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Thermodegradable polycarbonates: Effect of substituents on the degradation temperature

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Abstract: The thermal degradation process of some new polycarbonates is investigated from an experimental and theoretical point of view, in order to obtain insight into the microscopic aspects that influence the reaction mechanism and the process of thermolysis. In particular, attention is focussed on the influence of the type of substituents in the polymer chain on the degradation temperature. A series of novel polycarbonates were designed differing from each other by the groups attached at the α and β carbon atoms. Thermal behavior was characterized by thermogravimetrical analyses. The polymers undergo rapid and complete thermolysis at different degradation temperatures depending on the structure. The degradation products were separated by gas chromatography and analyzed by mass spectroscopy. The ratio of formed dienes in the product distribution depends on the heating rate. Furthermore, density functional theory calculations were performed on a series of model compound systems for the polycarbonates under study, in particular carbonate systems differing by the groups attached at the α and β carbons. The study proves that the thermal degradation route can be controlled by tailoring the polymer backbone structure. Moreover, *ab initio* calculations provide further insight into the microscopic ingredients that govern the degradation process and associated reaction rates.

Introduction

Currently there is a lot of interest in new polymeric materials the properties of which can be modified by heating or high-energy radiation [1]. As an example, thermally degradable polymers are very promising for the design of dry imaging systems such as printing plates. Recently, there is a tendency to use infrared laser technology to write information digitally on a printing plate instead of the formerly used techniques based on UV light sources in combination with photo-masks [2]. The new technique has a lot of advantages such as elimination of multi-step processing including photo-masks, the ability to work under daylight conditions, the absence of toxic solvents, etc.

Thermally or photochemically labile polycarbonates, which undergo drastic changes in properties when exposed to heat or radiation, have interesting potential applications [3-7]. As an example, aromatic polycarbonates are used on large scale for the production of CDs. The thermal properties of several aliphatic and aromatic poly-

carbonates [8-17] have been studied using various techniques such as differential scanning calorimetry (DSC), powder X-ray analyses at various temperatures and thermogravimetrical analyses (TGA). The main purpose of this paper is to study the thermal degradation route of some new polycarbonates with the main objective of understanding how the thermal degradation temperature can be controlled by tailoring the chemical structure of the polymer backbone.

Therefore, it is essential to have a fundamental understanding of the reaction mechanism controlling the decomposition process. Thermolytic cleavage is known to proceed by β-H elimination [18-22] or *syn*-elimination, as generally depicted in Fig. 1. This process, known as internal elimination (E_i), is generally believed to be a single step mechanism with a cyclic transition structure, as first proposed by Hurd and Blunck [19]. The detailed mechanism of these reactions and in particular the role and nature of substituents attached to the characteristic six-membered ring of the transition state was so far not completely understood.

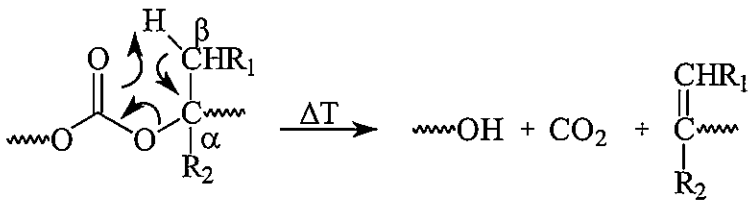

Fig. 1. Illustration of *syn*-elimination

The thermal degradability, characterized by the degradation temperature, can be experimentally determined by TGA. This technique is a valuable tool to detect the degradation temperature of polycarbonates since at degradation carbon dioxide is formed, which leads to a detectable weight loss. Other experimental techniques such as DSC are less suited since the degradation process of polycarbonates can be complicated by further decomposition of already formed degradation products.

In the Exptl. part, the preparation of a number of new designed polycarbonates with various substituents attached to the polymer chain is described. Thermal behavior was investigated by determining the degradation temperatures. Polycarbonates were prepared using a solid-liquid phase-transfer catalyzed polycondensation. The polycarbonates had a rather moderate molecular weight, but this was no obstacle to study the relation between chemical structure and thermal degradation. The products formed during thermal degradation were separated by gas chromatography (GC) and subsequently analyzed by mass spectroscopy (MS). At degradation, a mixture of various dienes can be formed, whereby the ratio depends on the heating rate.

In the theoretical part, the degradation mechanism of some model compound systems is studied which are representative of the polycarbonates. *Ab initio* density functional theory (DFT) calculations were performed on a series of carbonate systems differing by the groups attached at the α and β carbon atoms. Such calculations give further insight into mechanistic aspects such as the concerted nature of E_i elimination reactions and the kinematic details of the degradation process. Moreover, a good correlation is found between the experimentally derived degradation temperatures and the theoretically predicted reaction rates.

Results and discussion

1. Thermal properties of the polycarbonates

The degradation of polycarbonates containing a β-hydrogen atom has been documented before by Fréchet [3-6]. The degradation reaction proceeds by the cleavage of the C_α–O and the C_β–H bond, leading to the formation of dienes, diols and carbon dioxide.

One objective of this paper is to understand how the thermal degradation properties can be influenced by varying the substituents at α and β position in the polymer backbone. For that purpose, the thermal degradation temperatures for a series of novel polycarbonates were determined experimentally.

