Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 877–887

THE DEGRADATION MECHANISM USING TG-MS TECHNIQUE OF SOME AROMATIC POLYETHERS CONTAINING FLEXIBLE SPACERS

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(Received January 23, 2002; in revised form June 25, 2002)

Abstract

The paper presents a thermogravimetric study of some aromatic poly- and copolyethers, using mass spectrometry technique combined with thermogravimetric analysis. The polymers were synthesized by phase transfer catalysis technique, using bis(2-chloroethyl)-ether or 1,6-dichlorohexane as flexible spacers and various bisphenols (4,4'-dihydroxydiphenyl, 4,4'-dihydroxyazobenzene and bisphenol A). The presence of azobenzenic moieties in the chain induces a liquid crystalline behavior, but, due to the high values of the transition temperature, some precautions during the thermal characterisation are necessary. In the case of azobenzenic samples, the degradation reactions begin, as a function of the chemical structure, around 230–250°C. A degradation mechanism based on chain transfer reactions was proposed. The chain flexibility influences the thermal degradation mechanism, in the case of rigid polymers the chain transfer reactions being less probable. For the flexible chains, the thermal stability is not essentially influenced by the copolymerisation ratio between the two aromatic bisphenols.

Keywords: liquid crystals, mass spectrometry, polyethers, thermal stability

Introduction

Due to the unique behavior, combining two essential properties of the matter, order and mobility, polymers with liquid crystalline (LC) properties represent an interesting research field. In our previous studies, we reported the synthesis and characteriza-

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1418–2874/2002/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

tion of new polymers, some of them having LC properties [1–5]. Our attention was focused especially on the polyetheric structures obtained from bisphenols and dihalogenated compounds, the later one being chosen in order to permit a gradual modification of chain flexibility. Our synthesis strategy was to study the correlation between chain conformation, flexibility and inter-chain interactions on the capacity to generate LC behavior [6–9]. Because the polymers contain the mesogenic groups in the main chain, the values of the transition temperatures were situated near, or up to the thermal degradation limit. Therefore, in order to establish the temperature limits for DSC and optical microscopy characterization, a very careful study concerning the thermal stability was inevitable.

The present paper is focused on the thermal stability of some polyethers and copolyethers using a mass spectrometry (MS) technique combined with thermogravimetric analysis (TG). The polymers were synthesized starting from bis(2-chloroethyl)-ether or 1,6-dichlorohexane and various bisphenols, as follow: 4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD) and bisphenol A (BPA). Based on mass spectra, a degradation mechanism of polymers containing azobenzenic units was proposed.

Experimental

The polyethers were synthesized by phase transfer catalysis technique in a liquid/liquid system, details concerning the synthesis and characterization, being previously reported [1–10]. Numeric average molecular mass of the synthesized polymers were extracted from ^{1}H-NMR spectra, using the chains-ends (type CH_2-Cl).

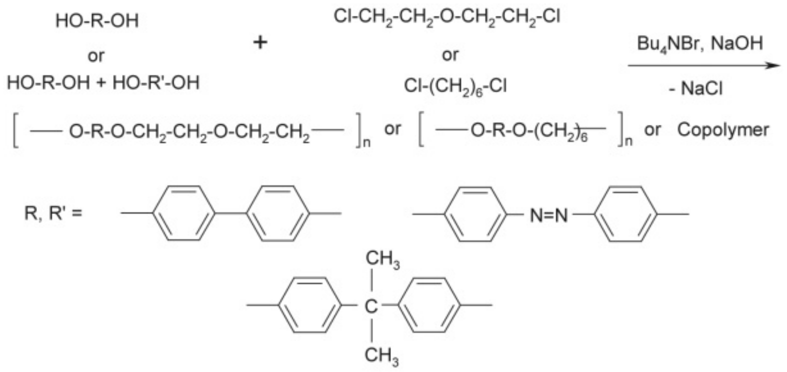
TG/DTG/DTA and MS measurements were effectuated using a SDT 2960 device (DuPont) coupled with a QMS 420 Mass Spectrometer (Balzers) via a capillary column heated at 200°C. For all the investigations, 3–7 mg of sample and Al_2O_3 as inert reference material were used. The registrations were carried out under dynamic atmosphere, beginning with ambient temperature and 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 0.5s/AMU. Air and argon with a flow of 10 L h^{-1} have been used as reaction gases. 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 sample holder and an empty aluminum pan as reference, on a 2920 DSC device.

