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Synthesis and physical characterization of poly(cyclohexane carbonate), synthesized from CO_2 and cyclohexene oxide

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Abstract

Using $[Zn(2,6\text{-difluorophenoxide})_2]_2(THF)_2$ as the catalyst, poly(cyclohexane carbonate) (PCHC) was synthesized from CO_2 and cyclohexene oxide. The ether content of the polymer was limited to a few mol%. The molecular weight distribution of the linear polycarbonate was broad, with $M_n = 42$ and $M_w = 252$ kg/mol. The recorded T_g was 115°C, which is in excellent agreement with the reported value of 116°C. In spite of its high molar mass, PCHC behaves like a brittle polymer, with an elongation at break of 1–2%. On the other hand, the tensile modulus of PCHC (3600 MPa) is much higher than the corresponding value for bisphenol-A polycarbonate (BP-A PC) (2400 MPa). Like the extremely tough BP-A PC, the PCHC exhibits a γ-transition around −110°C, the presence of which has been related to toughness. The magnitude of this γ-transition is lower than the corresponding value for BP-A PC, which indicates that the main chain of PCHC is less flexible than that of BP-A PC. Moreover, the low temperature relaxation of PCHC is probably related to chair–chair transitions of the cyclohexane side group. The brittle behavior of PCHC is expected from the relatively low plateau modulus of PCHC in the melt, from which a relatively high average molecular weight between entanglements (M_e) of ca. 15,000 g/mole was estimated, which is in the same order of magnitude as the M_e of the brittle polystyrene. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aliphatic polycarbonate; Tensile properties; γ-transition

1. Introduction

Prominent among the current efforts aimed at the chemical utilization of carbon dioxide is the copolymerization of epoxides and CO_2 to provide high molecular weight polycarbonates. This process represents an environmentally benign approach compared to the alternative route involving the use of phosgene. Although for sometime rather structurally undefined catalysts have been employed for the CO_2/epoxide copolymerization [1–4], there are reports of well-defined homogeneous catalysts which are more active [5]. Recently, in studies focusing on the coupling of cyclohexene oxide and carbon dioxide three quite active homogeneous catalysts have been described. These include; bisphenoxides of zinc [6,7], zinc carboxylates with perfluorinated tails [8,9], and three-coordinate zinc complexes containing β-diimine ligands [10]. Since CO_2 is a very cheap monomer, and the most frequently applied catalysts for the polymerization are based on relatively inexpensive zinc complexes, we have decided to investigate whether the new poly(cyclohexane carbonate) (PCHC) would posses interesting physical and mechanical properties. In particular we wish to communicate herein a comparison of the characteristics of PCHC with the widely applied bisphenol-A polycarbonate (BP-A PC).

Scheme 1 shows the general reaction scheme for the copolymerization of CO_2 and cyclohexene oxide. Thermal polymerization of cyclohexene oxide results in undesired ether linkages, whereas a successful copolymerization of cyclohexene oxide with carbon dioxide, under the influence of the applied $[Zn(2,6\text{-difluorophenoxide})_2]_2(THF)_2$ catalyst furnishes the desired aliphatic polycarbonate.

2. Experimental

2.1. Methods and materials

All manipulations were carried out under an inert atmosphere, unless otherwise indicated, using glassware which was flame dried prior to use. The solvents were freshly distilled before use. Cyclohexene oxide was purchased

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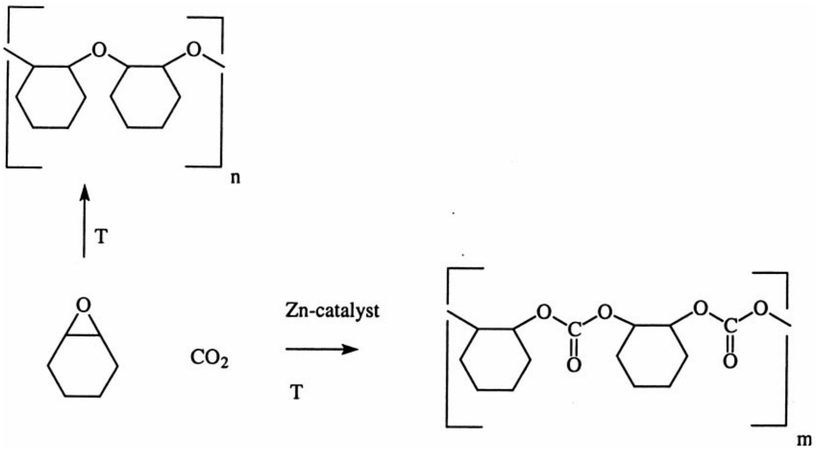

