

INFLUENCE OF THE SIZE OF METHYLENE SPACERS ON THE THERMAL BEHAVIOR OF SEVERAL ALIPHATIC-AROMATIC POLYESTERS

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Abstract: Polyesters have a wide range of technical applications and therefore their processing is of the utmost importance. Since polyesters are usually processed by melting, their thermal stability is an extremely important characteristic for the exact determination of the operational parameters. The thermal analysis was carried out using a MOM-Budapest derivatograph at the 10°C/min heating speed, aluminum oxide the reference material, and the air conditions were static. The study lead to conclusions on the thermal stability and degradation mechanism depending on the number of methylene groups in the spacer. Thermal stability is supported by the increase in the number of methylene groups in the spacer. The degradation mechanism is complex through successive reactions. The spacer size influences the nature of the micromolecules formed by spacer fragmenting and by the number of carbon atoms, respectively.

Keywords: *degradation mechanism, influence of the size spacer, polyesters, thermal analysis, thermal stability*

INTRODUCTION

Polyesters make up a class of materials with a wide range of technical applications [1 - 3] and therefore their processing is of the utmost importance. Since polyesters are usually processed by melting, their thermal stability is an extremely important characteristic for the exact determination of the operational parameters. Many new polyesters have been lately proposed by literature, whose extremely varied chemical structures require the development of a series of studies as complex as possible on the properties of these new materials. The special polyester properties are a consequence of strong electrostatic inter-chain interactions generated by the -CO-O- groups. Considering the numerous polyester applications in biology [4 - 6], our interest is raised by those structures that are able to interact with biomolecules [7, 8] by means of hydrogen bonds. Therefore, the amino-isophthalic acid present in the structure of a polyester chain may have, on the one hand, the advantage of the occurrence of several superior mechanical properties (due to the hydrogen bonds formed among the chains) and, on the other hand, it opens up new applications in biology, due to its interaction with biomolecules.

Consequently, our paper is designed as a comparative study of the thermal properties of a series of polyesters containing amino-isophthalic acid as well as different dihalogenated derivatives with hydrocarbon structure. Considering that the rigidity of a macromolecular chain is essential for polymer thermal stability, our study focuses on the influence of the size of flexible spacer on polyester thermal stability, as well as on elucidating the degradation mechanism.

MATERIALS AND METHODS

The investigated polyesters were synthesized in solution starting from 5-amino-sodium-isophthalate (5-ASIP) and different dihalogenated spacers according to Figure 1. Tetrabutyl ammonium hydrogensulfate (TBAHS) was used as catalyst [9 - 11].

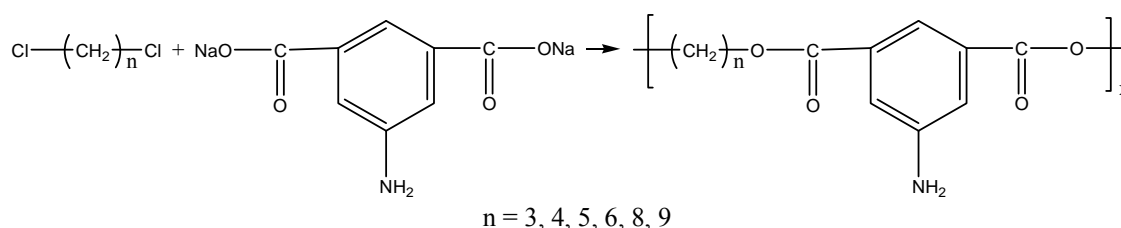


Figure 1. Synthesis of investigated polyesters

In a typical reaction, 3 mmol of 5-ASIP and 3 mmol dihalogenated spacer were introduced into a flask and dissolved in 15 ml N-methylpyrrolidone under stirring conditions. The reaction mixture was heated at 85 °C 5 hours and then precipitated in acidified (HCl) methanol, washed with water and methanol to remove the unreacted reagents and dried under vacuum (40 °C). The polymers structure was confirmed by ¹H-NMR analysis the typically signals being present at 7.3 ppm (2H) and 7.6 ppm (1H) for aromatic rings, 4.3 ppm (4H) for -CH₂- direct connected to the esteric group and 1.4 - 1.8 ppm region for central -CH₂- groups (as a function of the spacer length). Other

details concerning the synthesis and characterization procedures were previously reported [12].

