Thermal decomposition studies of highly alternating CO\textsubscript{2}-cyclohexene oxide copolymer

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Abstract: Highly alternating CO\textsubscript{2}-cyclohexene oxide copolymer, namely poly(cyclohexene carbonate) (PCHC), considered potentially to be microelectronic sacrificial material, was successfully synthesized by copolymerization of cyclohexene oxide and CO\textsubscript{2} in the presence of SalenAl(OiPr) catalyst. The obtained highly alternating PCHC copolymer were determined and proven to have superior thermal decomposition properties decomposing completely at 350 °C by thermogravimetric (TG) analysis under dynamic conditions. The thermal decomposition kinetics of the obtained PCHC was investigated by a different kinetic method using data from TG analysis. Based on the analytical, kinetic parameters were calculated and kinetic model of pyrolysis was proposed. TG-IR, Py-GC/MS, IR and \textsuperscript{1}H NMR techniques were applied to investigate the decomposition process. Based on Py-GC/MS and TG-IR techniques, carbon dioxide, 1,3-cyclohexadiene, cyclopentanecarbalkaldehyde, cyclohexene oxide, cyclohexanone and trans-1,2-carbonyldioxycyclohexane were identified as thermal decomposition products of PCHC. The solid residues of the PCHC with 25\% ether linkages decomposed at 200, 250, 300, 350 °C as determined by IR and \textsuperscript{1}H NMR. The results demonstrated that the carbonate content of the solid residues decreased gradually at elevated heat-temperatures and at 350 °C only few polyether linkages were observed.

Keywords: Polycarbonates, Thermal decomposition, Kinetics, Thermogravimetric analysis (TGA), Py-GC/MS

Introduction

The aliphatic polycarbonates, such as poly(ethylene carbonate), poly(propylene carbonate) and poly(cyclohexene carbonate), can be obtained from the copolymerization of carbon dioxide and epoxides with various catalysts [1-7]. It is well known that poly(ethylene carbonate) (PEC) has good bio-compatibility and biodegradability and can be used as surgery seam [8-10]. Poly(propylene carbonate) (PPC) is being used in packaging plastic [11,12], polyurethane synthesis [13], ceramic adhesives [14] etc. However, due to its low glass transition temperature (T\textsubscript{g}, 40 °C), modulus and tensile strength, its more extensive application was limited. At the same time, poly(cyclohexene carbonate) (PCHC), synthesized from CO\textsubscript{2} and cyclohexene oxide, exhibit excellent thermal and mechanical properties, which may potentially be applied in the field of microelectronics sacrificial material.

Over the past decade, different molecular weights of PCHC have been prepared, and the thermal and mechanical properties of these PCHC were investigated [15-17]. However, few reports focused on the thermal decomposition process of the PCHC...
which is helpful for application of the PCHC in the field of microelectronics sacrificial material. As microelectronics sacrificial material, PCHC must possess perfect alternating structure and should decompose completely at relatively lower temperature. In order to understand the effect of decomposition products on the processing and application, the thermal decomposition process and mechanism of the PCHC should be studied.

In this paper, the thermal decomposition of PCHC was investigated with dynamic thermogravimetry (TG), IR, TG-IR and Py-GC/MS techniques. The thermal decomposition kinetics of the highly alternating PCHC was studied and the thermal decomposition model of the PCHC was deduced. Then, apart from the identification of the decomposed products, the decomposition mechanism of the PCHC was also elucidated according to the general mechanism of polycarbonate degradation [18, 19].

Results and discussion

The highly alternating PCHC (the content of carbonate (m) =0.995, $M_n$=70100) was used for thermal TG-kinetics analysis. The structure and the $^1$H NMR spectrum of the PCHC are shown in Scheme 1 and Figure 1, respectively.

Scheme 1. The structure of the CO$_2$-CHO copolymer (PCHC).

Fig. 1. $^1$H NMR spectrum of the highly alternating PCHC.

