

Thermal behavior of some aromatic copolyethers containing a propylenic spacer

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Abstract: The main objective of this paper is to study the thermal stability of some aromatic copolyethers containing a propylenic spacer. Some of the investigated copolyethers displayed a liquid crystalline (LC) behavior, with the presence of the mesogenic groups in the main chain, inducing high values of the thermal transition temperatures. As a consequence, a thermal stability study was necessary to establish the maximum temperature value for the LC behavior characterization. A thermal degradation mechanism is proposed, taking into consideration the azobenzene unit as the weakest link in the polymer chain and thus, the starting point of the thermal degradation process. The degradation mechanisms were correlated with the chemical structure and the polarity and conformation of the chains. Conformational analysis was performed using molecular simulations. Freeman-Carroll and Coats-Redfern methods were used to calculate some kinetic characteristics.

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Keywords: Thermal stability, liquid crystalline copolyether, azobenzene, thermal degradation mechanism

1 Introduction

The structure-property relationship of materials, especially for polymers, has been attracting the attention of scientists over the past few decades. A better understanding of this relationship will enable scientists to control the material properties via order degree

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modification at supra-molecular level. A special attention has been given to liquid crystalline systems due to their unique behavior as a combination of two essential properties of the matter: order and mobility. There is growing interest in developing new materials exhibiting both LC properties and photochromism, and the polymers containing azobenzenic groups can be included in this class of materials. Development of various modern systems for data recording, transfer processing, nonlinear optics and visualization of images requires new materials capable of rapid and reliable response to the signals transmitted by electromagnetic fields, particularly by light and laser irradiation. The presence of the azobenzenic groups in the polymer chain (main chain or side chain) provides the structure with the ability to perform an induced conformational photo-response based on *trans-cis* transition of the azo-groups, under UV irradiation. The *trans-cis* transition will significantly influence some of the polymer properties, such as dipole-moment, inter-chain interactions, etc., with direct influence on the supramolecular order degree. Our previous work focused on the study of liquid crystalline polymers (LCP) containing mesogenic groups in the main chain, such as azobenzenic units [1-6]. But, due to the presence of the mesogenic groups in the main-chain, high transition temperatures values were observed. Therefore, some difficulties were encountered during the investigation of LC behavior and the thermal stability study is necessary.

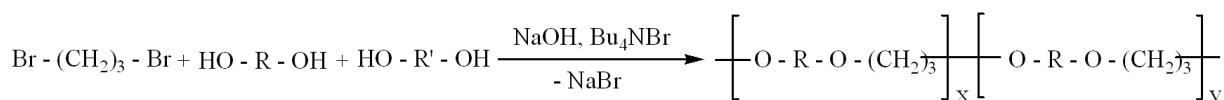
The present paper reports the thermogravimetric study of some aromatic copolyethers containing a propylenic spacer. A thermal degradation mechanism is proposed by taking into consideration the azobenzenic unit as the weakest link in the polymer chain and, therefore, the starting point of the thermal degradation process.

2 Experimental

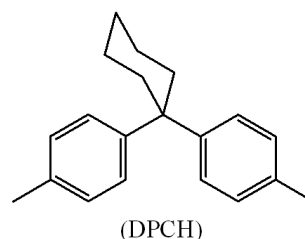
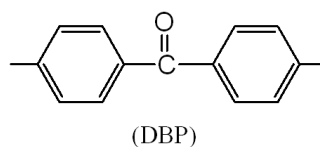
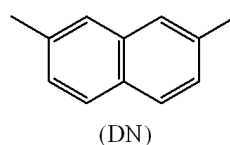
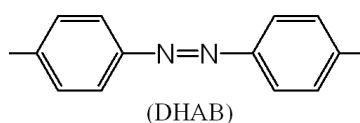
The copolymers were synthesized using phase transfer catalysis technique. Details concerning the synthesis procedure have been previously reported [1-3]. Polymers' thermostability was investigated using thermo-dynamic methods run on a MOM-Budapest apparatus. The thermograms were registered in air atmosphere over a temperature range 20 - 1000 °C, at a heating rate of 10 °C/min. Freeman-Carroll [7] and Coats-Redfern [8] methods were used to calculate the kinetic characteristics. The isokinetic temperature and the kinetic characteristics for maximum degradation rate were also calculated in agreement with the literature methods [9, 10]. The chains' conformations were obtained by molecular mechanics, using Hyperchem 4.5 software [11]. The molecular simulations were performed on the isolated chain, with a polymerization degree similar to the experimental ones (DP = 10-14). The initial geometry of the simulated copolyethers was optimized, the criterion of the energy convergence being less than 0.1 kJ/mol·Å. Minimization was performed using steepest descent and conjugate-gradient algorithms.