1.1. Synthesis of model polycarbonates

Polycarbonates were prepared starting from a diol and either carbonyldiimidazol or diethyl carbonate. A 1,4-diol was selected as building block for the polycondensation reaction [23-26], rather than a 1,2- or 1,3-diol [27]. The latter can undergo a competitive ring-closure reaction with formation of a five- or six-membered cyclic carbonate. Three commercially available 1,4-diols were selected: 1,4-butanediol (BD), 2,5-hexanediol (HD), and 2,5-dimethyl-2,5-hexanediol (DD).

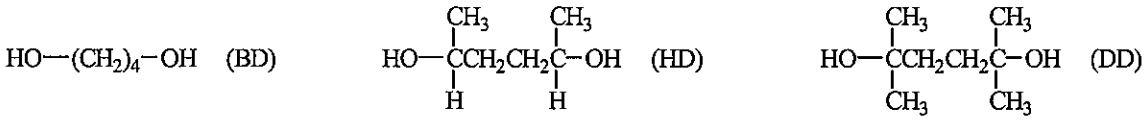

Fig. 2. Selected commercially available 1,4-diols

The polycarbonate based on 1,4-butanediol was synthesized in high yield by transesterification using diethyl carbonate in the presence of potassium tert-butoxide as catalysist.

Carbonate esters of alcohols can be prepared in good yield by reaction with phosgene or carbonyldiimidazol as described by Staab [28]. An approach described before by Fréchet [29] was used to prepare polycarbonates of 2,5-hexanediol (polymer II) and 2,5-dimethyl-2,5-hexanediol (polymer III) via a two-steps procedure (Fig. 3).

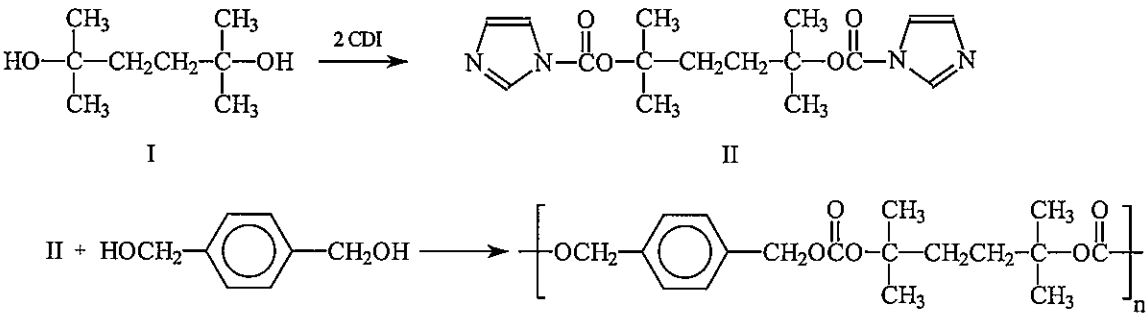

Fig. 3. Synthesis of polycarbonates using carbonyldiimidazol

In a first step, the diol was converted to a bis(carbonylimidazol) intermediate. Subsequently, the intermediate was treated with 1,4-benzenedimethanol using a basic catalyst, powdered anhydrous potassium carbonate and 18-crown-6-ether, to form the linear copolycarbonate.