Fig. 2 illustrates the TG and DTG curves of the PCHC thermal decomposition under nitrogen atmosphere at heating rate of 5, 10, 15, and 30 °C/min. The smooth TG curves show that the weight loss between 280 and 350 °C is completed in one step. The DTG curves show only one maximum weight loss rate peak at every heating
rate, which is at 307, 317, 325, and 334 °C, respectively. These indicate that the thermal decomposition of the highly alternating PCHC obeys a single-stage decomposition reaction. With increasing heating rate, the TG and DTG curves move towards the high-temperature region. However, the highly alternating PCHC can decompose completely before 350 °C, without any solid residues left. It indicates that the highly alternating PCHC possesses excellent thermal decomposition property. Consequently, the thermal decomposition kinetics and mechanism of the highly alternating PCHC were studied in detail.

![TG and DTG curves of the highly alternating PCHC thermal decomposition in N2 at different heating rate.](image)

**Fig. 2.** (a) TG and (b) DTG curves of the highly alternating PCHC thermal decomposition in N2 at different heating rate.

*The thermal decomposition kinetics of the highly alternating PCHC*

- Kinetics methods

Usually the non-isothermal decomposition of solid state material was subjected to equation (1) [20]:

\[
dt = \frac{1}{\beta} \left[ \frac{dW}{d\theta} \right]_{\text{rel}} \left[ \frac{dW}{d\theta} \right]_{\text{diff}}
\]
\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)
\]  

(1)

From the equation (1), the Ozawa-Flynn-Wall (OFW) equation and the Coats-Redfern equation were deduced.

**Tab. 1.** The algebraic expression of \(g(\alpha)\) and \(f(\alpha)\) functions commonly used in the kinetics of solid state reaction.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Rate-controlling process</th>
<th>(g(\alpha))</th>
<th>(f(\alpha))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_1)</td>
<td>Mampel power law, n=1/4</td>
<td>(\alpha^{1/4})</td>
<td>(4\alpha^{3/4})</td>
</tr>
<tr>
<td>(A_{1.5})</td>
<td>Random nucleation and growth, n=2/3</td>
<td>([- \ln(1-\alpha)]^{2/3})</td>
<td>(1.5(1-\alpha)[- \ln(1-\alpha)]^{1/3})</td>
</tr>
<tr>
<td>(A_2)</td>
<td>Random nucleation and growth,n=1/2</td>
<td>([- \ln(1-\alpha)]^{1/2})</td>
<td>(2(1-\alpha)[- \ln(1-\alpha)]^{1/2})</td>
</tr>
<tr>
<td>(A_3)</td>
<td>Random nucleation and growth,n=1/3</td>
<td>([- \ln(1-\alpha)]^{1/3})</td>
<td>(3(1-\alpha)[- \ln(1-\alpha)]^{2/3})</td>
</tr>
<tr>
<td>(A_4)</td>
<td>Random nucleation and growth,n=1/4</td>
<td>([- \ln(1-\alpha)]^{1/4})</td>
<td>(4(1-\alpha)[- \ln(1-\alpha)]^{3/4})</td>
</tr>
<tr>
<td>(R_2)</td>
<td>Phase boundary reaction, contracting cylinder, n=1/2</td>
<td>(1 - (1- \alpha)^{1/2})</td>
<td>(2(1- \alpha)^{1/2})</td>
</tr>
<tr>
<td>(R_3)</td>
<td>Phase boundary reaction, contracting cylinder, n=1/3</td>
<td>(1 - (1- \alpha)^{1/3})</td>
<td>(3(1- \alpha)^{2/3})</td>
</tr>
<tr>
<td>(D_1)</td>
<td>One-dimensional diffusion, parabolic law</td>
<td>(\alpha^2)</td>
<td>(1/(2\alpha))</td>
</tr>
<tr>
<td>(D_2)</td>
<td>Two-dimensional diffusion, Valensi equation</td>
<td>((1-\alpha)ln(1-\alpha) + \alpha)</td>
<td>([-ln(1-\alpha)]^{-1})</td>
</tr>
<tr>
<td>(D_3)</td>
<td>Three-dimensional diffusion, Jander equation , n=2</td>
<td>([1-(1-\alpha)!^{1/3}]^2)</td>
<td>(1.5[1-(1-\alpha)!^{1/3}]!^{-1}(1-\alpha)^{2/3})</td>
</tr>
<tr>
<td>(D_4)</td>
<td>Three-dimensional diffusion, Ginstling-Brounshtein equation</td>
<td>((1-2\alpha/3)-(1-\alpha)^{2/3})</td>
<td>(1.5[1-(1-\alpha)!^{1/3}]!^{-1})</td>
</tr>
<tr>
<td>(F_1)</td>
<td>Random nucleation with one nucleus on the individual particle</td>
<td>(-ln(1-\alpha))</td>
<td>(1-\alpha)</td>
</tr>
<tr>
<td>(F_2)</td>
<td>Random nucleation with two nuclei on the individual particle</td>
<td>((1-\alpha)^{-1})</td>
<td>((1-\alpha)^2)</td>
</tr>
<tr>
<td>(F_3)</td>
<td>Random nucleation with three nuclei on the individual particle</td>
<td>((1-\alpha)^{-2})</td>
<td>(0.5(1-\alpha)^{3})</td>
</tr>
</tbody>
</table>