3 Results and discussion

The copolymers were synthesized starting from 1,3-dibromopropan and various bisphenols: 4,4'-dihydroxyazobenzen (DHAB); 2,7-dihydroxynaphthalene (DN); 4,4'-dihydroxy (benzophenone) (DBP); 1,1'-bis(4-hydroxy phenyl)cyclohexane (DPCH) (Scheme 1).



where R or R' =



Scheme 1 General synthesis reaction.

Table 1 presents some characteristics of the investigated polymers.

Code number	Copolymer composition	Mn	Thermal behavior
1	DHAB/DBP = 3.1/1	1800	LC
2	DHAB/DBP = 1/1.1	1800	LC
3	DHAB/DBP = 1/2.9	1850	LC + SC
4	DN/DPCH = 3.2/1	2300	A
5	DN/DPCH = 1.1/1	2450	A
6	DN/DPCH = 1/2.7	2800	A

LC = liquid crystal;
 SC = semi-crystalline;
 A = amorphous.

Table 1 Characteristics of the investigated polymers.

For all polymers, the numeric molecular weights were calculated from $^1\text{H-NMR}$ data, and are situated at the boundary of oligomeric and polymeric domains. This oligomeric domain is preferred for two reasons: i) to avoid high transition temperatures (expected for these particular structures even at lower molecular weights), and ii) slight modifications in polymer chain shape will be easier seen as function of polymer composition.

The first group of polymers (Samples 1-3) exhibited strong polar inter-chain inter-

actions due to the presence of the polar azo and carbonyl groups. The second group (Samples 4-6) is characterized by a low chain polarity, as only ether groups are present in the structure. It is worth mentioning that these two polymer groups also differ in chain geometry. A linear geometry is characteristic for the polymers belonging to the first group (Figures 1-2), while the second group presents a disordered conformation induced by the side-chain cyclohexylic units (Figure 3). This conformational difference influences the thermal behavior; only Samples 1- 3 present ordering capacity either in solid or liquid state (LC or SC).

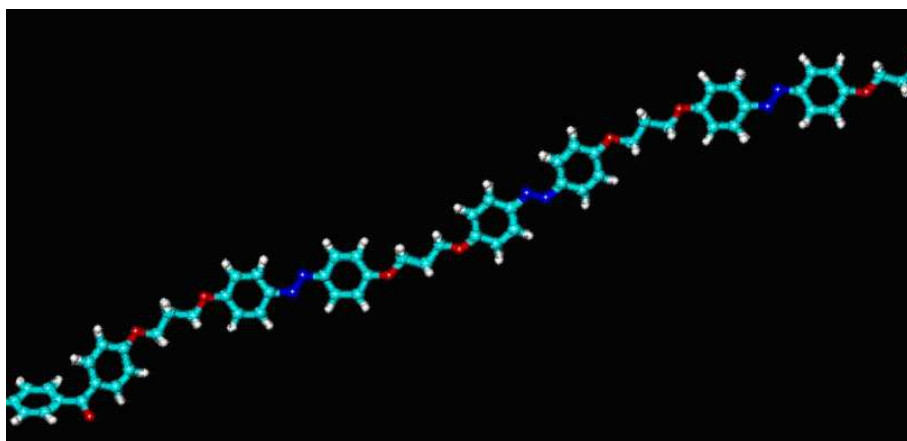


Fig. 1 Chain geometry corresponding to Sample 1.

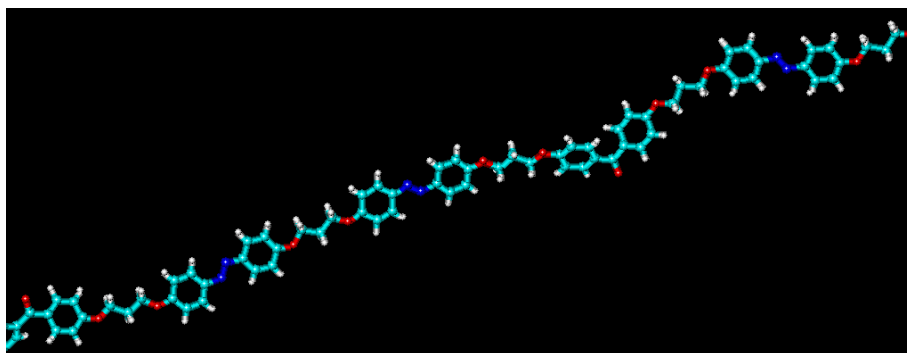


Fig. 2 Chain geometry corresponding to Sample 2.

