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THERMAL BEHAVIOR AND PRIMARY DEGRADATION MECHANISM OF SOME AROMATIC POLYETHERS WITH SEMI-FLEXIBLE CHAIN

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Abstract

The present paper describes a thermogravimetric study combined with mass spectrometry of some aromatic polyethers and copolyethers in order to obtain information on the degradation mechanism. The investigated polymers were synthesized starting from 3,3-bis(chloromethyl) oxetane and various bisphenols: 4,4'-dihydroxyazobenzene, 4,4'-dihydroxydiphenyl, bisphenol A and 4,4'-dihydroxydiphenylether. The presence of an oxetanic spacer in the structure, permitting the opening of the cycle, induces more complications in the characterization procedure. But, due to the possibilities relative to the modification of polymers or cross-linking reactions, the presence of the oxetanic moiety may offer some advantages.

Out of all the investigated polymers, those containing azobenzenic moieties have the lower thermostability. If the chain flexibility is augmented, the degradation mechanism is based on chain transfer reactions. All polymers present higher thermostability in an argon atmosphere. Based on mass spectra, a degradation mechanism sustained with the assumption that the oxetanic unit is the most labile was proposed. The opening of the oxetanic cycle begins with the most tensioned bond (–C–CH_2–) and generates a cross-linking process, which is more evident if the polymer melts below 200°C.

Keywords: mass spectrometry, oxetane, polyethers, thermal stability

Introduction

Due to the unique behavior, combining two essential properties of the matter: order and mobility, the polymers with liquid crystalline (LC) properties represents an inter-

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esting research field. In the last decade, liquid crystals and their use in the electronic displays became a subject of great interest. The presence of the azobenzenic units in the chains confers on the LC polymers the possibility of using them as optical memory systems. Thermotropic LC polymers containing mesogenic groups in the main chain have been studied systematically by Sirigu, Lenz, Percec and others [1–5]. Some of our previous papers presented the possibility of obtaining polyethers and polyesters, via phase transfer catalysis; some of these polymers presented LC properties [6–10]. Due to the presence of the mesogenic groups in the main chain, the synthesized polymers evidenced high values of the transition temperatures, near or up to the thermostability limit. As a consequence, we concluded that a very careful thermal stability study was necessary. Moreover, the presence of azobenzenic units, seems to induce some particularities to the mechanism of the degradation.

In order to obtain supplementary information on the degradation mechanism, the present paper is focused on a coupled thermogravimetric–mass-spectrometric (TG-MS) study.

The investigated polymers were synthesized starting from 3,3-bis(chloromethyl) oxetane (BCMO) and various bisphenols: 4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD), bisphenol A (BPA) and 4,4'-dihydroxydiphenylether (DDE).

The presence of an oxetanic spacer in the structure of the synthesized polymers, permitting the opening of the cycle, induces more complications in the characterization procedure. But, due to the possibilities relative to the modification of polymers or cross-linking reactions, the presence of the oxetanic moiety may offer some advantages [11–12].

Experimental

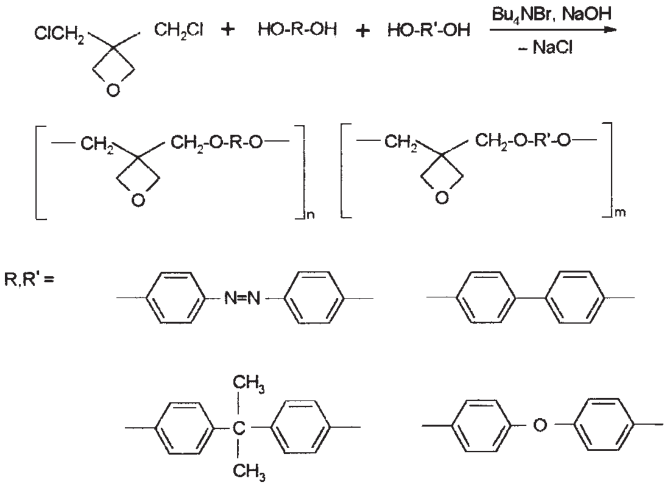
The polymers were synthesized by phase transfer catalysis in a liquid/liquid system [6–10]. The solvents and the phase transfer catalyst (tetrabutylammonium bromide) were supplied by Aldrich and were used without further purification. The composition of the copolymers and the molecular masses were calculated using ^{1}H-NMR spectra recorded on a Bruker Avence 300 MHz device (DMSO-d_6 as solvent).