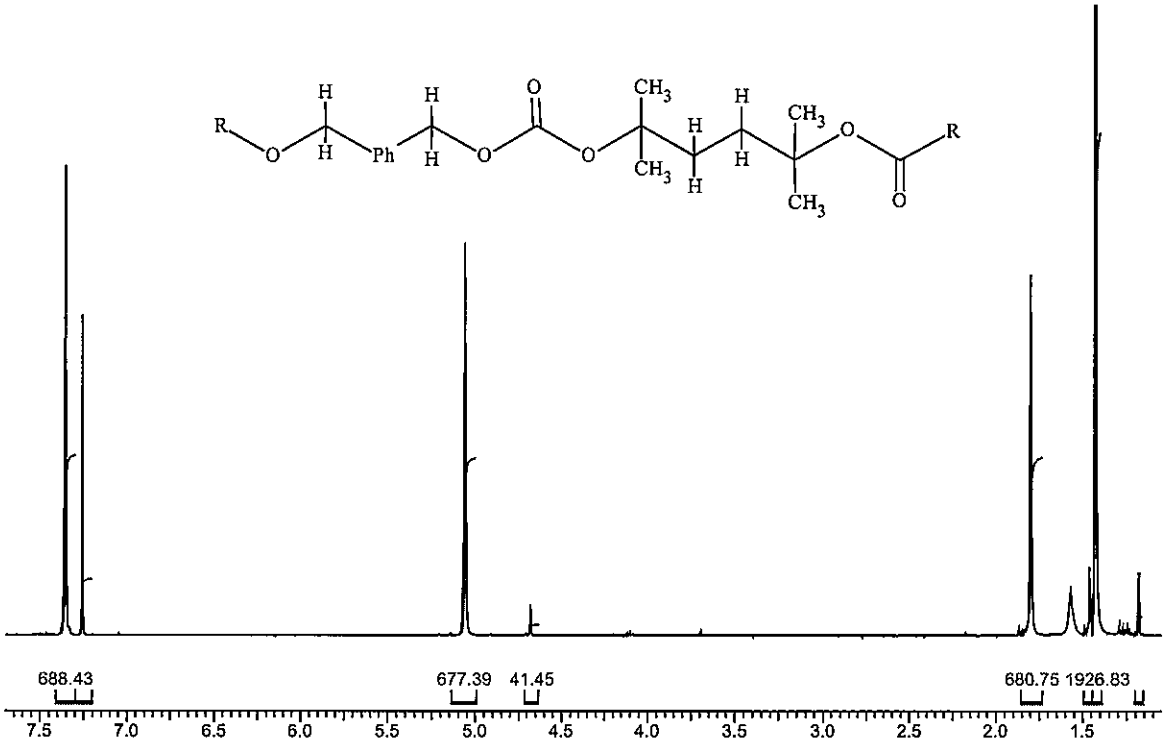

Fig. 4. ^{1}H NMR spectrum (in $CDCl_3$) of polycarbonate III based on 2,5-dimethyl-2,5-hexanediol; δ = 7.4 (aromatic protons, 4H); 5.1 (Ph$\underline{CH_2}$OC(O)O-, 4H); 4.7 (Ph$\underline{CH_2}$OH end group); 1.8 (-$\underline{CH_2CH_2}$-, 4H); 1.4 ($\underline{CH_3}$, 12H)); the structure shown in the NMR spectrum is a repeating unit of the polymer

The signal at δ = 5.1 in Fig. 4 clearly shows the presence of a carbonate structure in the obtained product. The absence of imidazol resonance peaks proves that the obtained polymer is purified. Finally, the signal at δ = 4.7 indicates one of the two possible end groups of the polymer. The other one cannot be observed in the ^{1}H NMR spectrum.

1.2. Thermogravimetric analysis of the polycarbonates

The TGA curves in Fig. 6 and the degradation temperatures in Tab. 1 confirm that this temperature is largely influenced by the substituents in α and/or β position. The polycarbonate based on 1,4-butanediol, characterized by a degradation temperature of 340°C [30], is included as the reference material.

The process of *syn*-elimination is known to proceed via a cyclic transition state. The results indicate that the mechanism is not fully concerted, but also has a partial ionic character, in which a partially positive and negative charge is formed on the C_α and C_β atom, respectively. This is also confirmed by theoretical calculations [36]. Introduction of alkyl substituents on the α-carbon atom decrease the degradation temperature due to delocalization and thus stabilization of the partial positive character of

the C_α atom in the transition state (hyperconjugation or inductive stabilization [31]). This effect is more pronounced when increasing the number of alkyl substituents on the C_α atom as evidenced for the following series: 1,4-butanediol, 2,5-hexanediol, and 2,5-dimethyl-2,5-hexanediol.

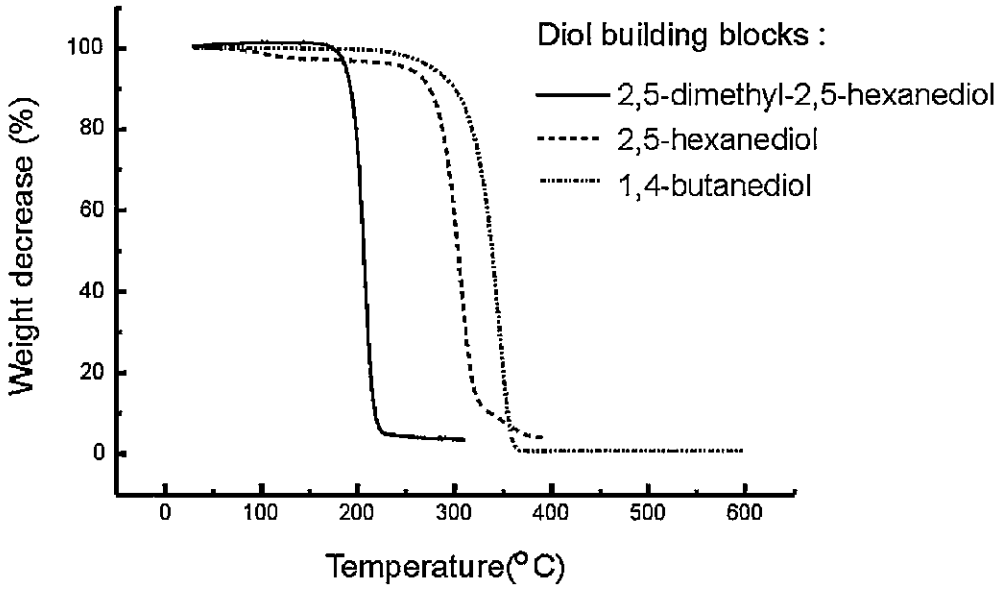

Fig. 5. TGA of polycarbonates

Tab. 1. Properties of co-polycarbonates and GC-MS analysis of thermolysis products

Polymer	M_w [a]	d [a]	T_d [b] in °C	Diene fragments	Characteristic peaks (m/e) [c]
I	6600	1.4	340	$CH_2=CHCH=CH_2$ Ia	72, 71, 57, 42
II	3550	1.7	300	$CH_2=CHCH_2CH_2CH=CH_2$ IIa	100, 85, 67, 56
				$CH_2=CHCH_2CH=CHCH_3$ IIb	100, 85, 67, 56
				$CH_3CH=CHCH=CHCH_3$ IIc	84, 67, 51, 39
III	7400	1.4	200	$(CH_3)_2C=CHCH=C(CH_3)_2$ IIIa	110, 95, 67, 55
				$CH_2=C(CH_3)CH_2CH=C(CH_3)_2$ IIIb	110, 95, 67, 55
				$CH_2=C(CH_3)CH_2CH_2C(CH_3)=CH_2$ IIIc	110, 95, 67, 55

[a] Via GPC, $d = M_w/M_n$. [b] Thermal degradation temperature defined as the maximum of the first derivative of weight loss (data not shown); heating rate 10°C/min. [c] Benzenedimethanol not detected, degradation products could remain on the Tenax® column.