Results and discussion

Tables 1 and 2 present some characteristics of the homopolymers and copolymers. Samples 1–3 present the same order of thermostability as compared with similar polymers containing other spacers (ex. oxetanic) [11]. The polymer containing azobenzenic groups presents the lower thermostability. This aspect was evidenced by other papers, too [12–13]. Nevertheless, the presence of azobenzenic moieties may be of interest for displays technology and optical storage materials.

The copolymers were obtained according to the following reaction scheme:



As compared with the other homopolymers, which are degraded in one main step, the degradation of Sample 1 occurs in two steps (Fig. 1). On the DTA curve No. 1 the strong exothermic effect is due to the nitrogen loss from the structure (this is the first step of decomposition). The phase transitions were discussed by DSC curves, not DTA (DTA curves have a low precision).

The mass spectrum of Sample 1 is less complicated as compared with the other homopolymers (Fig. 2). The signal *m*/*z* 28, corresponding to nitrogen elimination (pointed out in the case of the oxetanic spacer [11]) is not present in the spectra at lower

Table 1 Characteristics of the synthesized polymers

No.	Copolymerisation ratio	M_n	Behaviour
	Diethyletheric spacer		
1	DHAB	2.500	LC
2	DHD	4.000	SC
3	BPA	3.800	SC
4	DHAB/BPA=1/1	4.500	LC
5	DHD/BPA=2.5/1	4.000	SC
	Hexamethylenic spacer		
6	DHAB	2.400	LC
7	DHD	2.900	SC
8	BPA	3.200	SC
9	DHAB/DHD=2.5/1	2.050	LC
10	DHAB/DHD=1/1.2	2.300	LC
11	DHAB/DHD=1/3.1	2.250	LC

LC – liquid crystalline
SC – semi-crystalline

Table 2 Thermogravimetric characteristic of the synthesied polymers

No.	W_i /%	First step of degradation			Second step of degradation		Residue
		ΔT_1/°C	T_{1max}/°C	W_1/%	ΔT_2/°C	W_2/%	at 875°C/%
1	0.27	252–465	294	68.68	465–875	7.23	24.46
2	0.88	320–500	437	78.81	500–875	3.94	16.28
3	1.21	350–500	447	87.02	500–875	2.47	9.30
4	0.67	220–308	278	65.70	500–875	3.63	30.00
5	0.51	310–500	440	79.30	500–875	1.47	18.55
6	2.13	260–334	292	13.92	334–500	63.52	18.0
7	0.86	285–500	379	89.82	–	–	7.7
8	0.00	360–500	451	96.58	–	–	2.9
9	1.61	289–345	313	13.51	345–500	65.75	16.12
10	1.78	276–331	304	10.4	331–500	72.00	13.80
11	0.73	271–359	327	15.65	359–500	75.00	6.7

W_i=mass loss before degradation
W_1=mass loss in the first step of degradation
W_2=mass loss in the second step of degradation
ΔT_1 =temperature interval for the first step of degradation
ΔT_2 =temperature interval for the second step of degradation
T_{1max}=maxim temperatures in the first step of degradation