TG/DTG/DTA and MS measurements were effectuated using a SDT 2960 device (TA Instruments) coupled with a QMS 420 mass spectrometer (Balzers) via capillary column heated at 200°C. For the investigations, 3–7 mg of sample and Al_2O_3 as inert reference material were used. The runs were carried out under flowing air and argon (10 L h^{-1}), from ambient temperature up to 900°C using a heating rate of 10°C min^{-1}. The simultaneously recorded mass spectra in the range of 10 to 300 AMU were taken every 10°C using a scan rate of 0.5 s/AMU. As reaction gases, air and argon with a flow of 10 L h^{-1} were used. The mass spectrometric investigations were done in the so-called MID (multiple ion detection) mode.

DSC curves were obtained up to 300°C using an open aluminum pan as a sample holder and an empty aluminum pan as reference on 2920 DSC device.

Results and discussion

The copolymers were synthesized according to the following reaction scheme:



Scheme I

Table 1 presents some characteristics of the synthesized polymers.

Table 1 Some characteristics of the synthesized polymers

Sample code	Bisphenol composition	M_n	T_g/°C	T_t/°C
1	DHAB	4100	127	>270
2	DHD	5000	120	255
3	BPA	5000	87	253
4	DDE	7000	87	–
5	DHAB/DDE=1.1/1	3550	120	–
6	DHD/DDE=1/1.1	3550	115	–
7	BPA/DDE=1/2	3500	100	–

M_n – numerical molecular mass
T_g – glass transition temperature
T_t – melting transition temperature

The experimental data show that the degradation process is influenced by the conditions in which the investigation is performed (in air or argon). Table 2 presents the thermogravimetric data obtained in different conditions.

The lower thermostability corresponds to the homopolymers containing DHAB units (sample 1). In the presence of air, the degradation starts at around 240°C, in argon, this process begins at 275°C. The mass loss for the temperature domain 250–400°C is higher if the degradation takes place in an inert (argon) atmosphere.

Table 2 Thermogravimetric characteristics of investigated samples

Sample code	Bisphenol composition	W_i/%	First step of degradation				Second step of degradation			Residue at $T_{2\text{final}}$/%
			ΔT_1	$T_{1\ \max}$/°C	$T_{1'\ \max}$/°C	W_1/%	ΔT_2/°C	$T_{2\max}$/°C	W_2/%	
Air, 10 L h^{-1}, 10°C min^{-1}										
1	DHAB	1.3	240–403	332	–	17.2	403–650	566	75.3	6.0
2	DHD	4.3	235–459	374	434	19.6	459–650	584	75.3	0.6
3	BPA	1.1	315–532	407	440	67.6	532–650	586	30.6	0.5
4	DDE	0.8	323–466	435	–	36.6	466–590	538	56.1	6.5
Argon, 10 L h^{-1}, 10°C min^{-1}										
1	DHAB	1.3	272–500	323	426	40.4	500–875	–	10.2	48.1
2	DHD	4.4	295–500	381	438	44.2	500–875	–	10.6	40.8
3	BPA	0.5	356–500	443	–	75.6	500–875	–	7.9	16.0
4	DDE	1.1	350–500	417	–	53.9	500–875	–	7.2	37.7
5	DHAB/DDE	1.0	290–500	349	384	41.5	500–875	–	11.3	46.2
6	DHD/DDE	1.6	340–500	433	–	62.6	500–875	–	9.5	26.1
7	BPA/DDE	3.0	345–600	432	–	59.0	500–875	–	8.7	29.3

