

## Liquid-Crystalline Polymers

### Part II: Thermal Analysis of Some Copolyethers Based on Bisphenol A, 4,4'-Dihydroxyazobenzene, 4,4'-Dihydroxydiphenyl and 3,3'-Bis (Chloromethyl) Oxetane

Nicolae Hurduc

Department of Macromolecular Chemistry, Technical University " Gh. Asachi," Jassy, Romania

Dana Ionescu and Natalia Hurduc

Department of Physical Chemistry, " AL. I. Cuza " Univesity, Jassy, Romania

Alexandrina Bordianu

Research Center of Savinesti, Romania

Received: 8 May 1994; accepted 28 September 1994

#### ABSTRACT

The thermal stability of some polyethers and copolyethers, containing the oxetanic ring in the main chain, is presented. Some of these polymers can be used for obtaining liquid - crystalline thermoset materials. The presence of azo bonds in copolyethers reduces the thermal stability, but we can say that this presence is necessary if we wish to obtain polymers with LC properties.

#### Key Words

liquid - crystalline polymers, thermal stability, liquid crystalline thermoset, copolyethers, 3,3-bis (chloromethyl) oxetane

#### INTRODUCTION

In the last few years, a great number of papers have been devoted to the synthesis and characterization of polymers with liquid - crystalline (LC)

properties due to their important technical applications [1-12].

LC polymer processing generates materials with high mechanical resistance[13-15].

A relatively new method for obtaining high

resistance materials is the synthesis of thermoset LC polymers [16-19]. This method consists in the possibility of cross-linked reactions of macromolecules in the LC state, usually by the reaction between epoxidic rings and diaminic derivatives.

In our laboratory some LC polyethers and copolyethers containing the oxetanic rings in the main chain were synthesized [20,24,31,32].

The presence of oxetanic ring determines the appearance of some special properties, e.g., the transformation of bisphenol-A in a mesogenic unit [20-21]. This behaviour is the result of the interaction between oxetanic and phenolic rings. These interactions determine a rigid-structure of bisphenol-A and, as a consequence, the polymer presenting LC behaviour. These LC polymers can be modified by reactions of oxetanic rings offering the possibility of obtaining LC thermoset polymers.

Taking all these into account, it was necessary to know their thermal behaviour in order to establish the most convenient temperature domains for the cross-linking reaction.

The goal of this paper is the characterization of some polyethers and copolyethers by thermal analysis under nonisothermal conditions. The influence of chemical composition on the thermal stability in correlation with LC properties was also analyzed.

## EXPERIMENTAL

The TGA thermograms were recorded on a Du-Pont 2000 V4 apparatus in nitrogen atmosphere, heating rate 10 °C/min. The kinetic treatment data was performed using Freeman - Carroll's [27], Nicolae's [28] and Gorbachev's methods [29] and the compensation criterion ( $S_p$ ) [30].

The details regarding the synthesis and characterization of the copolyethers are described elsewhere [22].

## RESULTS AND DISCUSSION

The synthesis of copolyethers was performed by a polycondensation reaction, starting from 3,3'-bis(chloromethyl) oxetane (BCMO) and various bisphenols [4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD) or bisphenol-A (BPA)] (scheme below).

The ternary copolyethers were obtained by reaction between BCMO and various mixtures of bisphenols (BPA, DHAB, DHD) in different molar ratios.

The same method was used for the synthesis of binary copolyethers. The thermal behaviour of binary systems was the aim of a previous paper [26].

The thermal analysis reveals a 33-50% degradation process occurring up to 600 °C. The degradation process takes place in a single step or two or three steps depending on the

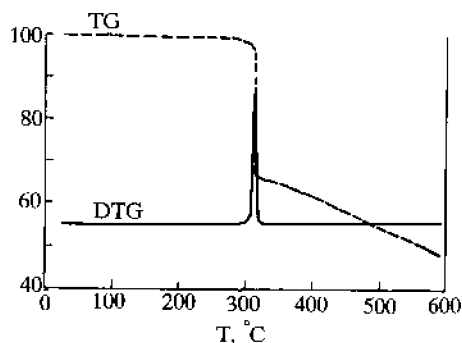
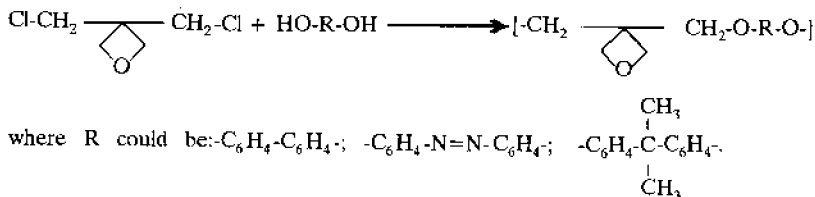


Fig.1



microstructure of the macromolecular chain. (Figures 1-3).