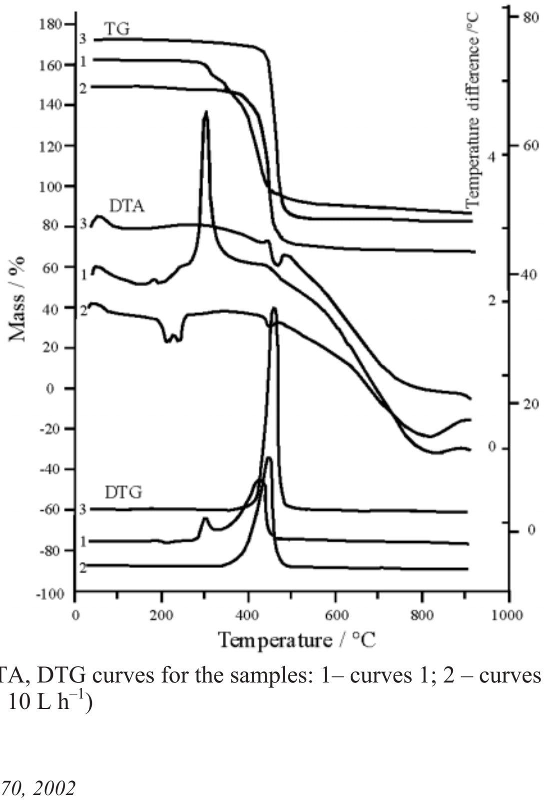


Fig. 1 TG, DTA, DTG curves for the samples: 1– curves 1; 2 – curves 2; 3 – curves 3; (argon, 10 L h^{-1})

temperatures, and appears only over 700°C. For comparison we present in Fig. 3 the mass spectra corresponding to an oxetanic polymer with azobenzenic groups.

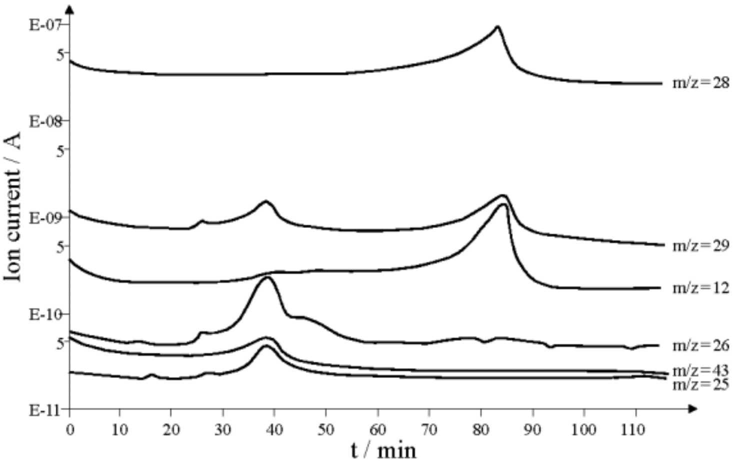


Fig. 2 Mass spectra corresponding to Sample 1

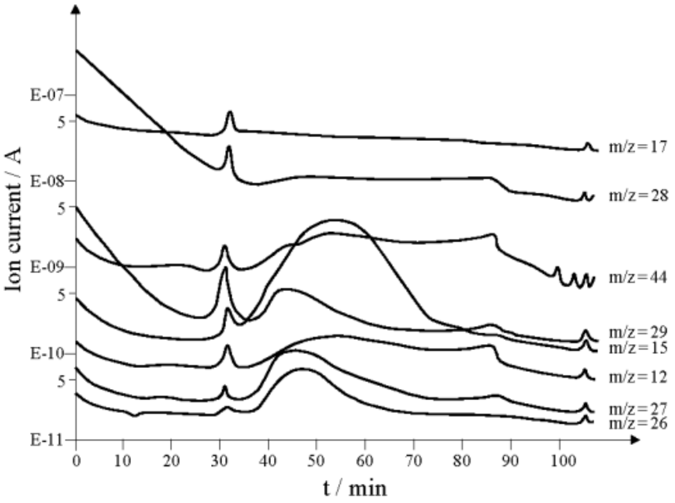
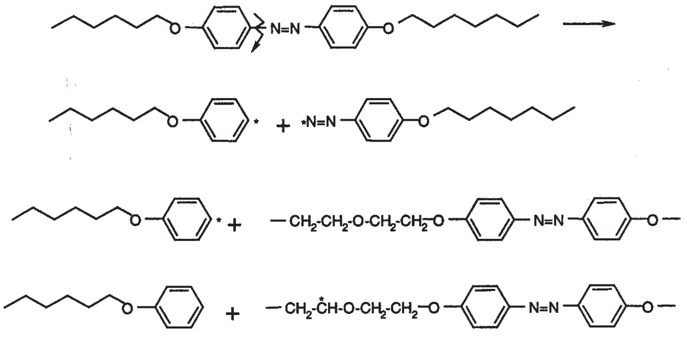