The thermal analysis was carried out using a MOM-Budapest derivatograph able to read and record simultaneously the thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal (DTA) analysis results. The heating speed was 10°C/min, aluminum oxide was the reference material, and the air conditions were static. The other operational parameters remained constant in order to achieve comparable data.

RESULTS AND DISCUSSION

Figure 2 shows the DTG curves, which suggest two degradation stages. The first stage includes successive separable processes depending on the spacer size. The second stage is similar to the analyzed samples and is characterized by mass losses constant in time. In fact, the DTA curves showed in Figure 3 lead to similar conclusions.

The thermal processes occurring during the first degradation stage suffer a series of changes depending on the spacer size, while the last stage witnesses the occurrence of a thermal oxidation-characteristic peak, which is also characteristic to several aliphatic-aromatic polyesters whose methylene spacer has different sizes [13 - 18].

Table 1 shows these thermogravimetric characteristics.

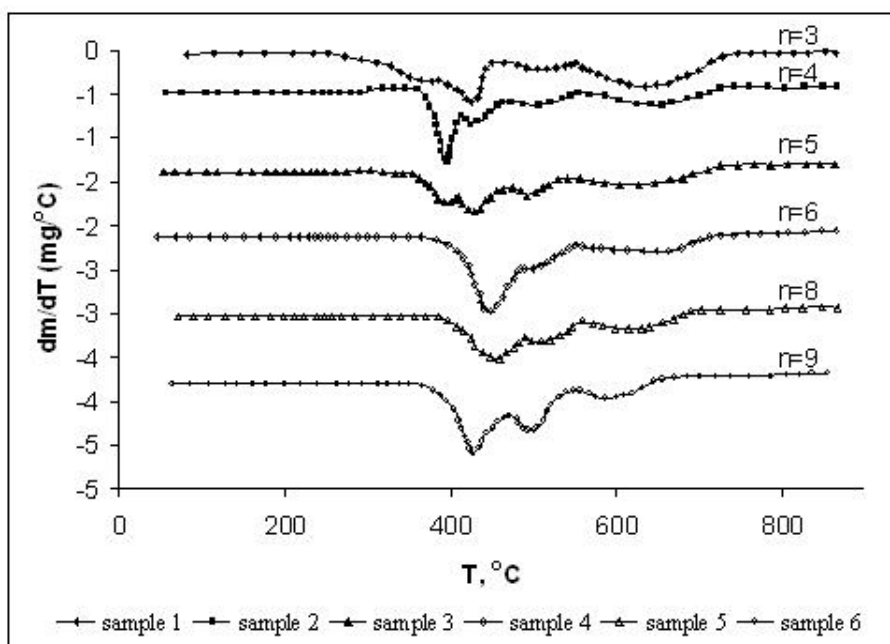


Figure 2. DTG curves

The temperature intervals of the two degradation stages are close for all the analyzed samples. The mass losses depend on the structure. According to the initial degradation temperature, we noticed that thermal stability increased with the spacer size.

Table 1 also shows the T_C temperature parameter calculated using the following ratio.

$$T_C = \frac{C_1 T_i + C_2 T_M}{C_1 + C_2} \quad (1)$$

where $C_1 = 5$, $C_2 = 3$ are values obtained after tests, T_i is the initial degradation temperature, T_M – the temperature of the highest degradation speed. This equation also has the advantage of pointing out the influence of the degradation speed.