Ozawa-Flynn-Wall (OFW) equation [21, 22]:

\[
\lg \beta = \lg \frac{A \cdot E}{R \cdot g(\alpha)} - 2.315 - 0.457 \frac{E}{RT}
\]

(2)

Coats-Redfern (C-R) equation [23]:

\[
\ln \frac{g(\alpha)}{T^2} = \ln \frac{A \cdot R}{\beta \cdot E} - \frac{E}{RT}
\]

(3)

where \(\alpha\) is the reaction fraction of decomposition, \(\frac{d\alpha}{dt}\) is the rate of conversion, \(\beta\) is the heating rate (\(^\circ\)C/min), \(A\) is the pre-exponential factor, \(E\) is the apparent activation energy (kJ/mol), \(T\) is the temperature (K), \(R\) is gas constant, and \(f(\alpha)\) and \(g(\alpha)\) is the differential and integral mechanism functions, respectively. The
algebraic expression of \( f(\alpha) \) and \( g(\alpha) \) functions commonly used in the kinetics of solid state reactions are shown in Table 1 [24-26].

**-Kinetic analysis**

With the OFW method and the experimental data obtained in the TG curves (Figure 2(a)), the apparent activation energy \( (E) \) of the PCHC at a different decomposition reaction fraction \( (\alpha) \) were estimated from the slope of a series of straight line of \( \ln \beta \) versus \( 1/T \). A mean value of 169.6 kJ/mol was obtained from the above data. The results show that the \( E \) values are almost constant with \( \alpha \) (Figure 3). Together with single-step decomposition in TG analysis, it suggests that the decomposition of the highly alternating PCHC obeys a single kinetic mechanism [27].

**Fig. 3.** The dependence of \( E \) obtained by OFW method for the decomposition of the highly alternating PCHC in N2 on the reaction fraction \( \alpha \).