The sharp and quantitative decrease in weight of the polymers at their degradation temperature indicates that degradation occurs almost simultaneously for all carbon-

ate units present in the polymer chain. It is know from literature [32] that thermal degradation of polycarbonates can proceed by a backbiting mechanism. This occurs if the degradation products are stable five- or six-membered rings. In this work, 1,4-diols were selected to avoid this cyclization mechanism during synthesis. The backbiting mechanism of these polymers would lead to the formation of unstable seven-membered ring structures. The degradation mechanism that occurs is only determined by the chemically active area of one carbonate unit and unaltered by its further chemical environment. This result is confirmed by the unaltered TGA curves of one type of polycarbonates with various molecular weights.

1.3. Analysis of the products of thermolysis

Interesting information about the decomposition mechanism can be obtained by mass spectral analysis of the degradation products. Therefore, polymers I, II, III (cf. Tab. 1) were heated until decomposition and the degradation products were captured on a Tenax® column [33]. The products were separated by gas chromatography and analyzed by mass spectrometry [34] (TGA-GC-MS). The polycarbonate derived from 2,5-dimethyl-2,5-hexanediol, and three diene dehydration products, viz. 2,5-dimethyl-2,4-hexanediene (IIIa), 2,5-dimethyl-1,4-hexanediene (IIIb) and 2,5-dimethyl-2,5-hexanediene (IIIc), were obtained in varying amounts (Fig. 6).

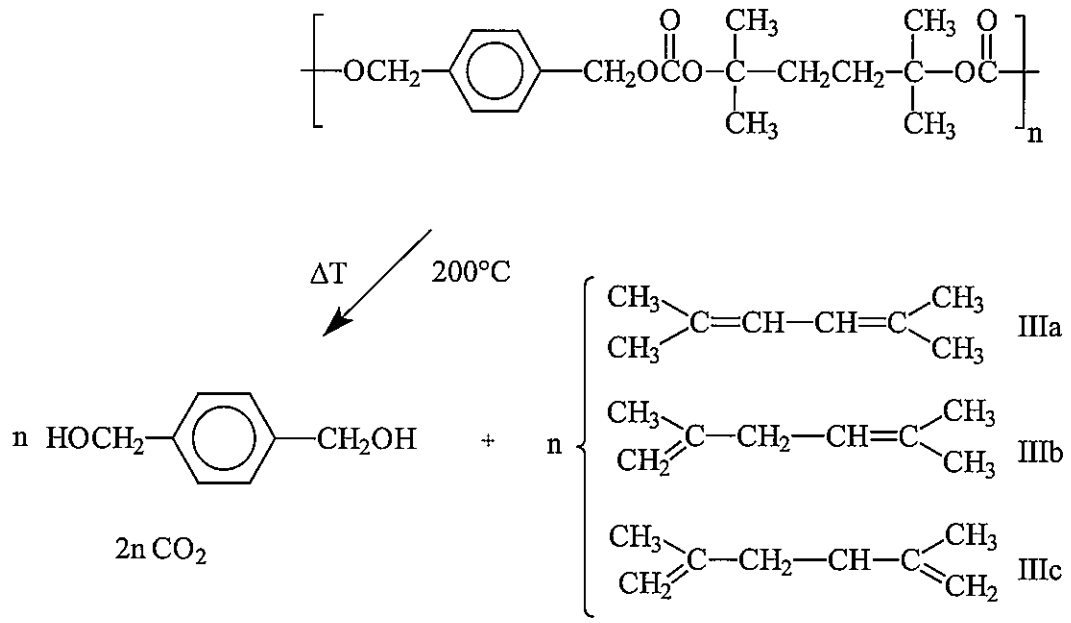

Fig. 6. Degradation products of polymer III

Degradation of the polycarbonate derived from 2,5-hexanediol results in the formation of three diene dehydration products, viz. 1,5-hexanediene (IIa), 1,4-hexanediene (IIb) and 2,4-hexanediene (IIc) in varying amounts. Finally, for the polycarbonate derived from 1,4-butanediol only one diene dehydration product is obtained, viz. 1,3-butanediene.

TGA-GC-MS results and the observation of a rapid and complete thermolysis indicate that the synthesized polycarbonates degrade by *syn*-elimination only. The ratio of the dienes in the product distribution can be calculated by calibration of the gas chroma-

tograms using commercially available dienes. Some interesting features about the thermolysis process can be obtained by studying the ratio of dienes in terms of the heating rate.