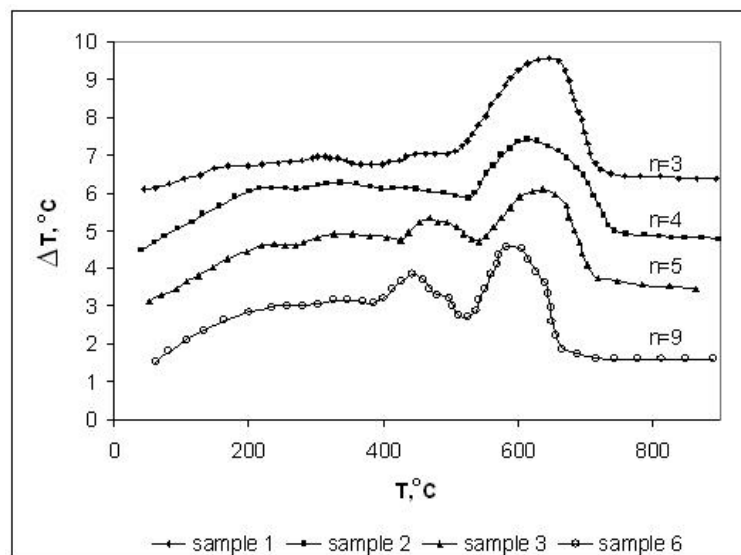


Figure 3. DTA curves

Table 1. Thermogravimetric characteristics upon the dynamic thermal degradation of several aliphatic-aromatic polyesters

Sample	$-(CH_2)_n-$	T_C (°C)	Stage I			Stage II	
			ΔT (°C)	W (%)	W^I (%)	ΔT (°C)	W^{II} (%)
1	3	293	250-480	48.57	61.43	570-730	38.57
			480-550	12.86			
2	4	348	320-420	30.76	71.14	580-760	30.19
			420-485	21.15			
			485-580	19.23			
3	5	353	330-430	21.00	68.30	570-760	31.58
			430-490	28.07			
			490-570	19.03			
4	6	380	340-490	52.46	75.41	550-740	24.59
			490-550	22.95			
5	8	380	340-495	51.85	77.77	560-740	22.20
			495-560	25.92			
6	9	378	340-495	45.16	74.16	580-740	25.80
			495-580	29.03			

ΔT – temperature interval; W – mass loss; W^I – total mass loss in the first stage; W^{II} – total mass loss in the second stage; n - number of methylene groups in the spacer; T_C – temperature parameter

Taking into account the initial degradation temperature and the temperature parameter defined by the ratio 1, the following thermal stability series were established:

$$1 < 2 < 3 < 4 \cong 5 \cong 6$$

The increase in the number of methylene groups in the spacer enhances thermal stability up to $n=6$, after which there are no more perceptible differences. Additional information on the influence of structure on thermal stability was obtained by means of conformational studies using the HyperChem 7.5 modelling program. Figure 4 shows the geometry of the investigated compounds corresponding to the minimum energy.

As one may notice, chain geometry is more consistently influenced by spacers with a lower number of methylene groups. If there is an odd number of methylene groups in the spacer, chain geometry deviates from linearity, which leads to higher inter-chain distances and implicitly to thermal stability decrease. Spacers with an even number of methylene groups generate linear geometries, which intensifies inter-chain interactions. This effect is very obvious in the first two compounds and it fades out with the increase in the spacer length. The fading out of the chain geometry effect with the increase in the spacer length is not surprising, considering that due to a better chain flexibility, linear geometry deviations are more easily compensated by the spacer. The increase in polymer thermal stability with the increase in the chain flexibility (spacer length) may be caused by the generation of a higher number of hydrogen bonds among the chains, given the easier repositioning of the $-NH_2$ groups as compared to the $-CO$ groups.