The apparent energy \( (E) \), \( \ln A \) and the linear correlation coefficients \( r \) of all kinds of mechanisms could be also obtained by C-R method. These kinetic parameters at 10 °C/min are listed in Table 2. Comparing the activation energies in Table 2, we found that the apparent activation energy corresponding to the \( A_2 \) type mechanism was very close to the value obtained from the OFW method \( (E=169.6 \text{ kJ/mol}) \). And the linearity of the plot of \( \ln[ (\alpha)/T^2] \) versus \( 1/T \) corresponding to \( A_2 \) mechanism model was very good \( (r \approx 0.9998) \). Hence the pyrolysis of the highly alternating PCHC probably followed \( A_2 \) type; that is, the rate-controlling process obeyed the Avrami-Erofeev equation (2), and \( f(\alpha)=2(1-\alpha)[-\ln(1-\alpha)]^{1/2} \). Putting the value of \( E \), \( A \) and \( R \) and the formula of \( f(\alpha) \) into the equation (1), achieved the thermal decomposition rate equation as follows: \( \frac{d\alpha}{dt}=9.84 \times 10^{14}(1-\alpha)[-\ln(1-\alpha)]^{1/2} \exp(-\frac{20242.9}{T}) \). In the purpose of estimating the uncertainty of the thermal decomposition rate equation, the theoretical value of \( \frac{d\alpha}{dt} \) were calculated by the rate equation and compared with the experimental value of \( \frac{d\alpha}{dt} \) obtained from the DTG data. At different heating rate, the theoretical value were similar to the experimental value, which indicated that
the rate equation can be applied in the thermal decomposition process at different heating rate for the high alternating PCHC.

**Tab. 2.** Kinetic parameter obtained by Coats-Redfern Method of several Solid-State Processes at 10 °C/min.

<table>
<thead>
<tr>
<th>No.</th>
<th>Symbol</th>
<th>( E ) (kJ/mol)</th>
<th>( \ln A )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( P_1 )</td>
<td>74.5</td>
<td>10.44</td>
<td>0.9941</td>
</tr>
<tr>
<td>2</td>
<td>( A_{1.5} )</td>
<td>227.7</td>
<td>46.28</td>
<td>0.9998</td>
</tr>
<tr>
<td>3</td>
<td>( A_2 )</td>
<td>168.3</td>
<td>33.83</td>
<td>0.9998</td>
</tr>
<tr>
<td>4</td>
<td>( A_3 )</td>
<td>109.1</td>
<td>21.31</td>
<td>0.9998</td>
</tr>
<tr>
<td>5</td>
<td>( A_4 )</td>
<td>79.4</td>
<td>14.92</td>
<td>0.9997</td>
</tr>
<tr>
<td>6</td>
<td>( R_2 )</td>
<td>304.6</td>
<td>61.34</td>
<td>0.9991</td>
</tr>
<tr>
<td>7</td>
<td>( R_3 )</td>
<td>317.9</td>
<td>63.78</td>
<td>0.9998</td>
</tr>
<tr>
<td>8</td>
<td>( D_1 )</td>
<td>543.9</td>
<td>110.84</td>
<td>0.9955</td>
</tr>
<tr>
<td>9</td>
<td>( D_2 )</td>
<td>591.3</td>
<td>120.17</td>
<td>0.9981</td>
</tr>
<tr>
<td>10</td>
<td>( D_3 )</td>
<td>645.7</td>
<td>130.16</td>
<td>0.9997</td>
</tr>
<tr>
<td>11</td>
<td>( D_4 )</td>
<td>609.4</td>
<td>122.50</td>
<td>0.9988</td>
</tr>
<tr>
<td>12</td>
<td>( F_1 )</td>
<td>346.4</td>
<td>70.93</td>
<td>0.9998</td>
</tr>
<tr>
<td>13</td>
<td>( F_2 )</td>
<td>441.9</td>
<td>91.19</td>
<td>0.9942</td>
</tr>
<tr>
<td>14</td>
<td>( F_3 )</td>
<td>553.0</td>
<td>116.89</td>
<td>0.9848</td>
</tr>
</tbody>
</table>

**Thermal decomposition mechanism of the PCHC**

To further study the thermal decomposition processes of the PCHC, Py-GC/MS and TG/IR techniques were applied to analyze the pyrolysates of the highly alternating PCHC \((m=0.995, \, M_n=70100)\); the solid residues of the PCHC with 25% polyether linkage were characterized by IR and \(^1\)H NMR spectrum, which finally led to the elucidation of the thermal decomposition mechanism of PCHC.