We can remark that the degradation process of ternary copolyethers takes place in three steps, independent of copolyethers composition. (Figures 4 and 5).

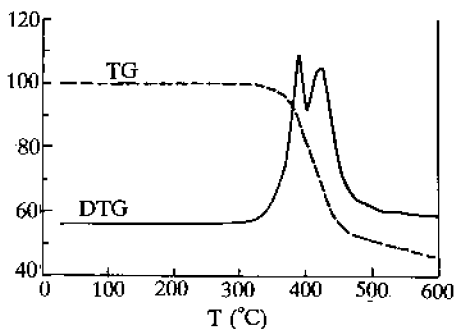


Fig.2

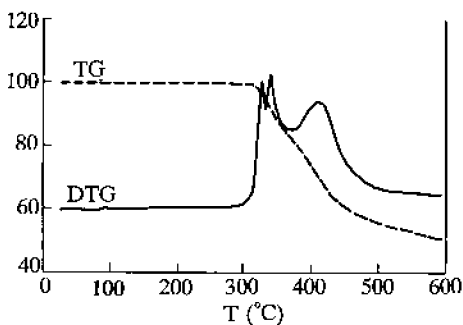


Fig.3

Table 1 contains the copolyethers composition determined by  $^1\text{H-NMR}$  spectroscopy.

The thermogravimetric and kinetic characteristics of the analyzed polyethers and copolyethers are presented in Table 2.

We mentioned that the cross-linked process of LC polymers takes place at about 250 °C.

The polyether based on DHAB and BCMO presents thermal stability up to 276 °C (identically for polyether based on BPA and BCMO) and it

Table 1. The composition for copolyethers studied.

	DHAB	DHD	BPA
1	2.8	1.5	1.0
2	2.0	3.4	1.0
3	1.0	1.1	2.0

can present LC phase between 175 °C and 250 °C (function of molecular weight). In principle, these copolyethers could suffer cross-link processes at 250 °C but the reaction time with diamines might be as short as possible to avoid the degradation processes.

The polymer which could be cross-linked without problems of degradation is the polymer based on DHD and BCMO (sample C from Table 2) the degradation process starts at 320 °C. It presents LC phase between 230 °C and 260 °C.

Taking into account the thermal behaviour of ternary copolymers we can mention that the degradation process starts at 280 °C, independent of chemical composition. So, by ternary copolymerization the thermal stability was not modified; in case of binary copolymerization this modification was possible. Using only two types of bisphenols, the thermal stability was increased towards 340 °C [26]. This high thermostability was obtained only for copolyethers without DHAB units in their chain. Even though the presence of DHAB units

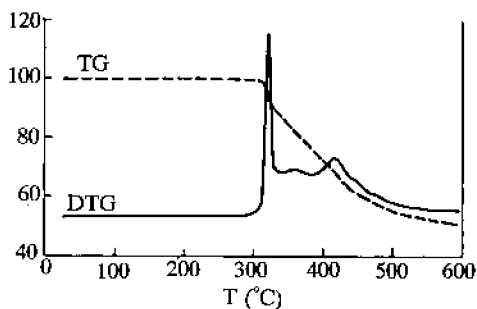


Fig.4

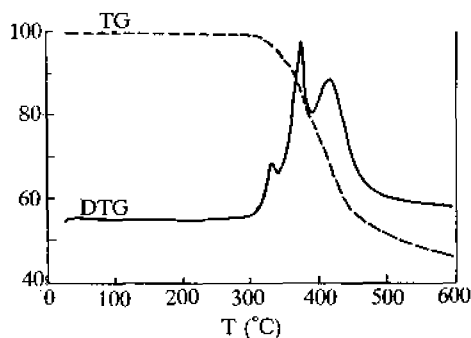


Fig.5

decrease thermal stability of the compounds we can say that this presence is necessary if we wish to obtain polymers with LC properties.

Thus, from these three copolyethers, only one which contains the highest percent of DHAB (sample 1 from Table 1) presents LC properties

between 170 and 220 °C [22] and is useful for our goals. The increasing of thermal stability for this polyether at 280 °C could allow a cross-linked process at 250 °C, but as in case of homopolymers, the time period of this process might be as short as possible.

we also remarked, that there is a dependence between the DHAB content and the maximum degradation rate for first step of degradation which is shown in Table 3.