W_i – mass loss before the starting degradation temperature; $W_{1,2}$ – mass losses in the first and the second degradation step; $\Delta T_{1,2}$ – temperature interval for first and second degradation step; $T_{1,1'\max}$ – temperature corresponding to the maximum in the first degradation step; $T_{2\max}$ – temperature corresponding to the maximum in the second degradation step

All the mass spectra present only the curves corresponding to the fragments with significant signals. The curves with low intensity signals were eliminated. The mass spectra were presented as a function of time for a better identification of the fragmentation processes that take place in the ionisation room (similar profiles of the curves suggest a fragmentation process in the ionisation room). The mass spectra are registered as a function of time because there is a small delay (3–4 min that correspond to 30–40°C on the temperature scale) between the elimination of the degradation fragments and the registration moment (for technical reasons).

The mass spectra recorded in an argon atmosphere, presenting a higher number of degradation fragments, permitted us to conclude that the degradation process is more complicated as compared with the similar recordings in the presence of the air. This observation is appropriate for all investigated samples. The different quality and amount of particular products measured by MS may be attributed to two factors. One is that the primary processes of the degradation may be different in an inert atmosphere or in air. The others is that the intermediate products of the primary degradation may take part in further decomposition and oxidation reactions, depending on the atmosphere.

Due to the possibility of the opening of the oxetanic cycle, the degradation processes seem to involve cross-linking reactions. Taking into account that the thermal degradation is a dynamic process (the heating rate being 10°C min^{-1}), we conclude that the degradation takes place at the same time with the opening of the cycles. As a function of the chemical structure and working atmosphere, cross-linking can be more or less intensive. A higher number of fragments in the MS spectra means a different degradation mechanism, which may be correlated with the cross-linking degree. Due to the existence of unfavourable sterical conditions for the cross-linking

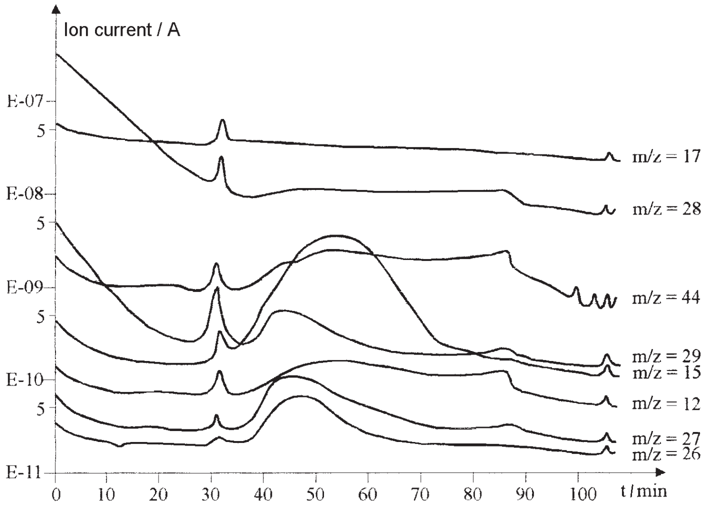
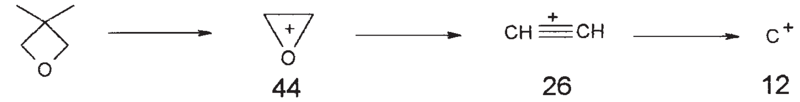


Fig. 1 Mass spectra corresponding to sample 1 (argon, 10 L h^{-1}, 10°C min^{-1})

process, in some cases the possibility to have only a ramification process of the polymer appears. The unfavourable geometry for a cross-linking process was evidenced by theoretical conformational analysis [13, 14].

In agreement with optical microscopy in polarized light (data obtained in isothermal conditions), the cross-linking process starts at around 250°C and, probably, is a consequence of the oxetanic ring opening. For the polymer containing DHAB units, the oxetanic ring opens at the same temperature when the degradation process starts. Moreover, the cross-linking reaction takes place only if the polymer is in an isotropic phase. In solid state, the lack of mobility of the polymer chain and sterical reasons make the cross-linking reactions less probable.