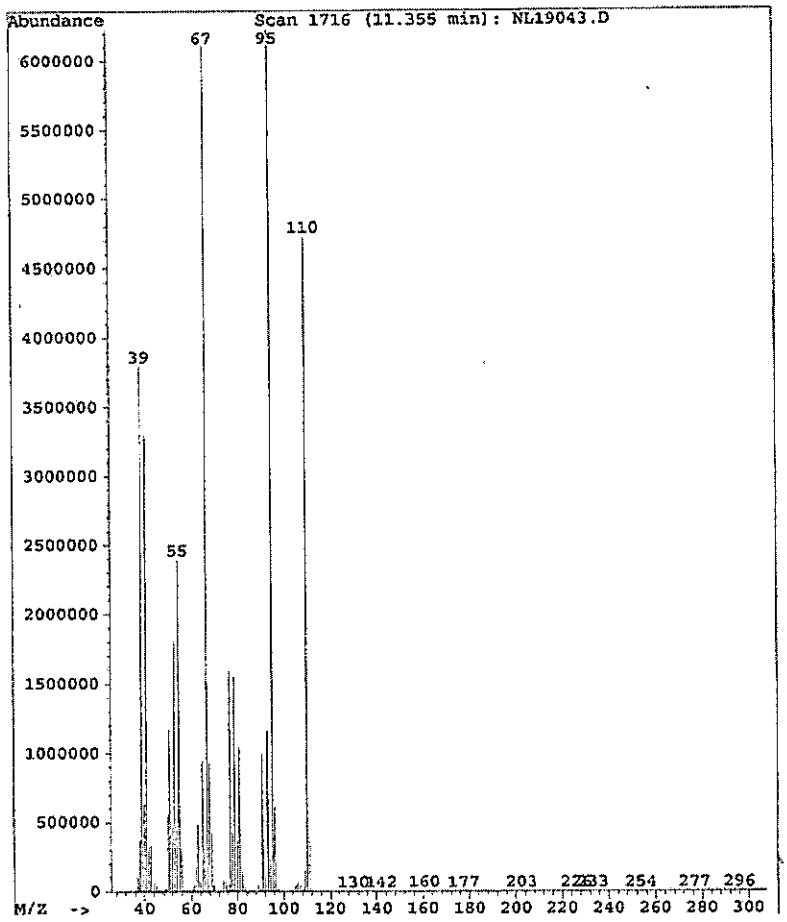

Fig. 7. Mass spectrum of polymer III

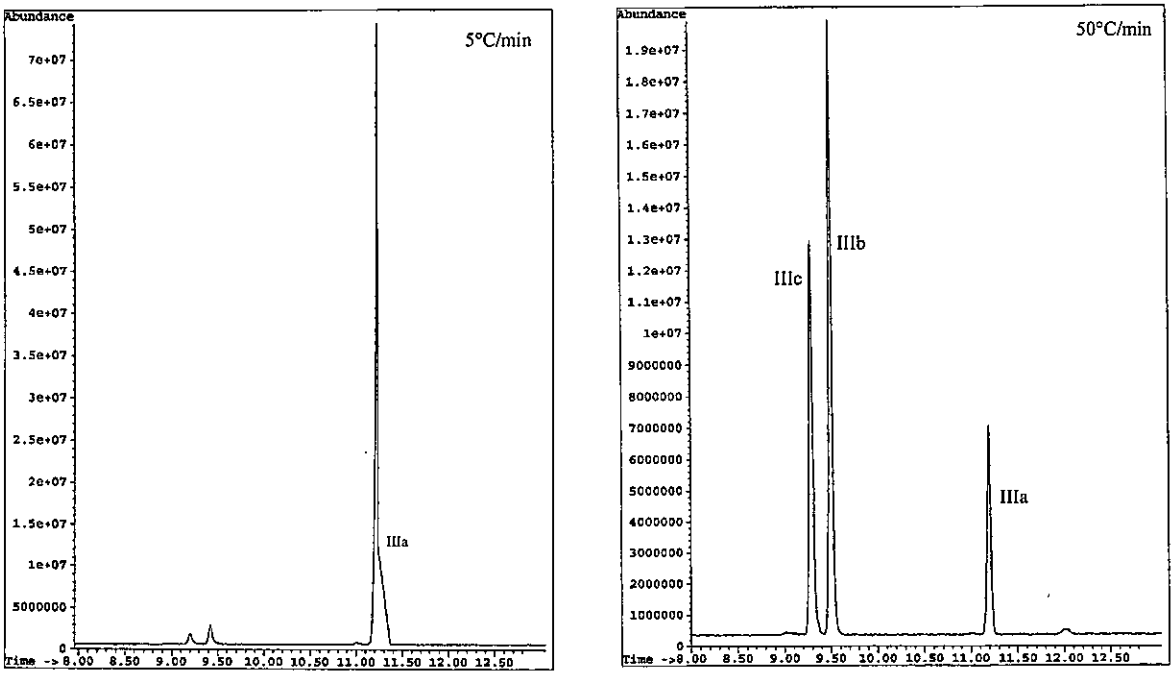

Fig. 8. Concentration of degradation products as a function of heating rate (e.g., yield of diene IIIa as a function of heating rate: 94% at 5°C/min, 18% at 50°C/min)

This aspect was investigated in more detail for the polymer derived from 2,5-dimethyl-2,5-hexanediol. Increasing the heating rate from 5°C/min to 50°C/min, the amount of the conjugated diene IIIa decreased from 94% to 18%. For polymer III, β-elimination can occur either by abstraction of a hydrogen atom from the side group (twelve available in each carbonate unit) or from the main chain (four available in each carbonate unit).