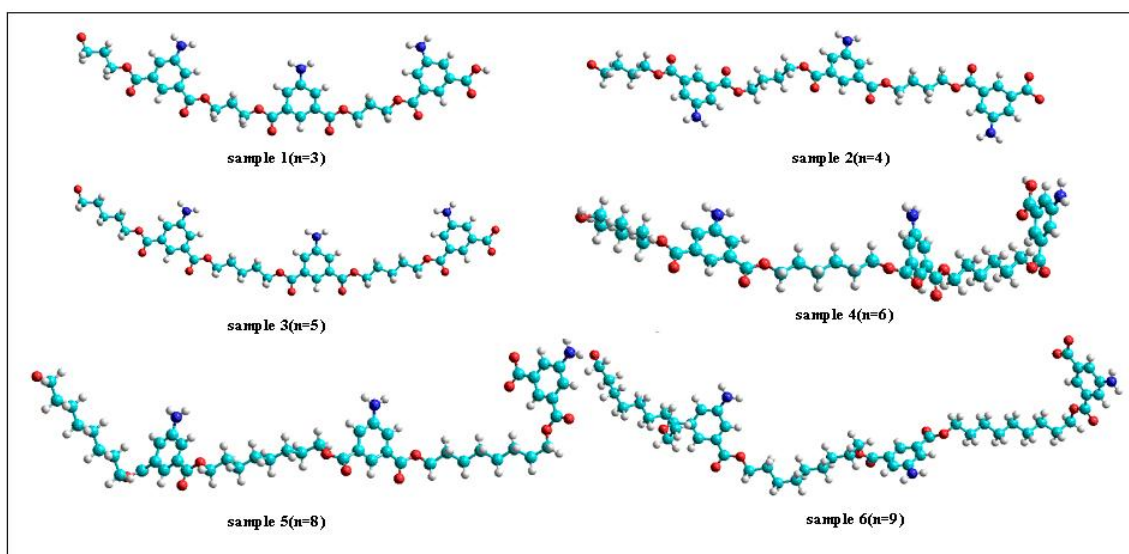


Figure 4. Geometry of aliphatic-aromatic polyesters obtained at a minimum energy level

In order to obtain information on the fragmenting of the structural unit, we carried out a calculation, whose results are shown in Table 2. If we compare the TGA data with the calculations performed, we notice that the degradation process starts with the release of several NH_3 , CO , CO_2 molecules, aldehydes with a variable number of carbon atoms, depending on the number of methylene groups in the spacer, leading to a residue which undergoes a degradation process of thermal oxidation. According to the mass losses, the

degradation mechanism consists of successive reactions, as shown in diagram presented in Figure 5.

Table 2. Mass losses calculated on structural unit fragmenting

Sample	$-(CH_2)_n$	X_1 (%)	X_2 (%)	X_3 (%)	X_4 (%)	X_5 (%)	Meanings X_i
1	3	7.69	32.57	13.57	12.22	33.93	$X_1 = NH_3$ $X_2 = CO_2 + CO$ $X_3 = R-C \begin{smallmatrix} H \\ \diagup \\ O \end{smallmatrix}$ $R = H$ $n=3, 4, 5$ $R = \dot{C}H_3$ $n=6, 8, 9$ $X_4 = -(CH_2)_{n-1}$ $n = 3, 4, 5$ $X_4 = -(CH_2)_{n-2}$ $n = 6, 8, 9$ $X_5 = Ar$
2	4	7.23	30.63	12.76	17.44	31.91	
3	5	6.82	28.91	12.05	22.08	30.12	
4	6	6.46	27.37	16.43	20.91	28.51	
5	8	5.84	24.74	15.12	28.52	25.77	
6	9	5.57	23.60	14.42	31.80	24.59	

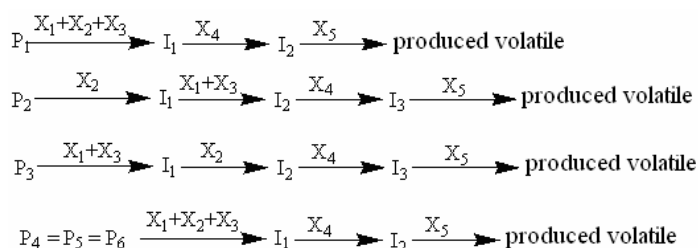


Figure 5. Compound degradation mechanism

In order to gather additional information, apparent activation energies were determined using the Coats-Redfern [19] and Reich Levi [20] methods.

The Coats-Redfern method uses the following equation:

$$\ln \left[\frac{F(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{aE} \right) \left(1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (2)$$

where $F(\alpha)$ is the conversion function, T – the temperature at different conversion degrees, R – the universal gas constant, a – the heating speed, A – the pre-exponential factor, E – the activation energy.

The value of the reaction order is established through successive tests for $F(\alpha)$ corresponding to the various values of the reaction order and when a line is obtained through the graphical representation of the values pairs $\left[\ln \left(\frac{F(\alpha)}{T^2} \right); \frac{1}{T} \right]$, the shape of the

conversion function indicates the reaction order, while the line slope helps calculating the apparent activation energy. Table 3 shows the results achieved.

