PHASE TRANSFER CATALYSIS IN POLYCONDENSATION PROCESSES
XVIII. Thermal properties and molecular simulation of some polyethers containing oxetane rings in the main chain

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Abstract

A study was made of the influence of the chemical structure of the chains on the thermal stability of a series of copolyethers obtained from 3,3-bis(chloromethyl)oxetane and various bisphenols: 4,4'-dihydroxyazobenzene, 4,4'-dihydroxydiphenyl, 4,4'-thiodiphenol, 1,1-bis(4-hydroxyphenyl)ethane and 4,4'-dihydroxydiphenylsulfone. For a better correlation between chemical structure and thermal stability, molecular simulations were performed, using the HYPERCHEM (version 4.5) program. The lowest thermal stability was exhibited by the polymers that contain azobenzene units. The best thermal stability was that of the polyethers containing thiodiphenyl and 1,1-bis(phenyl)ethane units.

Keywords: copolyethers, molecular simulation, oxetane, phase transfer catalysis, thermal stability

Introduction

A series of previous papers discussed the possibility of obtaining polyethers from 3,3-bis(chloromethyl)oxetane [BCMO] and various bisphenols by the application of phase transfer catalysis as a working method [1–4].

In the case of polyethers with liquid crystalline [LC] properties, the presence of the oxetane ring in the chain raised problems relating to mesophase characterization [2, 5, 6]. Such problems are caused by the limit of thermal stability, situated at around 270–300°C.

On the other hand, the presence of the oxetane ring in the chain also results in certain advantages. Thus, at 160°C, the oxetane ring may be opened under the action of an amine, which permits chemical modification of the chain [7]. When diamines are employed, crosslinking materials possessing non-linear optical properties may be obtained [8].

When the above considerations are taken into account, study of the thermal stabilities of the synthesized polyethers is clearly very important in order to determine the thermal domains in which the polymers may be used. The present study follows the influence of the chemical structure of the chain on the thermal stabilities of a se-

ries of copolyethers obtained from BCMO and five types of bisphenols: 4,4'-dihy-droxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD), 4,4'-thiodiphenol (TDP), 1,1-bis-(4-hydroxyphenyl)ethane (HPE) and 4,4'-dihydroxydiphenyl sulfone (DDS).

For a better correlation between the chemical structure of the chain and the thermal stability, molecular simulations were performed. Molecular simulations permit a better understanding of the chemical processes at both molecular and atomic levels, improve the characterization of polymers, assist in the design of new polymers and allow prediction of their properties in difficult conditions, such as temperature and pressure. The study analyzed the surface polar area and chain geometry, known to influence the ordering capacity and the thermal properties, too.

Experimental

The copolymers were synthesized by phase transfer catalysis, using BCMO and various bisphenols (DHAB, DHD, TDP, HPE and DDS). Details concerning the synthesis and characterization of the polymers were reported previously [1–3].

The solvents and the phase transfer catalyst (tetrabutylammonium bromide) were supplied by Aldrich and were used without further purification.

The compositions of the copolymers were determined by ^{1}H-NMR spectroscopy with a JEOL 60 MHz device (in CDCl$_3$ or DMSO).

The thermoanalytical curves were recorded on a MOM (Budapest) derivatograph (heating rate 13.7°C min^{-1}; temperature domain 20–1000°C).

For molecular simulation, the force-field program HYPERCHEM (version 4.5) was used [9].

Results and discussion

The copolymers were synthesized according to the following reaction scheme:
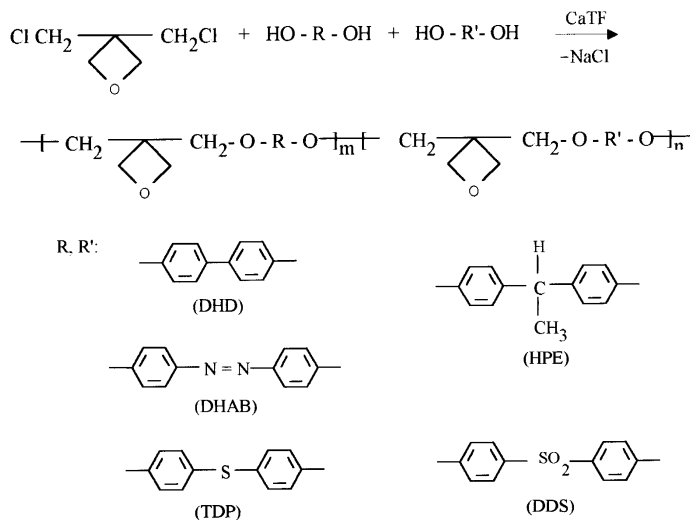
Table 1 presents the compositions of the copolymers corresponding to the synthesized polyethers. In consequence of the synthesis conditions, the molecular weights of the polyethers were low (8000–9200).