When the heating rate is low, the more stable product IIIa is formed in high yield, since the polymer can rearrange and induce E_i elimination from the main chain (thermodynamic reaction). When increasing the heating rate, *syn*-elimination from the side chain is preferred since more hydrogen atoms are available for this type of reaction. At high heating rates the process is kinetically controlled, yielding the less stable diene (IIIc). This is reflected in the degradation temperature of the poly-carbonate. Increasing the heating rate results in a higher degradation temperature, raising from 188°C at 5°C/min to 224°C at 100°C/min.

2. Theoretical ab initio calculations on carbonates

In addition, theoretical *ab initio* calculations were performed on some model carbonates which are representative of the chemically active area of the poly-carbonate to obtain more microscopic insight into the mechanistic and kinetic details of the degradation route. Due to increasing computer capabilities in recent years, it is now possible to study chemical systems of industrial importance by theoretical molecular modeling techniques. *Ab initio* density functional theory (DFT) calculations [35] at the B3LYP/6-311G** level were performed on a set of carbonates, differing from each other by the groups R_1 and R_2 attached at the α and β carbon atoms, as shown in Fig. 9. These results enable us to determine kinetic parameters which are, in this case of extremely volatile degradation products, also a qualitative measure for degradation temperatures. The details of the calculations have been discussed before [36]. Only those results are given which are needed to correlate the thermal degradation temperatures with theoretically predicted kinetic parameters. A first product, methyl ethyl carbonate having no substituents on the α and β carbon atoms is chosen as the reference. The other model compounds are obtained by substituting groups R_1 and R_2 (Fig. 1) by:

(i) two hydrogen atoms: methyl 1-methylpropyl carbonate (KI)

(ii) hydrogen atom and methyl group: methyl 1,1'-dimethylpropyl carbonate (KII)

(iii) phenyl group and hydrogen atom: methyl 1-benzylpropyl carbonate (KIII)

(iv) hydrogen atom and phenyl group: methyl (1,1'-methylphenyl)propyl carbonate (KIV)

(v) methyl group and phenyl group: methyl (1,1'-ethylphenyl)propyl carbonate (KV)

The designed carbonates are expected to undergo thermolysis to yield an olefinic species together with the volatile species carbon dioxide and methanol. For some carbonates, *syn*-elimination can occur at different places of the molecule, leading to a mixture of olefins. In this work, only E_i elimination from the side chain is considered. A study of the relative importance of competitive pathways, cf. section 1.3., on the thermal degradation process is in progress [37]. It is anticipated that this study will enable us to better understand the complexity of the thermal behavior of the polymer materials in terms of the heating rates.