The activation energy of the first process confirms that Sample 1 has the lowest thermal stability. The dependence of the apparent activation energy corresponding to the first stage processes suggests successive reactions with close activation energies, which requires a similar process. Sample 2 has a higher activation energy value although it has the same characteristics as the other samples. It also enjoys a mass loss constant in time and a strongly exothermal process. The different behaviour may be accounted for by the existence of an intermediary with a better ordered structure, determined by the initial packaging ordered as a result of the even/odd effect.

The Reich-Levi method enables researchers to establish the activation energy – conversion degree dependence. In order to calculate the activation energy through this method, we used the following ratio:

$$E = \frac{R \ln[(S_1 + S_2)/S_1]}{(1/T_1) - (1/T_2)} \quad (3)$$

where T_1 and T_2 are temperatures at different degrees of conversion, which define, in the dependence graph, the S_1 and S_2 areas between the conversion function corresponding to the reaction order and temperature.

Table 4 shows the values obtained for the apparent activation energies.

Table 3. Apparent activation energy assessed by the Coats-Redfern method for the reaction order zero (E_a , kJ.mol^{-1})

Sample	n*	Stage I	Stage II
1	3	68.07	106.37
2	4	138.77	191.47
		184.11	
		143.60	
3	5	166.49	105.60
		191.47	
		136.76	
4	6	136.76	127.65
		125.52	
5	8	95.73	95.73
		114.88	
6	9	108.22	93.60
		114.88	

* n = number of methylene groups in the spacer

The successive reactions degradation mechanism is confirmed for the first degradation stage, as the apparent activation energy changes with the conversion degree.

Table 4. Activation energy dependence on the conversion degree (Reich-Levi method)

Sample/ α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Stage I									
1 (n=3)	137.80	112.10	103.35	114.84	137.88	76.56	76.56	66.99	65.07
2 (n=4)	314.52	363.66	334.25	280.77	191.40	113.80	91.87	76.89	56.95
3 (n=5)	322.19	229.68	146.74	113.18	193.98	185.02	86.13	57.12	62.20
4 (n=6)	115.13	127.17	142.59	152.35	146.61	153.12	137.18	103.09	73.80
5 (n=8)	236.11	160.77	133.76	133.98	116.82	110.05	70.18	86.13	70.18
6 (n=9)	100.73	86.58	101.44	108.79	86.13	105.05	94.57	68.58	78.75
Stage II									
1 (n=3)	267.96	187.57	82.94	80.31	89.32	76.56	95.70	82.94	70.18
2 (n=4)	281.99	130.75	98.05	110.13	106.73	103.58	114.84	114.84	122.49
3 (n=5)	382.80	287.10	148.33	110.05	102.08	86.13	114.90	114.60	143.55
4 (n=6)	481.69	337.89	245.79	191.78	210.54	259.66	211.44	148.70	97.60
5 (n=8)	440.22	358.90	205.75	153.12	229.68	172.26	172.26	114.84	133.98
6 (n=9)	311.70	262.68	156.18	105.62	92.81	157.28	109.37	94.16	92.67

For the second degradation stage, low conversion degrees are accompanied by higher apparent activation energy values, and then its values fluctuate in a close field. These results may be accounted for by the initial fragmenting of the aromatic cycles, followed by a thermal oxidation process. The degradation mechanism in Figure 5 is thus confirmed.

CONCLUSIONS

The study performed by correlating the thermogravimetric and the kinetic data lead to conclusions on the thermal stability and degradation mechanism depending on the number of methylene groups in the spacer.

Thermal stability is supported by the increase in the number of methylene groups in the spacer. Thermal stability increase with chain flexibility increase (spacer length) may be accounted for by the generation of a higher number of hydrogen bonds among the chains, considering the easier positioning of the -NH₂ groups as compared to the -CO- groups. The degradation mechanism is complex through successive reactions. The spacer size influences the nature of the micromolecules formed by spacer fragmenting and by the number of carbon atoms, respectively.

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