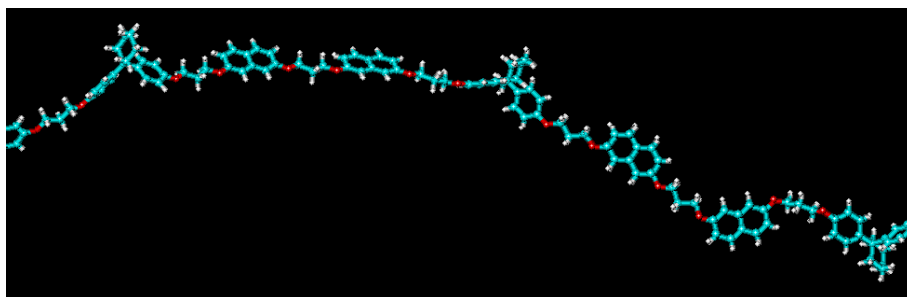


Fig. 3 Chain geometry corresponding to Sample 4.

The recorded thermograms suggest that the degradation process occurs in three steps

for the polymers containing azobenzene units, and in two steps for the other samples (Figures 4 and 5).

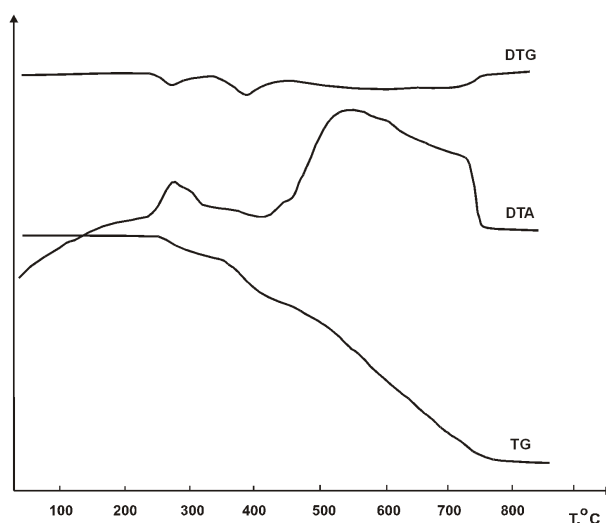


Fig. 4 Thermogram corresponding to the Sample 1 (TG = thermogravimetry; DTA = differential thermal analysis; DTG = derivative thermogravimetry).

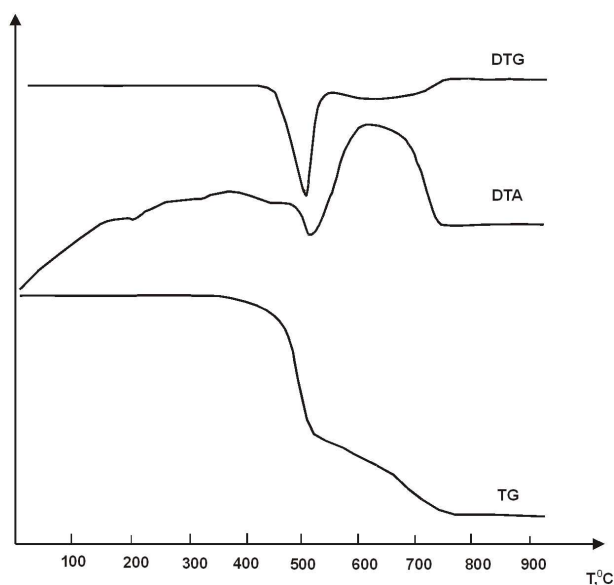


Fig. 5 Thermogram corresponding to Sample 4.

The last degradation stage is similar for all analyzed structures and shows a constant rate of weight loss as a function of temperature. This last stage is accompanied by a strong exothermal effect, with a profile of the DTA curves reflecting the polymers' structure: Samples 1 - 3 present an asymmetric DTA curve profile associate to a complex degradation process (a succession of elementary processes); Samples 4 - 6 are characterized by a symmetric DTA curve profile characteristic to an elementary degradation process. The thermogravimetric characteristics are listed in Table 2.

