	1682

obtained from calculating the electrostatic charge on oxygen atoms of different dicarboxylate and bisphenolate anions [10, 11]. These studies proved that the reactivity of the carboxylate anion is smaller than the hydroxylic anione. As a consequence, the hydroxylic anions will react first, therefore, the resulted species have only one active centre (Scheme III) for the reaction systems using SGu and Flu as dyes. As a result, the growing of the polymer chains is locked.

The SGe and EB molecules will be statistically connected to the macromolecular backbone because, according to Scheme IV, the resulted species have two active centres.

Owing to these reactions we expect that the $\overline{M}_n$ values for the systems containing SGe and EB are smaller than those recorded for the systems using SGu and Flu, as dyes. The data presented in Table 1 confirm this supposition. It is worth noting that the molecular weights of the synthesized polymers have
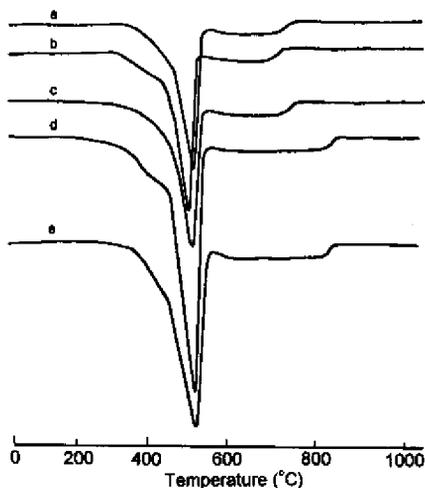
Figure 1. DTG Curves of chemically modified polyester with EB (a), SGe (b), SGu (c), Flu (d) and for pure polyester (e).

low values ($\overline{M}_n$ = 1500–2000).

Figure 1 presents the DTG curves of the obtained homo/ and chemically modified polyesters.

As one can see, for all studied samples, the degradation processes take place over the same temperature range, in two steps; the only difference between them is the increase of peaks asymmetry.
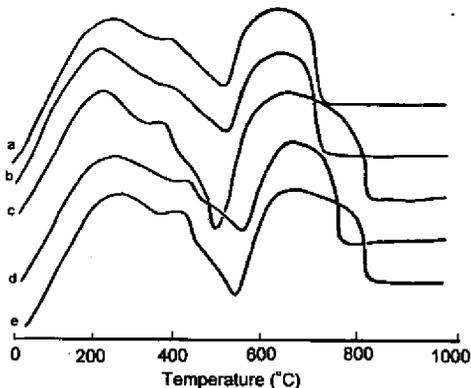

Figure 2. DTA Curves of chemically modified polyester with SGe (a), EB (b), Flu (c), SGu (d), and for pure polyester (e).

The final values of the degradation temperature are different and decreasing of the degradation domain may be also evident.

The DTA curves, shown in Figure 2, have the same shape, suggesting that the degradation process has an endothermic effect, for the first stage, while for the second stage the effect is an exothermic process.

In order to establish how the degradation process depends on the dye's presence, the thermal behaviour of the polyester, dye, physical mixture of dye with polyester and chemically modified polyester with dyes, was analyzed. The obtained DTG curves (the dye used was EV) are presented in Figure 3.

It is obvious that the thermal behaviour of the dye (Figure 3, curve b) is much different from that corresponding to the polyester (Figure 3, curve c). Thus, the degradation process of dye starts at 100 °C and has three stages.

For the physical mixture of EB with the polyester, the second stage of the degradation process takes place within the same temperature range, which corresponds to the second degradation step of homopolyesters; thus, a level is attained.