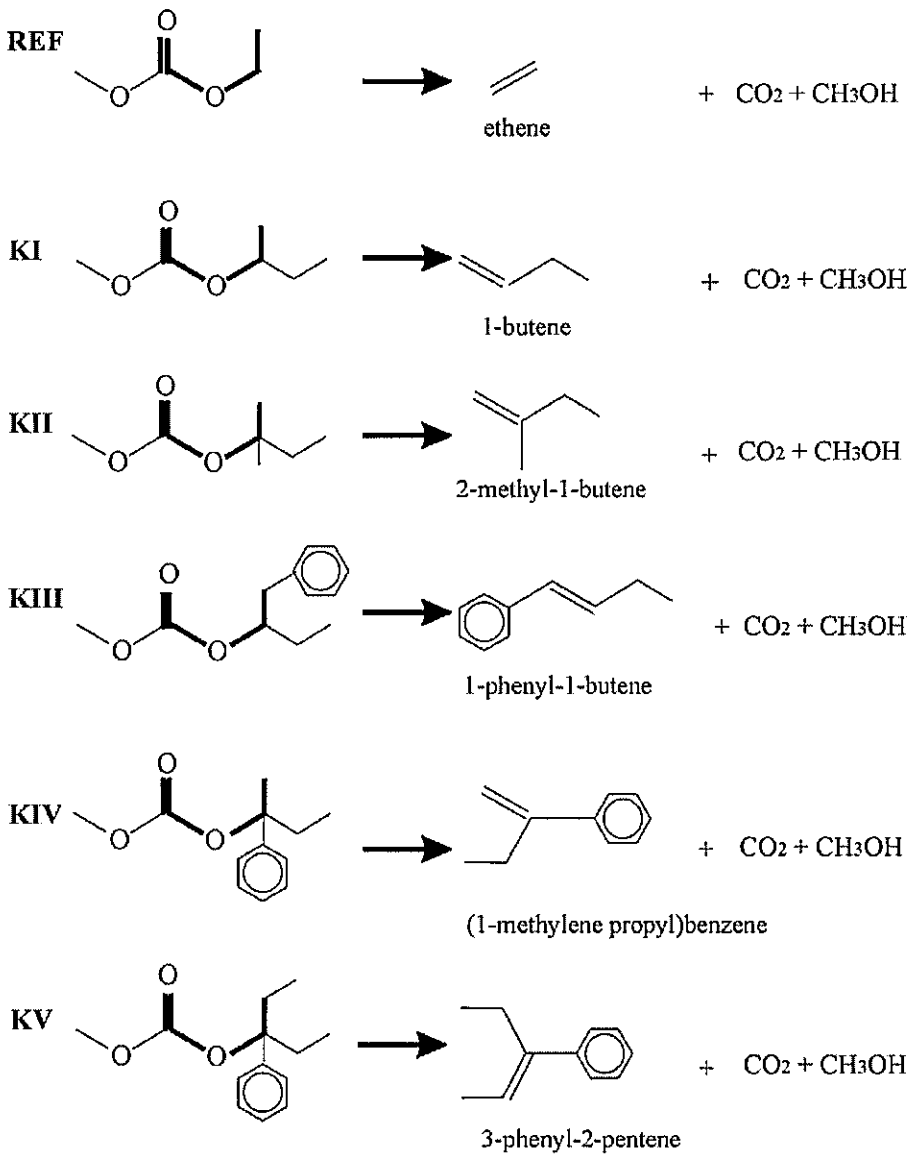

Fig. 9. Representation of β-eliminations

A conformational analysis of reactants, products and transition states reveals information on the mechanistic details of the reaction. The geometries of the transition states confirm that the *syn*-elimination reaction proceeds by a six-membered activated complex in which a partial positive charge is formed on the C_α atom. It can be proven that in the transition state, the C_α-O bond is relatively more extended, developing some carbocation character on the C_α atom [36], followed by abstraction of the β-hydrogen atom.

For all compounds, kinetic parameters are calculated for the E_i elimination reaction by means of transition state theory (TST) [38]. To explain the effects of substituents on the reaction rates, we mainly concentrate on the activation energies, since the pre-exponential factors are more sensitive to the approximations made in the *ab initio* calculations, as explained [37]. Comparison of the activation energies reveals the following trend for the reaction rates: REF < KI < KIII < KIV < KII < KV. This sequence indicates that the presence of alkyl groups and aromatic groups on the α carbon atom substantially decreases the activation energies. This can be explained

by the effect of inductive and resonance stabilization of the carbocation character of the C_α atom in the transition state. Placing alkyl groups and aromatic groups on the C_α atom also increases the reaction rates. It is found that the primary effect of substituents on the C_β atom is the remote stabilizing effect on the partial positive charge on C_α [38]. In this respect, calculations indicate that breakage of the C_α-O bond is the rate determining step.

Tab. 2. Kinetic parameters obtained from theoretical calculations on a set of carbonates. E_a is the activation energy while A is the pre-exponential factor as defined by the Arrhenius rate law $k(t) = A\, e^{-E_a/(RT)}$

Carbonate	E_a / (kJ·mol^{-1})	A / s^{-1}	T_d in °C	Polymer
REF	174.912	$1.5 \cdot 10^{13}$	340	I
KI	162.149	$2.4 \cdot 10^{13}$	300	II
KII	135.925	$6.1 \cdot 10^{13}$	200	III
KIII	154.483	$1.2 \cdot 10^{13}$		
KIV	138.985	$2.0 \cdot 10^{13}$		
KV	131.452	$1.9 \cdot 10^{13}$		

In addition, the theoretically predicted influence of substituents in the α and β position of carbonates agrees very well with the experimental findings for the degradation temperatures on corresponding polycarbonates (cf. Tab. 2). Lower activation energy for the carbonates induces a decrease of thermal stability for the corresponding polycarbonates.

These results show that calculations on small model systems which are representative of the chemically active area of the polycarbonate can provide additional microscopic information on the reaction mechanism. Such calculations can help the experimentalist, interested in designing new polymers with controlled thermal behavior, in understanding the microscopic factors that govern the degradation process.

Experimental part

Materials

1,1'-Carbonyldiimidazol (Merck), *p*-benzenedimethanol (Acros), diethyl carbonate (Acros), 18-crown-6 (Acros), 2,5-hexanediol (Fluka), and 2,5-dimethyl-2,5-hexanediol were used as received. 1,4-Butanediol (Aldrich) was purificied by destillation under reduced pressure over CaH_2. All solvents used in the reactions were dried prior to use.

Methods

The average molecular weights M_n and M_w of the copolymers were determined by gel permeation chromotography (GPC) on a PL-Gel Mixed D-5 7.8 x 600 mm column calibrated by polystyrene standards with chloroform as an eluent using a MELZ LCD-212 refractive index detector. ^{1}H NMR analyses were carried out on a Bruker AM 360

MHz instrument with tetramethylsilane as internal standard. IR measurements were recorded on a Perkin Elmer 1600 Series FT-IR spectrometer. Thermogravimetrical analysis was performed on a Hi-Res TGA-2950 apparatus of TA-instruments under nitrogen atmosphere.

Synthesis of the polycarbonates

Via transesterification

Synthesis of poly(oxycarbonyloxytetramethylene) (I): A solution of 1,4-butanediol (10 g, 0.11 mol), diethyl carbonate (13.11 g, 1 eq.) and tert-butoxide (2 mol-%) was gradually heated until 130°C, whereby ethanol was distillated from the reaction mixture. After 24 h, the mixture was stirred under reduced pressure (18 Torr) for another 24 h. The mixture was dissolved in dichloromethane and the organic layer was extracted with brine and $NaHCO_3$ solution and dried over $MgSO_4$. The product was isolated after precipitation in diethyl ether. The product was analyzed by ^1H NMR and IR.

^1H NMR (ppm, $CDCl_3$): $\delta = 4.5$ (m, 4 H); 3.65 (t, 4H); 1.75 (m, 4H); 1.6 (t, 4H).