Scheme II

The mass spectra presented in Fig. 1 demonstrate evidence that the degradation processes are strongly influenced by temperature. Fragments *m/z* 12, 26, 28, 29 and 44 are detected for the first step of degradation and they correspond to the maximum degradation intensity ($T_{1\max}$ from Table 1).

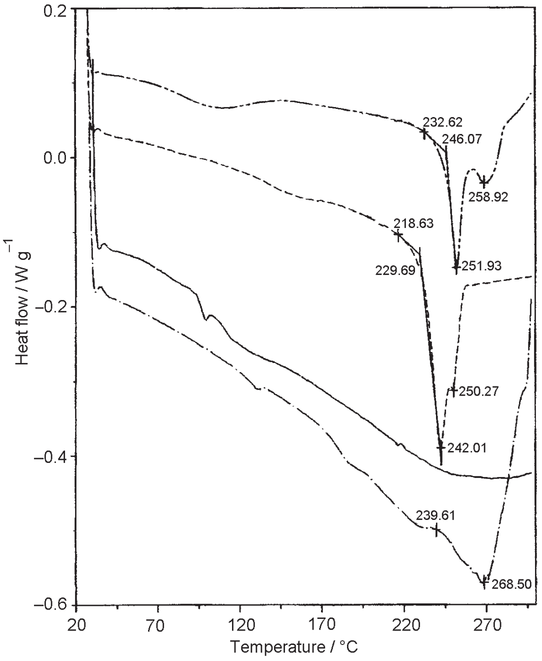


Fig. 2 DSC curves corresponding to homopolymers (samples 1, 2, 3 and 4).
— DDE+oxetan, - - - BPA+oxetan, – · – DHAB+oxetan, —— - - — DHD+oxetan

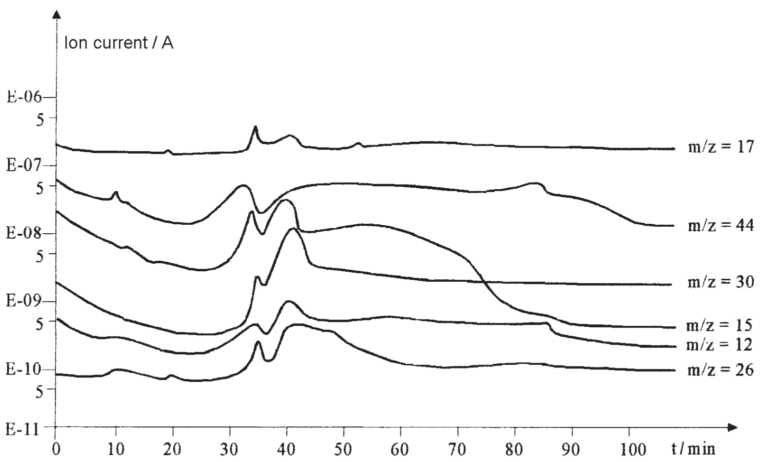


Fig. 3 Mass spectra corresponding to sample 2 (argon, 10 L h^{-1}, 10°C min^{-1})

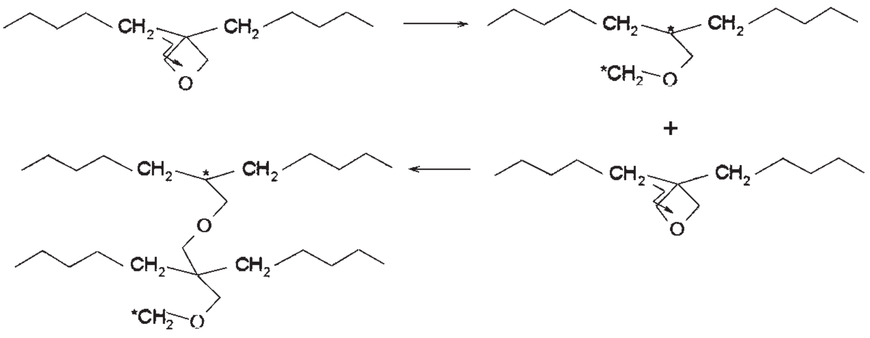
The presence of the peak *m/z* 28 could be explained by the elimination of nitrogen molecules. But, at the same time, the oxetanic ring is broken, leading to an epoxy fragment (44). In agreement with Scheme II, this fragment leads to an acetylenic one (*m/z* 26) and, finally, to carbon atoms (*m/z* 12).