The behaviour of copolyester is almost similar with that of the homopolyester. Therefore, incorpor-
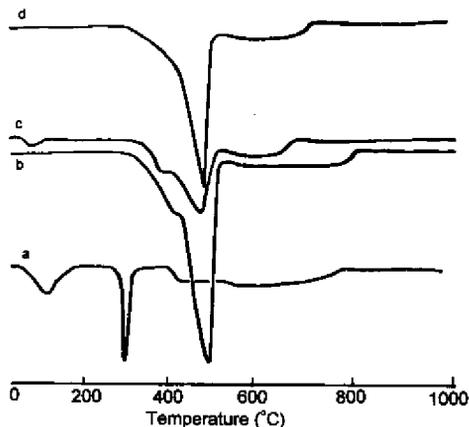

Figure 3. DTG Curves of EB dye (a), pure polyester (b), physical mixture of dye with polyester (c) and chemically modified polyester with EB (d).
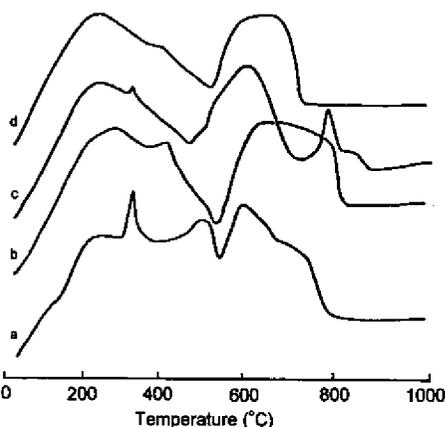
Figure 4. DTA Curves of EB dye (a), pure polyester (b), physical mixture of dye with polyester (c) and chemically modified polyester with EB (d).

Figure 5. DTG Curves of SGe dye (a), pure polyester (b), physical mixture of dye with polyester (c) and chemically modified polyester with SGe (d).

ation of the dye into the polyesters chemical structure does not modify its thermal stability.

The same conclusion may be reached when taking into consideration the data of DTA curves shown in Figure 4.

Replacement of EB with SGe does not produce essential modification in the thermal behaviour of the polyester, as the DTG and DTA curves presented in
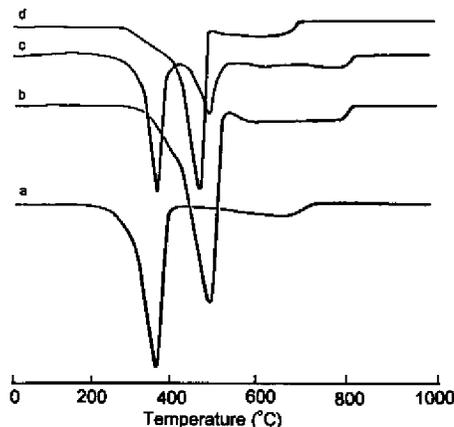
Figures 5 and 6 suggest.

The thermal characteristics of the analyzed samples are presented in Table 2.

As to the samples' thermal stability, it is observed that the newly synthesized polymers present a smaller thermal stability than the starting polyester. Taking into consideration the temperature values corresponding to a conversion equal to 0.1, the lowest

Table 2. Thermogravimetric characteristics of the studied samples (heating rate: 13.7 °C/min).

Sample	First stage					Second stage	
	T_i (°C)	T_α (°C)	T_M (°C)	ΔT (°C)	W_∞ (%)	ΔT (°C)	W_∞ (%)
SGe	220	322	380	220–480	75	480–750	25
EB	280	320	340	280–370	44	530–790	56
SGu	250	430	468	250–500	22	500–740	78
PES	340	407	516	340–540	80	550–820	20
PES + SGe	245	285	345	245–420	74	530–760	26
PES + EV	300	360	480	300–510	70	525–820	30
PESSGe	300	352	500	300–530	80	520–745	20
PESEB	305	380	515	305–540	76	540–740	34
PESSGu	304	360	500	304–514	80	514–724	20
PESFlu	310	375	510	310–560	78	560–860	22

T_i - Temperature at which the degradation process starts (°C); T_α - Temperature corresponding to a conversion of 0.1 (°C); T_M - Temperature corresponding to the maximum degradation rate (°C); ΔT - Temperature interval for decomposition (K); W_∞ - weight loss (%).