**Analysis of gas pyrolysates**

The pyrolysates of the highly alternating PCHC under fast pyrolysis were examined by Py-GC/MS. The Py-GC/MS experiments were carried out at different pyrolysis temperatures, namely, 180, 350 and 600 °C. The total ion chromatograms of the PCHC sample at 350 °C are shown in Figure 4. The chemical name, molecular formula, molecular weight and content of all identified decomposition volatile products at all pyrolysis temperature labeled in Table 3. It is shown that the volatile products of the PCHC are carbon dioxide, 1,3-cyclohexadiene, cyclopentanecarboxaldehyde, cyclohexene oxide, cyclohexanone, and trans-1,2-carbonyldioxycyclohexane, while trans-1,2-carbonyldioxycyclohexane is the main gas pyrolysite. Table 3 also shows that at lower pyrolysis temperature of 180 °C, little CHCl\(_3\) come from solvents in pretreatment of PCHC samples. The PCHC is stable at 180 °C and the evolved gas remained in solvent CHCl\(_3\). Upon increasing the pyrolysis temperature, the percentage of trans-1,2-carbonyldioxycyclohexane quickly increased to 86%. It indicates that higher temperature pyrolysis is apt to form trans-1,2-carbonyldioxycyclohexane.

With the help of TG/IR technique, the thermal decomposition dynamic process of the PCHC can be followed. Three-dimensions TG-IR spectrum of the highly alternating PCHC is shown in Figure 5. Due to its small amount, no signal of CHCl\(_3\) is observed.
**Fig. 4.** Py-GC spectrum of the highly alternating PCHC at 350 °C pyrolysis temperature.

**Tab. 3.** The thermal decomposition volatile products of the highly alternating PCHC.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compound name</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Percentage* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>180 °C</td>
</tr>
<tr>
<td>1</td>
<td>Trichloromethane</td>
<td>CHCl₃</td>
<td>118</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>44</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1,3-cyclohexadiene</td>
<td>C₆H₈</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Cyclopentane-carboxaldehyde</td>
<td>C₆H₁₀O</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexene oxide</td>
<td>C₆H₁₀O₂</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Cyclohexanone</td>
<td>C₆H₁₀O</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Tran-1,2-Carbonyl-dioxycyclohexane</td>
<td>C₇H₁₀O₃</td>
<td>142</td>
<td>0</td>
</tr>
</tbody>
</table>

* the percentage of the compound in the total ion chromatogram at certain temperature

Figure 6 represents the IR spectrum of pyrolysate at 160 °C, 328 °C and 343 °C. At lower temperature (160 °C), only CO₂ characteristic peak (2360 cm⁻¹) can be observed in Figure 6 (A). But in Figure 6(B) (328 °C), apart from CO₂ (absorption bands at 2358 and 669 cm⁻¹), ester carbonyl peak at 1863 cm⁻¹ and ether –O– peak at 1064 and 1142 cm⁻¹ can also be observed, which further validate the presence of tran-1,2-carbonyldioxycyclohexane. Two peaks at 2960 and 2982 cm⁻¹ are signals of υ(C-H) vibrations. The other carbonyl peak at 1738 cm⁻¹ due to carbonate compound is medium intensity at 328 °C, but disappears at 343 °C. It may be that there are low molecular weight carbonate compounds at 328 °C, but all carbonate linkage decomposed completely at 343 °C. At lower temperature, the unzipping of the PCHC give low molecular weight carbonate compounds and trans-1,2-carbonyldioxycyclohexane; by about 350 °C all of carbonate compounds decomposed completely.
**Fig. 5.** TG-IR analysis of the highly alternating PCHC in air.

**Fig. 6.** IR spectrum of the highly alternating PCHC thermal decomposition products at (A) 160 °C, (B) 328 °C, (C) 343 °C in air.