The fragment *m/z* 29 could be the CHO ion resulted from the oxetanic unit.

The second investigated polymer is based on DHD (sample 2). Again, the thermal behavior in argon is different as compared with air. The decompositions begin to appear at a temperature value close to the ones of DHAB based substances. DSC curves (Fig. 2) reflect that the melting temperature of this polymer is similar to sample 1 (between 240–270°C).

The fragments *m/z* 12, 26, 30 and 44 (Fig. 3) suggest a similar degradation mechanism proposed for sample 1. Similarly to the case of sample 1 these fragments correspond to the maximum intensity of the degradation process of the first step (374°C). The fragment *m/z* 30 could be due to the presence of a CH_2O group.

Because the mass loss starts over 300°C, one can conclude that the thermostability of the polymer is better in an inert atmosphere as compared with air. For the



Scheme III

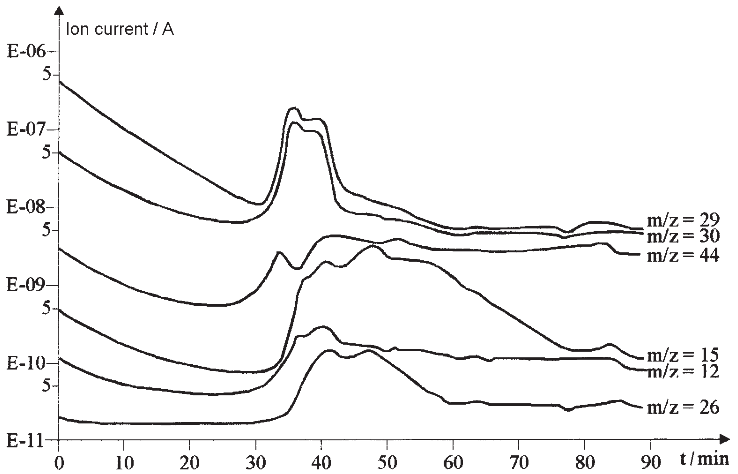


Fig. 4 Mass spectra corresponding to sample 3 (argon, 10 L h^{-1}, 10°C min^{-1})

same temperature interval, the mass loss is much higher in an inert atmosphere. This behavior suggests that the degradation mechanism is of a radical character.

The nature of the opening of the cycle is quite surprising. Contrary to our expectation, the breaking of the cycle begins with the most strain bond of the system (C–CH_2).

This proposed mechanism (Scheme III) is supported by the presence of the signal *m/z* 30, corresponding to a CH_2O fragment. Probably, this fragment forms in the scission of the exo-cyclic bond –C–CH_2–O–CH_2•, preceding the formation of an epoxy cycle.

The third investigated homopolymers is based on BPA (sample 3). Although the initial decomposition temperatures are very close, this polymer has a more rigid chain