IR: 3547, 2962, 1739, 1457, 1402, 1324, 1242, 1026, 904 cm^{-1}.

GPC: M_w = 6600 g/mol, d = 1.4.

Via polycondensation with carbonyldiimidazol

Synthesis of the bis(carbonylimidazolide) of a 1,4-diol

A solution of the 1,4-diol (1 eq.), dissolved in 10 w/v % dry THF, was treated with 0.025 eq. potassium metal under argon atmosphere. The reaction mixture was refluxed until all the potassium metal dissolved. The temperature was lowered to 30°C and the solution was transferred, under argon, into a flask containing a stirred suspension of 1,1'-carbonyldiimidazol (2 eq.) in 50 w/v % THF. After complete addition, the mixture was heated to 65°C for 1 h. Workup was done by adding ethyl acetate to the reaction mixture and extracting the resulting solution with distilled water. The organic layer was dried over anhydrous magnesium sulfate. The final product was obtained as a solid after evaporation of the solvent (yield 65 %). The product was analyzed by ^1H NMR and IR.

Bis(carbonylimidazolide) of 2,5-hexanediol

^1H NMR (ppm, $CDCl_3$): δ = 8.1 (s, 2 H); 7.4 (s, 2H); 7.1 (s, 2H); 5.2 (m, 2H); 1.8 (m, 4H); 1.4 (d, 6H).

IR: 3409, 2978, 1752, 1631, 1381, 1290 cm^{-1}.

Bis(carbonylimidazolide) of 2,5-dimethyl-2,5-hexanediol

^1H NMR (ppm, $CDCl_3$): $\delta = 8.1$ (s, 2 H); 7.4 (s, 2H); 7.1 (s, 2H); 1.6 (s, 12H).

IR: 3411, 3053, 2983, 1755, 1712, 1629, 1472, 1382, 1297, 1180, 1094, 1002, 837 cm^{-1}.

Synthesis of poly(oxycarbonyloxy-1,4-dimethyltetramethyleneoxycarbonyloxy-methylene-1,4-phenylenemethylene) (II)

A solution consisting the bis(carbonylimidazolide) of 2,5-hexanediol (1 eq.) in 50 w/v % dry CH_2Cl_2 was treated with 1.35 g (1 eq.) *p*-benzenedimethanol along with 1/15 eq. 18-crown-6-ether and 5 eq. of finely ground powdered anhydrous potassium carbonate. The reaction mixture was stirred for 24 h at 40°C under argon atmosphere. Workup was done by extraction of the organic layer with distilled water and a $NaHCO_3$ solution and drying with $MgSO_4$. The final product was obtained after evaporation of the solvent (yield 70 %).

^{1}H NMR (ppm, $CDCl_3$): δ = 7.4 (s, 4 H); 5.1 (s, 4H); 4.8 (m, 2H); 4.7 (s, 4H); 3.7 (m, 2H); 1.5 - 1.8 (m, 4H); 1.3 (m, 6H).

IR: 3408, 2972, 2934, 1740, 1654, 1454, 1458, 1381, 1268, 1129, 949 cm^{-1}.

GPC: M_w = 3550 g/mol, d = 1.7.

Synthesis of poly(oxycarbonyloxy-1,4-tetramethyltetramethyleneoxycarbonyloxy-methylene-1,4-phenylenemethylene) (III)

This polymer was prepared in analogy to the procedure described before for II.

^{1}H NMR (ppm, $CDCl_3$): δ = 7.4 (s, 4 H); 5.1 (s, 4H); 4.7 (s, 4H); 1.8 (s, 4H); 1.4 (s, 12H).

IR: 3408, 2970, 1738, 1519, 1475, 1450, 1380, 1370, 1258, 1205, 1160, 1086 cm^{-1}.

GPC: M_w = 7400 g/mol, d = 1.4.

Conclusions

In this paper, we succeeded in establishing a correlation between the thermal degradation temperature of polycarbonates and the nature of substituents attached to various points on the repeating unit of the polymer. The experimental results were confirmed by theoretical *ab initio* calculations. Experimentally, a TGA-GC-MS study on some novel polycarbonates was performed. The polycarbonates were synthesized using a solid-liquid phase-transfer-catalysed polycondensation in the presence of powdered potassium carbonate. The diols were converted to the corresponding bis(carbonylimidazolide) intermediate which was subsequently reacted with a second diol. The degradation temperature of the polycarbonates ranged between 100°C and 350°C and depended on the substituents at the C_α and C_β atoms. The degradation temperature decreased by the substitution of alkyl groups at the C_α atom. The degradation products were separated by gas chromatography and analysed by mass spectrometry. The ratio of the formed dienes depended on the heating rate. At higher heating rates, the thermolysis reaction was kinetically controlled, while at lower rates the reaction was controlled thermodynamically. This study clearly demonstrates that the degradation temperature of polycarbonates can be varied over a wide range by proper selection of the building blocks. Moreover, it was shown that the nature of the degradation products depends on the heating rate.

Ab initio calculations on a set of small model carbonate systems gave us additional insight into the reaction mechanism. The structures of the activated complexes confirmed the mechanistic details of this type of E_i elimination reactions. The C_α-O bond was relatively longer than the C_β-H bond in the transition state developing some

carbocation character on the α carbon atom. Furthermore, a correlation was found between the theoretically predicted activation energies and experimentally derived degradation temperatures.

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