For DHAB polymers, the copolymerization ratio does not influence the starting degradation temperature and the first temperature degradation domain. The degradation pro-

Polymer sample	W ₁ (%)	ΔT ₁ °C	W ₂ (%)	ΔT ₂ °C	W ₃ (%)	ΔT ₃ °C	T _α
1	7.9	270-390	20.1	390-535	72.0	535-925	680
2	5.0	270-400	19.3	480-530	75.7	550-940	705
3	3.5	270-395	28.5	395-550	68.0	535-975	670
4	-	-	66.8	365-575	33.2	575-765	510
5	-	-	68.4	350-540	31.6	540-745	515
6	-	-	62.7	355-535	37.3	535-765	510

ΔT - the temperature domain corresponding to the degradation process;

W - the weight loss corresponding to the degradation process;

T_α - the temperature corresponding to 50 % weight loss.

Table 2 Thermogravimetric characteristics of the synthesized polymers.

cesses of Samples 1-3 start at 270 °C. An explanation of this thermal behavior could be based on the fact that the degradation starts in the LC state (for all the samples the isotropization take place above 300 °C). In the LC state, the electrostatic inter-chain interactions may play a role in the degradation process. This influence of the chain polarity on the thermal behaviour is also supported by similar studies previously performed on the copolyethers containing a propylenic spacer. It was established that if the structural unit of the copolymer contains only one “polar” bisphenol (such as DHAB), and the other co monomer is either biphenyl or bisphenol A, the starting degradation temperature depends on the copolymer composition [12].

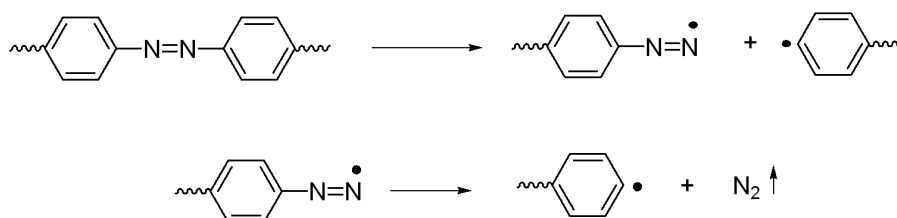
Taking into consideration our previous study related to the azobenzene containing copolyethers, the first degradation stage, situated in the interval 270-400 °C, was attributed to the nitrogen elimination process from DHAB units. As a direct consequence, the characterization of polymers LC property is not possible above 220-240 °C when degradation processes starts. In these circumstances, the isotropization process can not be monitored. The weight loss corresponding to the first degradation stage is in agreement with the DHAB content of the copolymer (Table 3).

Some considerations regarding the degradation mechanism can be stated, based on theoretical and experimental values of the weights' loss, corresponding to different stages of degradation (Table 3). For azobenzenic polymers (Samples 1-3), the degradation process starts with an elimination process of nitrogen molecules (Scheme 2) and data presented in Table 4 show a very good agreement between theoretical nitrogen content and experimental weight losses. These first reactions generate free radicals able to induce further degradation of the propylenic units in the next step via chain transfer reactions (Scheme 3).

Spl. code	W ₁ (%)		W ₂ (%)		W ₃ (%)	
	Experimental weight loss	N ₂ content (%)	Experimental weight loss	-(CH ₂) ₃ - content (%)	Experimental weight loss	Residual carbon (%)
1	7.9	8.2	20.1	22.4	72.0	37.9
2	5.0	5.5	19.3	22.8	75.7	37.9
3	3.5	2.8	28.5	22.8	68.0	37.9
4	-	-	66.8	25.2	33.2	34.9
5	-	-	68.4	22.4	31.6	33.1
6	-	-	62.7	20.2	37.3	32.0

Table 3 Theoretical and experimental weight losses of the synthesized copolymers.

W₁, W₂ and W₃ have the same significance as in the Table 2.

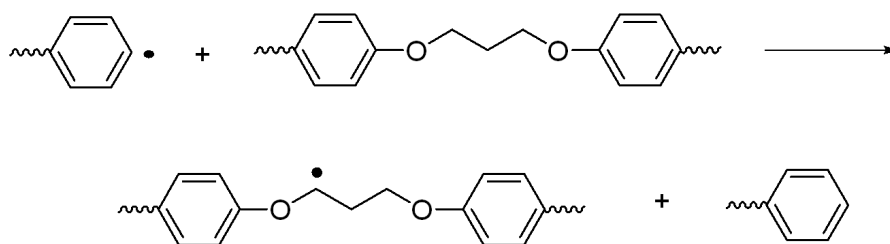


Scheme 2 Radicals' formation process on the first degradation step.

The nitrogen elimination mechanism supposition is based on the previous studies of the degradation process, and was based on Mass Spectrometry-Thermogravimetric analyses [13-14]. These studies demonstrated the presence, in the first decomposition step, of a signal $m/z = 28$ (specific only to the azobenzenic polyethers) which was attributed to the nitrogen elimination.