Fig. 3 Mass spectrum corresponding to an oxetanic polymer with azobenzenic groups [11] (argon, 10 L h^{-1}, 10 ºC min^{-1})

This fact could be a consequence of a different degradation mechanism in rapport with oxetanic spacer. Taking into consideration that the order of homopolymers thermostability is not changed, the absence of the signal *m*/*z* 28 could be explained through a stabilization reaction of the macro-radicals formed by chains' scission (Scheme 2). The stabilization probably takes place through a chain transfer reaction.



This modification of the degradation could be explained taking in consideration the chain flexibility and melting temperatures. In the case of oxetanic polymers (containing DHAB units), the degradation starts immediately after the melting point, situated around 250°C. In these conditions, we can anticipate a supplementary energy accumulation in the main chain, maintained in solid phase up to 250°C. This fact, combined with the chain's rigidity, will decrease the probability of the chain transfer reactions and results in the nitrogen elimination immediately after the melting. In the case of polymers with diethyl-ether spacer, the melting processes are taking place at lower temperatures. More of that, Sample 1 shows liquid crystalline properties, the polymer being in the fluid state after 190–200°C (Fig. 4).

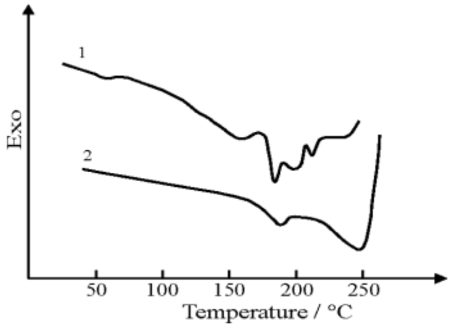


Fig. 4 DSC curves (first heating, argon 10 L h^{-1}, 5°C min^{-1}) for the samples: 1 – curve 1; 6 – curve 2

Combined with the chain flexibility, this manner will generate a higher mobility of the radical chain-ends obtained by the scission of the bond C–N. The radical chains could be stabilized by reaction with a hydrogen atom coming from a neighbor chain.

The mass spectra of all the homopolymers belonging to this group (Samples 1–3) present the same signals produced by spacer degradation (*m/z* 43 for C_2H_3O, *m/z* 29 for CHO, *m/z* 26 for C_2H_2 and *m/z* 25 for C_2H). For Sample 2 (based on DHD) a supplementary signal (*m/z* 78) appears in the mass spectra over 500°C. This signal may indicate an aromatic fragment (Fig. 5).

The absence of *m/z* 28-signal characteristic to N_2 elimination is valuable too, in the case of the copolymers based on DHAB and diethyletheric spacer.