These results suggest that the attack takes place at azo bond, with preferential liberation of nitrogen.

In order to obtain some information regarding the mechanism of thermal degradation of these polymers we performed the kinetic mode of behaviour (Table 4).

The analysis of these data suggest the existence of a compensation effect, this effect is verified, too, by the graphical representation of dependence  $\ln A = f(E)$  which shows a statistical

Table 2. Thermogravimetric and kinetic characteristics for polyethers and copolyethers studied.

The sample	I						II						III					
	$\Delta T$ (%)	W (%)	TI (°C)	$T_M$ (°C)	$v_M$ (%/°C)	E (kJ/mol)	$\Delta T$ (%)	W (%)	TI (°C)	$T_M$ (°C)	$v_M$ (%/°C)	E (kJ/mol)	$\Delta T$ (%)	W (%)	TI (°C)	$T_M$ (°C)	$v_M$ (%/°C)	E (kJ/mol)
A	276-593	33	316	327	4.25	184												
B	276-395	36.6	341	353	0.98	306	395-553	22	447	429	0.49	96						
C	321-402	18.7	391	390	0.66	191	402-526	31	462	423	0.61	68						
1	280-335	12	324	326	0.93	269	339-388	11.47	331	366	0.27	269	388-541	23	425	0.31	42	
2	285-335	5	326	330	0.40	356	335-372	11.47	347	345	0.43	144	372-539	29	413	0.35	39	
3	282-344	3.9	337	334	0.18	221	343-392	18.06	355	366	0.57	239	392-555	30	429	0.46	53	

$T$ - interval of decomposition (°K)

W- loss of weight (%)

TI- isokinetic temperature (°K)

$T_M$ - temperature corresponding to the maximum heating rate (°C)

E- activation energy (kJ/mol)

$v_M$ - maximum rate of decomposition (%/°C)

distribution according to a straight line (Fig. 6).

The compensation parameters are in agreement with those computed by Nicolaev's method. So, we propose the following equation:

$$\ln A = 3.10^4 E - 0.4$$

**Table 3. The dependence between the maximum degradation rate and DHAB content of polymer.**

Sample	DHAB (%)	T <sub>M</sub> (°C)	V <sub>M</sub> (%°C)
A.(Tab.2)	100	327	4.25
1.(Tab.1)	54.1	324	0.93
2.(Tab.1)	33.2	326	0.40
3.(Tab.1)	24.5	337	0.18

**Table 4. The compensation parameters for polyethers and copolyethers studied.**

The sample	I				II				III						
	Nicolaev		Gorbachev		Nicolaev		Gorbachev		Nicolaev		Gorbachev				
	a.10 <sup>4</sup>	b	ln A	Ti(K)	S <sub>p</sub> =ln A/E	a.10 <sup>4</sup>	b	ln A	Ti(K)	S <sub>p</sub> =ln A/E	a.10 <sup>4</sup>	b	ln A	Ti(K)	S <sub>p</sub> =ln A/E
A	3.7	0.3	28	589	4.9										
B	3.5	1.2	58	614	5.1	3.0	0.4	15	720	5.0					
C	3.2	0.5	34	664	5.5	2.9	0.5	11	735	6.0					
1	3.6	0.1	52	597	4.9	3.0	-0.7	6.3	704	5.3	2.8	-0.7	6.2	776	6.4
2	3.6	1.3	70	599	5.0	3.5	-0.1	27.4	620	5.1	2.8	-0.7	5.9	772	6.4
3	3.6	0.08	41	610	5.07	3.4	-0.07	44.6	638	5.0	2.9	0.2	8.6	743	6.2

a,b- compensation parameters

Ti- isokinetic temperature °(K)

S<sub>p</sub>- compensation criterion

A- pre-exponential factor

The kinetic characteristics suggest the same mechanism of degradation, which consists in generation of micromolecules until 600°C, followed by a cross-linked process. The obtained structures are able to decompose at elevated temperatures (higher than 600 °C).

The compensation effect represents a kinetic law and the modifications of kinetic parameters are a function of the nature of micromolecules liberated from the system.

## CONCLUSION

- The thermostability depends on the micro-structure of polymeric chain; the presence of DHAB, independent of percent content, determines the same initial temperature of degradation and the increasing of number for compounds reduce the degradation rate.

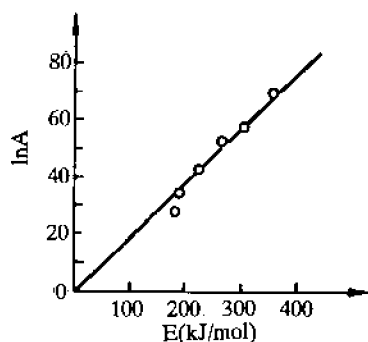


Fig.6

- The compensation effect is real depending on the mechanism of thermal degradation.