The hydrogen elimination from the propylenic units has, as a result, chain scissions and, finally, only aromatic fragments will be present in the system. The propylenic units' elimination is not accompanied by the aromatic hydrogen scission, or by oxygen elimination process. This supposition is supported by the residual carbon content values; the experimental weight loss in the third degradation step is much higher than the residual carbon content (calculated with Van Krevelen [13] relation). Therefore, the system should contain aromatic fragments containing hydrogen and oxygen atoms besides the expected residual carbon. The presence of the complex aromatic fragments also justifies the asymmetric profile of the DTA curves (Fig. 4), corresponding to the last degradation step (a succession of elementary processes).

The degradation mechanism is different for the polymers from the second group (Samples 4-6). In this case, although the (theoretical) propylenic content values are not correlated with the experimental weight loss corresponding to the first degradation step (Table 4), the weight losses occurring during the second degradation step are in a very good agreement with the theoretical residual carbon content. These results support the idea that in the first degradation step, a statistical radical process takes place accompanied by the oxygen and aromatic hydrogen elimination reactions. As a result, only



Scheme 3 Radical attack of the propylenic units.

residual carbon will constitute the substrate of the second stage of degradation. This supposition is also emphasized by the characteristic symmetric profile of the DTA curves (on the second degradation step) usually associated with elementary reactions (Fig. 5).

The differences between the degradation mechanisms of these two groups of polymers can be related to the conformational aspects. The presence of the cyclohexylic units in the side-chain and a disordered chain conformation might favor a statistical radical process, with direct consequences concerning the hydrogen and oxygen atoms elimination from the system (after the first degradation step residual carbon will be predominant in the system).

To obtain supplementary information concerning the activation energy and reaction degradation order, the experimental kinetic data were calculated using Freeman-Carroll and Coats-Redfern methods (Table 4).

Sample code	Freeman-Carroll method (ΔT_2)		Coats-Redfern method (ΔT_3)	
	n	Ea (kJ/mol)	n	Ea (kJ/mol)
1	1	285	1	48
2	1	181	1	70
3	1	200	1	57
4	1	293	1	83
5	1	191	1	96
6	1	275	1	96

n = reaction order;

Ea = activation energy of the degradation process;

ΔT_2 and ΔT_3 have the same significance as in the Table 2.

Table 4 Kinetic parameters evaluated from thermogravimetric data.

For the ΔT_2 temperatures interval, the activation energies vary as a function of the copolymer composition and structural units' type. One can observe that for the last degradation step there is a difference in the activation energy values between the two polymeric groups. The first group presents lower energy values, in agreement with the presence of complex aromatic residues. For the second polymer group, higher activation energy is necessary to obtain the residual carbon.

The kinetic characteristics corresponding to maximum degradation rate are summarized in Table 5.

Sample code	T_M (°C)	T_{cr} (°C)	$k_M \cdot 10^3$ (s ⁻¹)	$v_M \cdot 10^3$ (s ⁻¹)
1	450	452	10.9	5.12
2	460	455	6.7	2.83
3	470	477	7.2	2.46
4	500	504	5.8	2.01
5	500	507	5.8	1.71
6	510	511	9.2	3.12

T_M = temperature value corresponding to the maximum degradation rate;
 T_{cr} = critical temperature;
 k_M = rate constant at T_M ;
 v_M = degradation rate at T_M .

Table 5 Kinetic characteristics corresponding to the maximum degradation rate, on the temperature domain ΔT_2 .

The critical temperature values are much closer to the maximum degradation rate temperature values.

For the azo-copolymers (Samples 1-3), T_M values are lower than those corresponding to the second group of polymers, due to the presence of azo units. The azobenzene content influences the maximum degradation rate values, especially in the case of a large excess of azo units (Sample 1).

4 Conclusions

The thermogravimetric study enables us to establish that temperature limits (230–240 °C) should be taken into consideration for the study of liquid crystalline properties of the polymers containing azobenzene moieties. It was not possible to record some isotropization transitions, likely situated around 300 °C. Some problems might occur even for the evaluation of crystalline melting points (situated at 235–250 °C) and heating rate values of 20 °C/min are highly recommended.

The degradation mechanism is related with the polymer structure; in the case of azobenzene based polymers, the degradation process starts with the nitrogen elimination (at 270 °C) for all the samples, while higher starting degradation temperature (350–360 °C) are recorded in the absence of the azobenzene moieties.

For the degradation processes taking place in the liquid crystalline state, an influence of the chain polarity upon the starting degradation temperature is seen for those polymers containing only a “polar” bisphenol.

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