**Analysis of solid residues**

The PCHC \((m=0.75)\) cannot decompose completely at higher temperature \((350 \, ^\circ\text{C})\) and always have some solid residues (Figure 7). Figure 8 shows the IR spectrum of the PCHC and its solid residues at different decomposition temperatures in air. It can be seen that the IR spectrum of solids residues at 200 °C and 250 °C are similar to the IR spectrum of the initial PCHC. But the IR spectrum of solid residue at 300 °C is different. The intensity of signal at 1760 cm\(^{-1}\) is unchanged in Figure 8 (A, B, C) and it indicates that the carbonate remains unchanged till 250 °C. But at 300°C, the signal at 1760 cm\(^{-1}\) turn weak and the double linkage peak at 1600 cm\(^{-1}\) appears. It indicates that carbonate linkage of the PCHC decomposes slowly before 250 °C, but at 300°C the carbonate linkage breaks down quickly and some unsaturated compounds are formed. Figure 9 shows the \(^1\text{H}\) NMR spectrum of the PCHC and its solids residues at 250 °C and 350 °C.
**Fig. 7.** TG curves of the PCHC A (m=0.75) and B (m=0.995). Heating rate: 10 °C/min, atmosphere: N₂.

**Fig. 8.** IR spectrum of the initial PCHC (m=0.75) (A) and its decomposition residues at 200 °C (B), 250 °C (c), 300 °C (D) in air.

**Fig. 9.** 1H NMR spectrum of the initial PCHC (m=0.75) (A) and its decomposition residues at 250 °C (B), 350 °C (C) in air.
The content of the carbonate (m) of the initial PCHC is 0.75, but at 250 °C the content of the carbonate of the solids residues reduce to 0.64, at 350 °C the carbonate linkage even disappears and ether linkage signal almost stay unchanged. It implies that carbonate linkage can decompose completely at about 350 °C, and the ether linkage is stable even at 350 °C.

**Evaluation of mechanisms**

Inoue et al. [18] suggested that the thermal decomposition of PPC take place in two ways: the main chain random scission and unzipping. With Py-GC/MS and TG/IR techniques Meng et al.[19] concluded that lower molecular weight PPC with active terminal –OH groups is susceptible to unzipping. Unzipping of PCHC produces trans-1,2-carboxyldioxycyclohexane. The percentage of trans-1,2-carboxyldioxycyclohexane is about 80% (Figure 4 and Table 3), which indicates thermal decomposition mechanism of the lower molecular weight PCHC (M_n=70100) is unzipping. In the mean time, due to the breakage and rearrangements of C-H and C-O bonds in trans-1,2-carboxyldioxycyclohexane, small amount of carbon dioxide, 1,3-cyclohexadiene, cyclopentanecarbaxaldehyde, cyclohexene oxide, and cyclohexanone are formed. The thermal decomposition mechanism of the PCHC is proposed in Scheme 2.

![Scheme 2. The thermal decomposition mechanism of the PCHC.](image)

**Conclusions**

To meet the needs of microelectronic sacrificial material, the highly alternating PCHC copolymer was synthesized. The highly alternating PCHC copolymer (m=0.995) started to decompose at 250 °C, and decomposed completely without solid residue at 350 °C. The thermal decomposition kinetics of the PCHC under N_2 was studied. The apparent activation energy calculated by Ozawa-Flynn-Wall method was 169.6 kJ/mol. There is a good fitting between OWF method and C-R method. The A_2 type thermal decomposition mechanism model of the PCHC was followed according to the Coats-Redfern method. With the C-R method, ln A and the probable conversion function, f(α) for the decomposition of PCHC were calculated. The thermal
decomposition rate equation is\[ \frac{d\alpha}{dt} = 9.84 \times 10^{14} (1 - \alpha) \left[ - \ln(1 - \alpha) \right]^{1/2} \exp\left( -\frac{20242.9}{T} \right). \]
By means of Py-GC/MS and TG/IR measurement, the volatile decomposition products of the PCHC were identified as mainly trans-1,2-carbonyldioxycyclohexane due to the unzipping of PCHC. Little thermal decomposition products of trans-1,2-carbonyldioxycyclohexane such as carbon dioxide, 1,3-cyclopentanecarbaxaldehyde, cyclohexene oxide, and cyclohexanone were observed. Together with IR and \(^1\)H NMR analysis of the solid residual of the CO\(_2\)-CHO copolymer (m=0.75), it was found that carbonate linkages decreased gradually upon increasing the temperature and ether linkages remained unchanged till 350 °C.