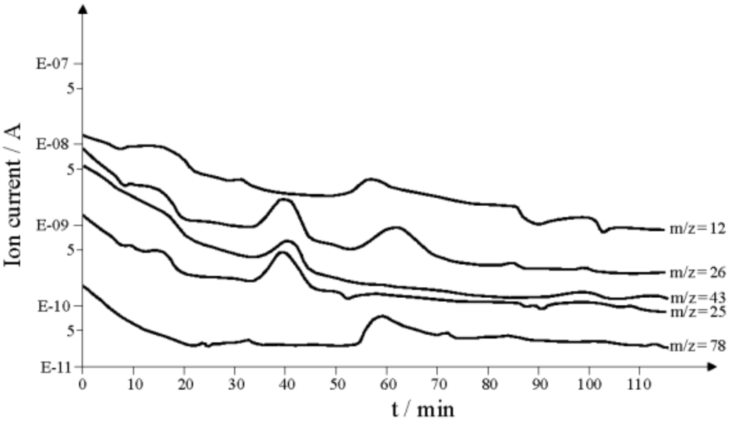


Fig. 5 Mass spectrum corresponding to Sample 2

The behavior of the Sample 4 is in agreement with the proposed mechanism. This polymer becomes isotropic at a lower temperature than the Sample 5. The result will be the decreasing of the starting decomposition temperature (220°C). The DSC curve shows that the polymer is in anisotropic phase at 180°C. This is favorable for transfer chain reactions and leads to the acceleration of the degradation processes and, consequently to the decreasing of thermal stability. The proposed mechanism seems to be the same in the case of the hexamethylenic spacer, when the same absence of the signal *m*/*z* 28 has been observed.

The next investigated group contains a hexamethylenic spacer (Samples 6–11). Generally, these polymers present the same characteristics like the group with diethyletheric spacer (Fig. 6). The order of the thermostability is similar, the sample containing DHAB being the less stable, while the sample with BPA is the most stable. The starting degradation temperature (evidenced by the exothermal effect) for the homopolymer containing DHAB is very close to the same term with diethyletheric spacer (260°C Fig. 4).

Similar with the previous case, the degradation takes place in two steps. The DSC curve (Fig. 4) shows a melting process from crystal to liquid crystal at 175°C, but the sample can not be isotropised because the degradation starts at 260°C. The mass spectra shows the same particularity like in case of diethyl ether spacer (the absence of signal *m*/*z* 28). The proposed mechanism is the same and is based on the macro-radicals stabilization formed through C–N bond scission. This stabilization occurs *via* transfer chain reactions. Similarly, with the group containing BCEE, the mass spectrum of the Sample 6 (Fig. 7) evidence signals at higher *m*/*z* values (*m*/*z* 78). The others fragments are obtained by flexible spacer degradation: *m*/*z* 68 (C_5H_8); *m*/*z* 57 (C_4H_9); *m*/*z* 44 (C_2H_4O); *m*/*z* 41 (C_3H_5); *m*/*z* 26 (C_2H_2); *m*/*z* 15 (CH_3); *m*/*z* 12 (C).

The homopolymer based on DHD presents a simillar thermal stability, the mass losses starting for 285°C. This polymer is in fluid phase starting with 215°C.

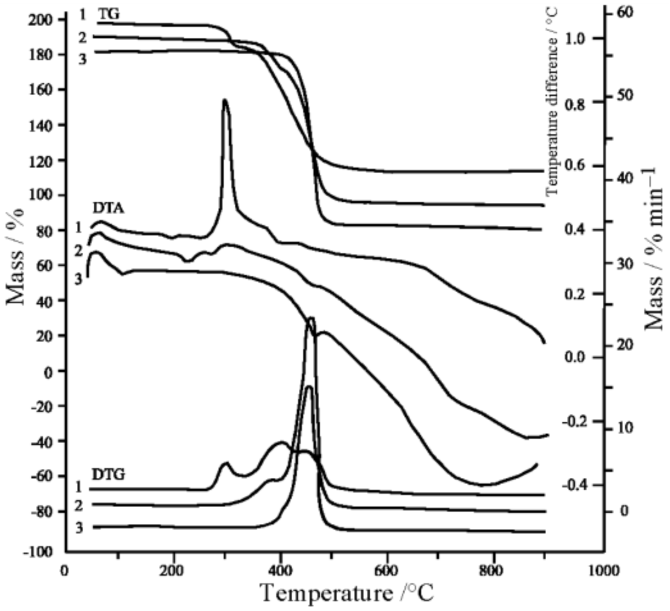


Fig. 6 TG, DTA, DTG curves corresponding to the samples: 6 – curves 1; 2 – curves 7; 8 – curves 3; (argon, 10 L h^{-1})