Table 1 Copolymer compositions of synthesized polyethers

Sample no.	Type of bisphenol	Copolymer composition
1	DHD/TDP	2.8:1
2	DHD/TDP	1:1.1
3	DHD/TDP	1:3
4	DHAB/TDP	2.9:1
5	DHAB/TDP	1:1.2
6	DHAB/TDP	1:3.1
7	HPE/DDS	2.8:1
8	HPE/DDS	1:1
9	HPE/DDS	1:2.9
10	DHAB/DDS	2.1:1
11	DHAB/DDS	1:1.1

The molecular simulations were performed by using chain segments with DP=4 (in order to estimate polar area) and DP=8 (for the conformation of the chains), which permit modification of the compositions of the copolymers in agreement with the experimental results (three ratios of bisphenols were used: 3:1, 1:1 and 1:3). In order to obtain the chain geometry of minimum energy, a force-field (MM+) program was used (convergence criterion 0.01 kcal $\mathring{A}^{-1}$ mol^{-1}). The total and polar surface areas were calculated with the 'Quantitative structure-property relations' (QSPRs) module. Table 2 lists some geometrical and electrical parameters of the tetramers.

The thermal stability studies were performed under dynamic conditions of temperature, by applying thermogravimetry, derivative thermogravimetry and differential thermal analysis, the same operational parameters being used in order to obtain comparable results (an atmosphere of air under static conditions, a quartz capsule, aluminium oxide as reference, sample mass 50 mg, heating rate 13.7^{o}C min^{-1}). Kinetic calculations were carried out with the differential Freeman-Carroll [10] and integral Reich-Lewi [11] methods.

The DTA and DTG curves plotted in Fig. 1 suggest a degradation process in two steps, the first up to 600°C, and the second between 600 and 1000°C.

The second degradation step displays the same characteristic for all polymers: a constant mass loss; the thermal characteristics are presented in Table 3.

With reference to their LC properties, the most interesting polymers are those containing an excess of DHAB relative to the other bisphenol. Unfortunately, it is

these structures that exhibit the lowest thermostability (samples 4–6 and 10–11). For samples 4–6, initiation of the degradation process can be observed below 335°C. However, mention should be made of a mass loss of only 30%, as compared with other samples having no azo groups.

Table 2 Geometric and electric properties of synthesized polymers

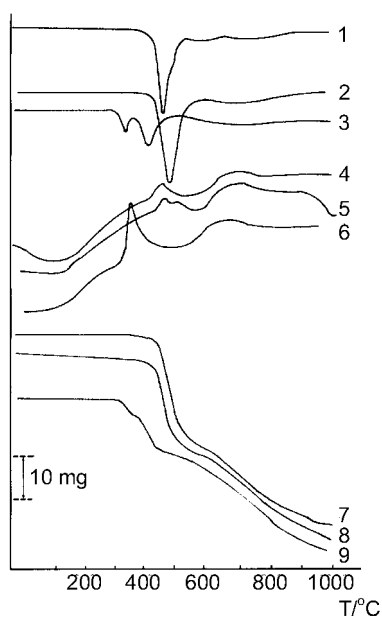| Sample no.	Total surface area/Å^2	Polar surface area/Å^2	Tetramer length/Å
1	1718	121.0 (7.0%)	57
2	1772	151.2(9.3%)	58
3	1731	208.6(12.0%)	58
4	1839	160.8(8.7%)	62
5	1870	183.3(9.8%)	64
6	1827	195.2(10.7%)	62
7	1884	161.2(8.5%)	57
8	1885	227.0(12.0%)	57
9	1884	314.7(16.0%)	57
10	1860	194.7(10.5%)	62
11	1902	250.6(13.2%)	64