**Experimental part**

**Materials**
Commercial Carbon dioxide of 99.99% purity was used without further purification. Cyclohexene oxide (CHO) was treated over calcium hydride prior to use to reduce the water content to less than 100 ppm as determined by Kart Fisher titration. SalenAl(O\(_i\)Pr) was prepared according to literature procedures [28]. 4-dimethylamine pyridine (DMAP) were purchased from Acros and used as received. All solvents (tetrahydrofuran, methanol, chloroform etc) were purchased from commercial sources and treated with 4Å molecular sieves prior to use.

**Synthesis and Characterization of the PCHC**
Poly(cyclohexene carbonate) (m=0.995) was synthesized by the copolymerization of carbonate dioxide and cyclohexene oxide with SalenAl(O\(_i\)Pr) as main catalyst and DMAP as cocatalyst at 80 °C under 4 MPa pressure of CO\(_2\). Poly(cyclohexene carbonate) (m=0.75) was synthesized according to literature [29]. The copolymer was extracted as a chloroform solution and subjected to repeated precipitation with methanol. The structure of the PCHC is shown in Scheme 1. The PCHC was analyzed by \(^1\)H NMR in CDCl\(_3\), and the \(^1\)H NMR spectrum of the highly alternating PCHC is shown in Figure 1 (the letters correspond to the structure formula). The content of carbonate linkages (m) of the PCHC copolymer was determined by integrating the \(^1\)H NMR peaks corresponding to the methane protons of polyether at ~3.45 ppm and polycarbonate at ~4.6 ppm [2, 30, 31]. The number average molecular weight (\(M_n\)) of the PCHC was obtained by gel permeation chromatography (GPC).

**Thermal analysis**
Thermogravimetry (TG) was performed on a Perkin Elmer Pyres 1 thermoanalyzer. About 10 mg highly alternating PCHC (m=0.995, \(M_n=70100\)) sample was heated from 50 °C to 400 °C at a heating rate of 5, 10, 15 and 30 °C/min under a nitrogen atmosphere.

**Infrared (IR) measurement**
The thermal decomposition solid residues of the PCHC with 75% polycarbonate linkages heated at 200, 250, 300, and 350 °C for 4 hours in muffle in air atmosphere were collected and analyzed using the standard KBr-pellet technique by IR analyzer (RFX-65A).
**TG-IR measurement**

A TG/IR system, namely a Netzsch 209 TG analyzer coupled with a Bruker Vector 22 IR spectrometer, was used to perform the TG-IR analysis. About 5 mg highly alternating PCHC samples were pyrolyzed in the TG analyzer, and the evolved gases were led to the IR spectrometer directly through a connected heated gas line to obtain three dimensional IR spectrum. TG analysis was conducted under air atmosphere from 50 °C to 400 °C at a heating rate of 10 °C/min.

**Py-GC/MS measurement**

The Py-GC/MS experiments were carried out using a PYR-4A Pyroprobe Pyrolyzer coupled with a QP2010Plus Gas Chromatograph/Mass spectrometer. About 1.00 mg highly alternating PCHC sample was pyrolyzed at 180, 350, and 600 °C respectively in a quartz capillary sample holder, followed by introduction of the pyrolyzed products into GC and separation using helium as carrier gas and then characterized by mass spectrometer. The GC column was a DB-5HT (30 m - 0.25 mm i.d. with a coated film thickness of 0.1 um). The GC oven temperature was initially held at 50 °C for 2 min, then programmed to 280 °C at a heating rate of 10 °C/min and held for 5 min. The GC/MS interface was set at 280 °C. The mass spectrums were recorded under electron impact ionization energy at 70 eV.

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**References**