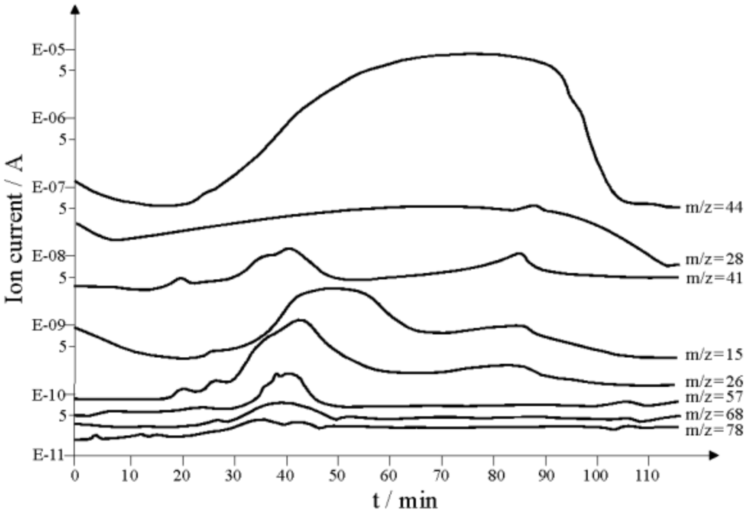


Fig. 7 Mass spectrum corresponding to sample 6

The mass spectra shows some common characteristics with the sample containing DHAB. These characteristics are imposed by the flexible spacer nature. The difference from the previous spectra consists in the shape of the signals. The signal *m*/*z* 78 is also present, and can be assigned to the aromatic ring. The other signals are coming from the spacer degradation: *m*/*z* 68 (C_5H_8); *m*/*z* 57 (C_4H_9); *m*/*z* 44 (C_2H_4O); *m*/*z* 41 (C_3H_5); *m*/*z* 26 (C_2H_2); *m*/*z* 15 (CH_3); *m*/*z* 12 (C).

The next polymer (Sample 8) presents the highest thermostability, the mass losses starting at 360°C. Up to 500°C, the polymer is almost totally (degraded) decomposed. The mass spectrum shows the presence of some common fragments, but there are differences due to the absence of some hydrogen atoms. For example, instead of fragments *m*/*z* 68 and, *m*/*z* 57 the spectra presents fragments *m*/*z* 67 (C_5H_7) and *m*/*z* 55 (C_4H_7), respectively. The other fragments are the same like in the previous spectra.

For a better understanding of the degradation mechanism of the polymers based on DHAB, three new copolymers have been investigated (Samples 9–11). Due to their potential application as optical storage materials, the polymers containing azobenzenic moieties present a high practical interest. These copolymers have the same structure, but the composition was changed gradually. All these copolymers present LC properties, but they cannot be isotropised because the degradation starts in the temperature domain 270–290°C. Neither of these samples shows the signal *m*/*z* 28.