Fig. 1 DTG(1–3), DTA(4–6) and TG(7–9) curves corresponding to samples: 1 – curves 1, 4 and 8; 9 – curves 2, 5 and 7; 11 – curves 3, 6 and 9

**Table 3** Thermogravimetric characteristics of synthesized polyethers

Sample no.	$\Delta T^{I}/^{\circ}C$	$w^{I}/\%$	$\Delta T^{II}/^{\circ}C$	$w^{II}/\%$	$T_{\alpha=0.05}$
1	360–550	48	550–900	52	420
2	370–480	50	490–960	50	400
3	340–520	50	520–950	50	400
4	335–420	15	430–980	85	420
5	330–500	29	500–950	71	380
6	320–470	31	470–980	69	400
7	340–500	40	500–900	60	360
8	350–500	49	500–940	51	420
9	400–550	56	550–940	44	420
10	320–390 390–490	27	490–1000	73	350
11	320–390 390–480	29	490–1000	71	360

I – first step of degradation
II – second step of degradation

Another observation is that the introduction of polar groups into the molecular chain increases the thermal stability (samples 10 and 11), from the aspect of the activation energies (Table 4). This observation is in agreement with conformational analyses, which reflect an increase of the polar surfaces for samples 10 and 11 (Table 2), the chain geometries being the same for samples 4–6 (Fig. 2). For this class of polymers, the dipole–dipole interactions represent the most intense physical forces. It may therefore be expected that they will play an essential role in the supramolecular ordering and implicitly in the thermal stability of the studied polymers.

Figure 2 presents the geometry of the macromolecular chains corresponding to samples 5 and 11.

Structure 5

Structure 11
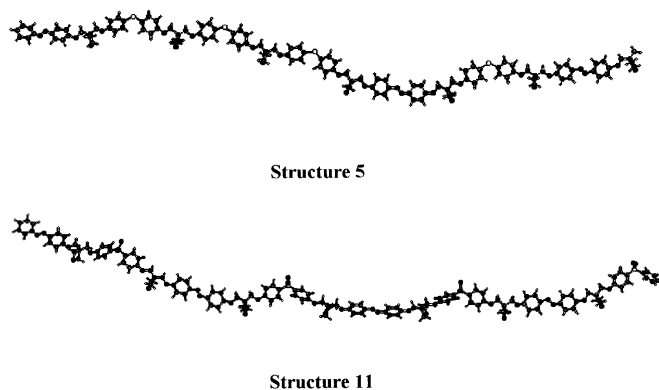
Fig. 2 Chain geometry corresponding to samples 5 and 11
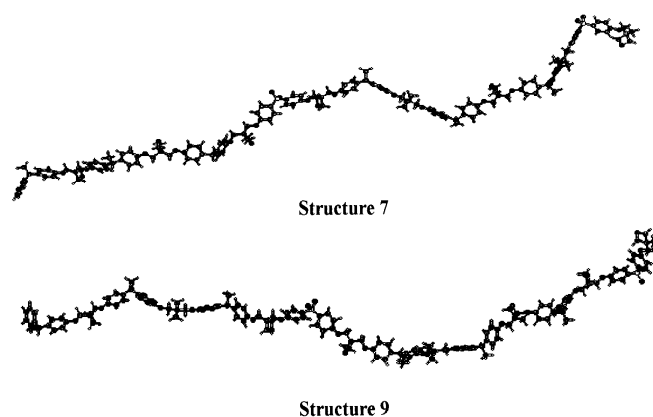
Structure 7

Structure 9

Fig. 3 Chain geometry corresponding to samples 7 and 9

Samples 7–9 form the most representative group reflecting the correlation between the dipole–dipole interactions and the thermal stability. In this group, the geometry of the bisphenols and hence of the macromolecular chains is similar, whatever the composition of the copolymer. Figure 3 depicts the chain geometries corre-