Table 3. Kinetic characteristics corresponding to the first degradation stage of the studied samples.

Sample	F.C.			R.L.			C.R.		
	n	E_a (kJ/mol)	ln A	n	E_a (kJ/mol)	ln A	n	E_a (kJ/mol)	ln A
SGe	0	80	22	0	90	23.8	0	80	22
EB	0	110	26.3	0	102	24.8	0	115	26
SGu	0	150	29.7	0	107	22.6	0	90	22
PES	1	130	24.5	1	115	22	0	83	19.5
PES+SGe	1	133	21.6	1	140	22	0	86	–
PES+EB	1	123	25.2	0	76	–	1	94	15
PESSGe	1	96	19	1	90	18	0	76	16
PESEB	0	96	21	0	80	19	0	78	18
PESSGu	0	87	20	0	80	19	0	78	18
PESFlu	0	105	23	0	120	22.4	0	92.	21.2

thermal stability corresponds to copolyester PESSGe. The weight loss of this sample is about 80% in the first stage of degradation.

For setting information on the mechanism of thermal degradation, the kinetic mode of behaviour was performed by the methods mentioned by previous workers [7–9]. The results are presented in Table 3.

Analysis of the data presented in Table 3 suggests the existence of a good agreement between the activation energy and the thermal characteristics.

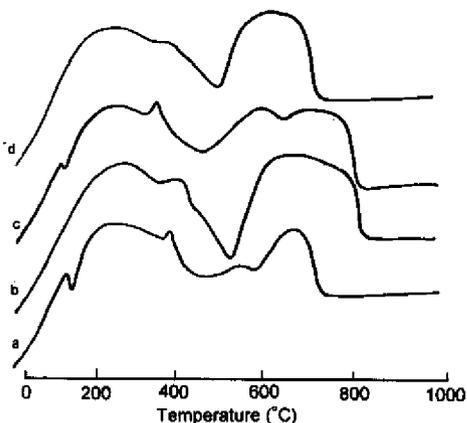It is worth mentioning that the obtained values

are placed in the range of allowable errors.

Dye's incorporation into polyesters main chain modified their supramolecular structure. Thus, the more amorphous domains present, there should be greater decrease in thermal stability.

The FC methods have evidenced two different processes, proving the existence of successive reactions with similar thermal effects.

The kinetic characteristics corresponding to the second stage of the degradation process are presented in Table 4.

As one can see, even where the weight loss process is constant the degradation of the copolyesters obeys the same first order law . The activation energy

Figure 6. DTA Curves of SGe dye (a), pure polyester (b), physical mixture of dye with polyester (c) and chemically modified polyester with SGe (d).

Table 4. Kinetic characteristics corresponding to the second stage of the degradation process.

Sample	R.L.	
	n	E_a (kJ/mol)
SGe	0	115
EV	1	160
SGu	–	134
PES	1	126
PES + SGe	0	136
PES + EB	1	102
PESSGe	1	143
PESEB	1	134
PESSGu	1	122
PESFlu	1	165

values vary between 122 and 165 kJ/mol.

Taking into consideration all the above observations, one can deduce that the degradation process occurs with the formation of a carbonic residue; as its chemical structure depends on polymer supramolecular structure.

As already known the thermo-oxidative processes are favoured by the existence of an amorphous structure. The results obtained for PESFI suggest a higher degree of ordering.

CONCLUSION

Polyesters, modified chemically with various dyes, were synthesized. Their thermal stability was seen as not depending on the presence and amount of dye.

The mechanisms of degradation for the chemically modified polyesters and homopolyesters are almost the same.

The physical mixtures of polyester with different dyes have smaller thermal stability because of the reduced dyes' thermal stability.

As one can see, all studied polyesters could be used as precursors for the potential NLO materials; their degradation temperatures (>200 °C) are situated over the temperature value at which cross-linking processes start (160 °C).

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