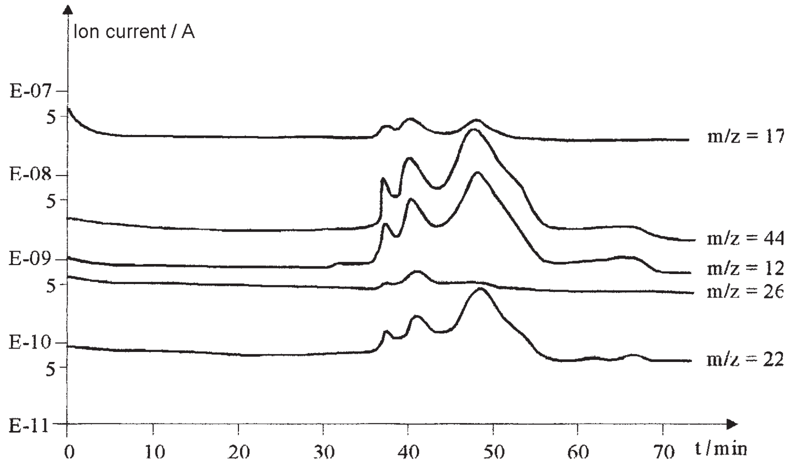


Fig. 5 Mass spectra of the sample 4 (air, 10 L h^{-1}, 10°C min^{-1})

as compared with sample 4. In spite of this, for temperatures going up to 470°C, the mass loss is much higher (around 60%). This result could be explained taking into consideration the cross-linking degree, which is probably lower as compared to sample 4, but higher than that of samples 1 and 2.

As compared with other samples, the mass spectra presented in Fig. 4 are more complex, new signals, corresponding to CH_2O and CH_3 groups (*m*/*z* 30, 29, 15) being present.

The fourth of the investigated homopolymers (sample 4) presents the highest thermostability in air. This is quite surprising because, due to the presence of an oxygen atom between the two aromatic rings, this polymer has the most flexible chain. If we take into consideration only the chain flexibility, this polymer should have the lowest thermostability.

On the contrary, the mass loss starts at 325°C. This polymer presents an amorphous structure, the DSC curve revealing only the glass transition (85°C). This sample is in liquid state under 200°C and as a consequence, the cross-linking process can start earlier: the result is a better thermostability. The mass loss up to 470°C is only 36.6%, this aspect being in agreement with the existence of an intensive cross-linking process.

The corresponding mass spectra in air are less complex (Fig. 5). The main important fragments are *m*/*z* 44, 26 and 12.

The behavior of these 4 homopolymers leads to the conclusions that cross-linking processes take place between 200–230°C, this interval being below the estimated values obtained by optical microscopy.

In order to test the assumption of the thermal stabilization through cross-linking reactions, some copolymers containing the most stable structural unit (DDE-BCMO) were investigated. As one can see on the DSC curves, all these copolymers present an amorphous structure, up to 300°C only the glass transition being observed.

The presence of the azobenzenic units in the main chain decreases the thermostability, sample 5 being the less stable. For sample 7, the initial degradation temperature is very close to that of the component homopolymers. The mass spectra of copolymers are more complex as compared with the homopolymers ones.

The copolymer containing DHAB and DDE presents some signals corresponding to the oxetanic ring scission (*m*/*z* 44, 26, 12) and $–CH_2O$ –CHO, groups respectively (30 and 29). The signal corresponding to the nitrogen elimination (*m*/*z* 28) disappeared, this aspect being quite interesting. This behavior could be explained by the augmentation of the chain flexibility due to the presence of the etheric groups. In the case of flexible chains, a different degradation mechanism, based on the chain transfer reactions, was evidenced for azobenzenic polymers, without nitrogen elimination [15].

All mass spectra corresponding to samples 5, 6 and 7 present signals corresponding to the fragmentation of the oxetanic ring (*m*/*z* 12, 26, 44) and to the presence of CH_2O groups (*m*/*z* 29, 30).

Conclusions

Out of all the investigated polymers, those containing azobenzenic moieties have the lowest thermostability. Nevertheless, the presence of these azobenzenic moieties is essential to obtain LC properties. For the azobenzenic polymers with a semi-rigid chain, the degradation mechanism starts with the elimination of nitrogen molecules. If the chain flexibility is augmented, the degradation mechanism is strongly influenced and is based on chain transfer reactions.

All polymers present a higher thermostability in an argon atmosphere.

Based on mass spectra recorded by the TG–MS system, a degradation mechanism is proposed assuming that the oxetanic unit is the most unstable.

The opening of the oxetanic cycle begins with the most tensioned bond (–C–CH_2–) and generates a cross-linking process, which is more evident if the polymer is in the molten state below 200°C.

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