Table 4 Kinetic criteria concerning the characterization of thermal stability

Sample no.	First step of degradation			Second step
	FC $\ln A$	FC E_a/kcal mol^{-1}	RL E_a/kcal mol^{-1}	RL E_a/kcal mol^{-1}
1	39.5	200	200	50
2	49.50	248	248	50
3	35.14	172	160	50
4	–	–	80	50
5	20.36	90	120	50
6	–	–	90	50
7	35.47	180	160	50
8	38.22	190	200	50
9	50.05	274	250	50
10	21.29; 33.84	88; 176	175	70
11	20.18; 32.39	80; 164	170	70

FC – Freeman and Carroll method
RL 0150 Reich and Lewi method extrapolated to $\alpha=0$
E_a – activation energy of thermal degradation process

sponding to samples 7 and 9. However, the length of the molecular chains corresponding to samples 7–9 is the same (Table 2).

As a consequence of the presence of the sulfone groups in the chains, the polar surface area is hardly modified by the composition of the copolymers. Thus, the polymer corresponding to sample 9 has double the polar area obtained for sample 7. Sample 9 exhibits the best thermal stability in this group. This thermal stability is confirmed by the temperature corresponding to a 5% loss in mass ($T_{\alpha=0.05}$), regarded as a criterion of stability. The activation energy of the degradation process too supports these observations (Table 4).

Table 4 presents the activation energies of the degradation processes corresponding to the synthesized polymers, calculated by the Freeman-Carroll and Reich-Lewi methods. For the Reich-Lewi method, the value extrapolated to $\alpha=0$ was used.

From this point of view, the polymers containing azo groups display the lowest thermal stability.

It is not still established whether the flexibility of the chains influences or not the thermal stability of these polyether groups. It is well known that increase in the rigidity of the chains induces better thermal stability. Since we used a rigid and a flexible bisphenol in the synthesis, samples 1, 4, 9 and 10 should exhibit the highest thermostability. This is true for samples 1, 4 and 9 (though for sample 9 the differences are not relevant), but it is not true for sample 10. Additional investigations employing two rigid bisphenols are still necessary for complete clarification of such aspects.

Conclusions

1. Of the investigated polymers, those containing DHAB units display the lowest thermal stability, although from the aspect of the LC properties these polymers are the more interesting.

2. The polymers containing HPE and DDS groups present the best thermal stability.

3. Conformational analysis can furnish useful information on the thermal properties of these polymers. For structures with comparable rigidities, a direct relation was evidenced between the polar surface area and the thermal stability. Additional studies are still necessary to find a better correlation between the chain geometry, polar interactions and thermal properties.

References

1 N. Hurduc, V. Bulacovschi and C. I. Simionescu, Eur. Polym. J., 28 (1992) 791.
2 N. Hurduc, V. Bulacovschi, D. Scutaru, V. Barboiu and C. I. Simionescu, Eur. Polym. J., 29 (1993) 1333.
3 N. Hurduc, D. Scutaru, V. Barboiu, D. Vizitiu, C. I. Simionescu, J. M. Buisine and A. Daoudi, J. Macromol. Sci.-Pure Appl. Chem., A33 (1996) 1745.
4 N. Hurduc, A. Daoudi, J. M. Buisine, P. Decock and Gh. Surpateanu, Eur. Polym. J., 33 (1997) 187.
5 N. Hurduc, A. Stoleru, D. Pavel and C. I. Simionescu, J. Thermal Anal., 47 (1996) 735.
6 A. Daoudi, J. M. Buisine, N. Hurduc and C. I. Simionescu, J. Macromol. Sci.-Pure Appl. Chem.-A35 (1998) 151.

7 N. Hurduc, J. M. Buisine, P. Decock, J. Talewee and Gh. Surpateanu, Polym. J., 28 (1996) 550.
8 Ying-Ling Liu, Ging-Ho Hsiue, Yie-Shun Chin and Ru-Yong Jeng, J. Polym. Sci. Part A: Polym. Chem., 32 (1994) 3201.
9 HyperChem 4.5, Hyperchem Computational Chemistry, Autodesk Inc.
10 L. Reich and D. W. Lewi, Macromol. Chem., 66 (1963) 102.
11 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.