For all these samples, the thermogravimetric curves (Fig. 8) and the mass spectra are very similar. Due to the composition modifications, there is a small difference regarding the shape of the signals in the mass spectra, but this difference does not change very much the degradation mechanism. For all these polymers, one can ob-

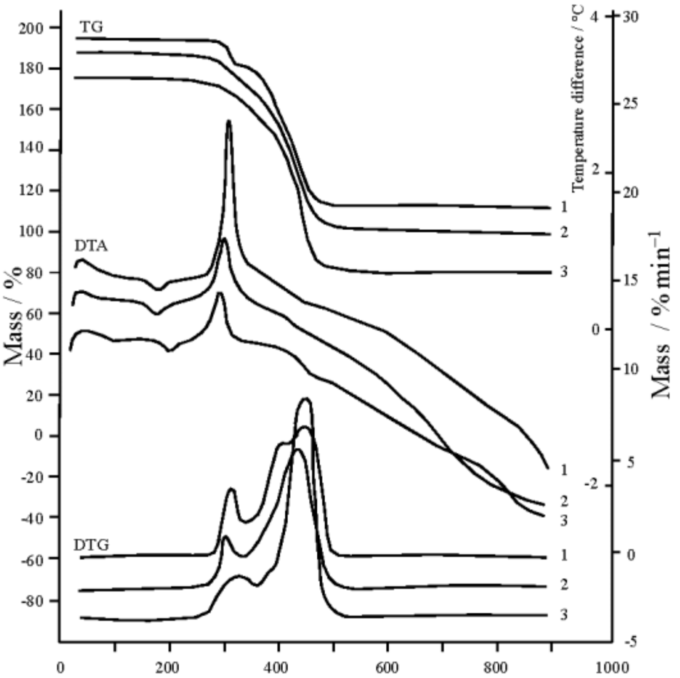


Fig. 8 TG, DTG, DTA curves corresponding to the samples: 9 – curves 1; 10 – curves 2; 11 – curves 3; (argon 10 L h^{-1})

serve the lack of the signal *m/z* 78, the other fragments corresponding to the hexamethylenic spacer degradation being present: *m/z* 67 (C_5H_8); *m/z* 57 (C_4H_9); *m/z* 44 (C_2H_4O); *m/z* 41 (C_3H_5); *m/z* 26 (C_2H_2); *m/z* 15 (CH_3); *m/z* 12 (C).

We assume that the polymers containing a flexible spacer, being in a fluid phase before the degradation starts, possess a common characteristic concerning the degradation mechanism. The chain transfer reactions are supposed to appear only for the case when the first chain scission takes place at low temperatures (in the presence of an atom or a group of atoms thermally labile). The thermal stability is not influenced by the ratio between the mesogenic groups (DHAB and DHD).

A very important conclusion for the characterization of liquid crystalline polymers based on DHAB is that the scission of the azobenzenic groups may start under 250°C. In consequence, for avoiding decomposition processes (on DSC analyses or optical microscopy), we recommend high heating rate (15–20°C min^{-1}). The interpretation of the phase transitions on the DSC curves (present over 220°C) must consider the possibility of the degradation of the azo units. Consequently, between the first and the second heating scan, a non-reproducibility of the intensity of DSC signals could appear and signals over 220°C may disappear. In this case, we recommend (for the CL polymers with DHAB units) the interpretation of the DSC signals only for the first cycle heating-cooling. This is quite unusual during the DSC curves interpretation for liquid crystalline polymers, when, due to the history of the sample that can influence the DSC curves profile is strongly recommended to ignore the first cycle and to consider only the second or third heating cycles.

Conclusions

- The most important conclusion is associated with the thermal characterization of the liquid crystalline polymers containing azobenzenic groups in the main chain. If the temperature transitions are situated above 220°C, a heating rate of 15 or 20 °C/min (for DSC analysis) and the interpretation of the first heating/cooling scan is recommended.
- The chain flexibility influences the thermal degradation mechanism. In the case of flexible chains, in the presence of thermo-labile group, a thermal decomposition through chain transfer reaction takes place. If the polymer is rigid, the chain transfer reactions are less probable.
- A chain degradation mechanism for flexible polymers containing azobenzenic groups was proposed.
- In the case of flexible polymers, the thermal stability is not essentially influenced by the copolymerisation ratio; the most thermo-labile group will impose the stability limit.

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