- The most recommended polymer for obtaining LC thermoset substances is the polymer based on DHD and BCMO; in case of other compounds with LC properties, it is recommended to carry out a short time for cross-linked process, or decrease the cross-linked temperature at 230-240 °C.

## REFERENCES

- Percec V., Nava H., and Rodriguez Parada J.M., *J. Polym. Sci., Polym. Lett. Edn.*, **22**, 523, (1984).
- Percec V., Nava H., and Jonson H., *J. Polym. Sci.: part A: Polym. Chem.*, **25**, 1943, (1987).
- Shaffer T.D., and percec V., *J. Polym. Sci.: part A: Polym. Chem.*, **25**, 2755, (1987).
- Schneider H.A., Stocker W., Korn N., Kricheldorf H.R., and Percec V., *Mol. Cryst. Liq. Cryst.*, **57**, 196, (1991).
- Sato T., Teramoto A., Weng D. and Green M.M., *Polym. Prep.*, **33**, 292, (1992).
- Hirschmann H., Meier W. and Finkelmann H., *Makromol. Chem., Rapid Commun.*, **13**, 385, (1992).
- Piercount S., Lacoudre N., Borgue Le A., Spassky N., Friedrich C. and Noel C., *Makromol. Chem.*, **193**, 705, (1992).
- Sze J.Y. and Gibson H.W., *Polym. Prep.*, **33**, 331, (1992).
- Aoki K., Seki T., Sakmagi M. and Ichimura K., *Makromol. Chem.*, **193**, 2163, (1992).
- Stebani J., Nuyken O., Lippert T. and Wokamm A., *Makromol. Chem., Rapid Commun.*, **14**, 365, (1993).
- Werth M. and Spiess H.W., *Makromol. Chem., Rapid Commun.*, **14**, 329, (1993).
- Borgue Le A., Trentin V., Zacoudre N. and Spassky N., *Polymer Bull.*, **30**, 1, (1993).
- Wan-Chung Lee, Dibenedetto A., Grourek I., Nobile M., Acierio D., *Polym. Eng. and Sci.*, **33**(3), 156, (1993).
- Wan-Chung Lee, Dibenedetto A., *Polym. Eng. and Sci.*, **32**, (6), 400, (1992).
- Isayev A., Suhrmanian P., *Polym. Eng. and Sci.*, **32**(2), 85, (1992).
- Mormann W., Irlé Ch., Zimmermann J., *Polym. Prep.*, **34**(2), 704, (1993).
- Robinson A., McNamee S., Freidzen Y., Ober C., *Polym. Prep.*, **34**(2), 743, (1993).
- Yang Y., Kloczkowski A., Mark J., Erman B., Bahar I., *Polym. prep.*, **34**(2), 729, (1993).
- Cada L.G., Chien L. C., *Polym. Prep.*, **34**(2), 700, (1993).
- Hurdac N., Bulacovschi V. and Simionescu C.I., *Eur. Polym. J.*, **28**, 791, (1992).
- Hurdac N., Surpateanu Gh. and Bulacovschi V., *Eur. Polym. J.*, **28**, 1589, (1992).
- Hurdac N., Bulacovschi V., Scutaru D., Barboiu V. and Simionescu C.I., *Eur. Polym. J.*, **29**, 1333, (1993).
- Hurdac N., Bulacovschi V. and Surpateanu Gh., *Polym. Bull.*, **30**, 69, (1993).
- Hurdac N., Bulacovschi V. and Simionescu C.I., *Polym. Bull.*, **29**, (1993).
- Unpublished data from our laboratory.
- Ionescu Dana, Hurdac N., Hurdac Natalia, *Polym. Bull.*, - submitted for publication.
- Freemann E.S. and Carroll B., *J. Phys. Chem.*, **62**, 394, (1958).
- Nicolaev A.V., Logvinenko V.A., *J. Therm. Anal.*, **10**, 363, (1976).
- Gorbachev V.M., *J. Therm. Anal.*, **8**, 585, (1975).
- Somaskharan K.N. and Kalpagam V., *J. Therm. Anal.*, **32**, 1471, (1987).
- Bulacovschi V., Hurdac N., Scutaru D. and Simionescu C.I., *Ukrainian Polymer Journal*, **1**, 282, (1992).
- Bulacovschi V., Hurdac N., Scutaru D. and Simionescu C.I., *Journal of the Indian Chemical Society*-in press.