Scheme 1.

from Aldrich Chemical Co. and was distilled over calcium hydride. 2,6-difluorophenol, sodium bis-trimethylsilyl amide, and anhydrous zinc chloride were purchased from Aldrich Chemical Co. 2,6-difluorophenol was sublimed slowly at room temperature prior to use. $Zn[N(SiMe_3)_2]_2$ was prepared according to a published procedure [7]. $[Zn(2,6\text{-difluorophenoxide})_2]_2(THF)_2$ was synthesized through an analogous route of reacting one equivalent of $Zn[N(SiMe_3)_2]_2$ and two equivalents of 2,6-difluorophenol [7]. The dimeric structure of this catalyst in the solid state differs from previous well characterized monomeric zinc phenoxide systems as indicated by X-ray crystallographic analysis [11].

The reference bisphenol-A polycarbonate (Xantar® 22R) was obtained from DSM.

2.2. Copolymerization of cyclohexene oxide and carbon dioxide

A typical copolymerization run was as follows: 0.100 g $[Zn(2,6\text{-difluorophenoxide})_2]_2(THF)_2$ was dissolved in 20.0 ml of cyclohexene oxide. The solution was loaded via an injection port into a 150 ml Parr autoclave which had been previously dried under vacuum at 80°C. The autoclave was then pressurized with 40–50 bar of carbon dioxide and heated at 80°C for 48 h. After the allotted time, the reactor was allowed to cool and the polymer was extracted. High molecular weight polycarbonate was separated from low molecular weight polycarbonate and unreacted monomer by repeated precipitation of polymer from a dichloromethane solution with methanol. The resulting polymer was then placed into a vacuum oven and allowed to dry overnight.

2.3. Molecular characterization of the zinc catalysts and the polycarbonates

Molecular characterization of the zinc catalysts, performed by ^1H NMR in deuterated THF solution, confirmed the expected structure.

The synthesized poly(cyclohexane carbonate) samples were first analyzed, by means of ^1H NMR in $CDCl_3$ solution, for percentages of ether and carbonate linkages (^1H NMR: 3.4 and 4.6 ppm, respectively). ^1H NMR was also used to detect the presence of cyclohexene oxide located at 3.1 ppm. ^{13}C NMR was used to determine the stereoregularity of the polymer. The two ^{13}C resonances at 153.7 and 153.1 ppm correlate with those of polymers made from previous zinc phenoxide systems [6,7].

The absolute molecular weight of the poly(cyclohexane carbonate) was determined by size exclusion chromatography on a HP-1090M, equipped with a UV-diode array detector and a Viscotek differential viscosimeter detector, model 200 (SEC-DV). PS standards were used for the universal calibration. The solvent/eluent was THF, the flow rate was 1.0 ml/min, and 4 PL-gel Mixed C columns were applied.

2.4. Bulk characterization by DSC, mechanical and rheological properties

Differential Scanning Calorimetry was performed under nitrogen on a Mettler thermal analyzer. The heating and cooling rate was 10°C/min.

After drying at 80°C under vacuum and a small nitrogen flow, the synthesized poly(cyclohexane carbonate) and a bisphenol-A polycarbonate reference sample (Xantar® 22R) were compression molded according to the following procedure: 5 min, 190°C, 0 kN; 3 min, 190°C, 10 kN; 5 min, 190°C, 50 kN; Cooling to 25°C under 180 kN.

Testbars with a length of 60 mm, a width of 10.0 mm and a thickness of 1.0 mm were machined from the molded plates to allow a Dynamic Mechanical Test on a Rheometric Scientific ARES Analyzer. This measurement was performed with a torsional load at a frequency of 1 Hz, from −150°C to 200°C, at a heating rate of 3°C/min.

In addition, tensile testbars were machined from the compression molded plates. The tensile tests were performed according to the ISO 37 standard. The drawing

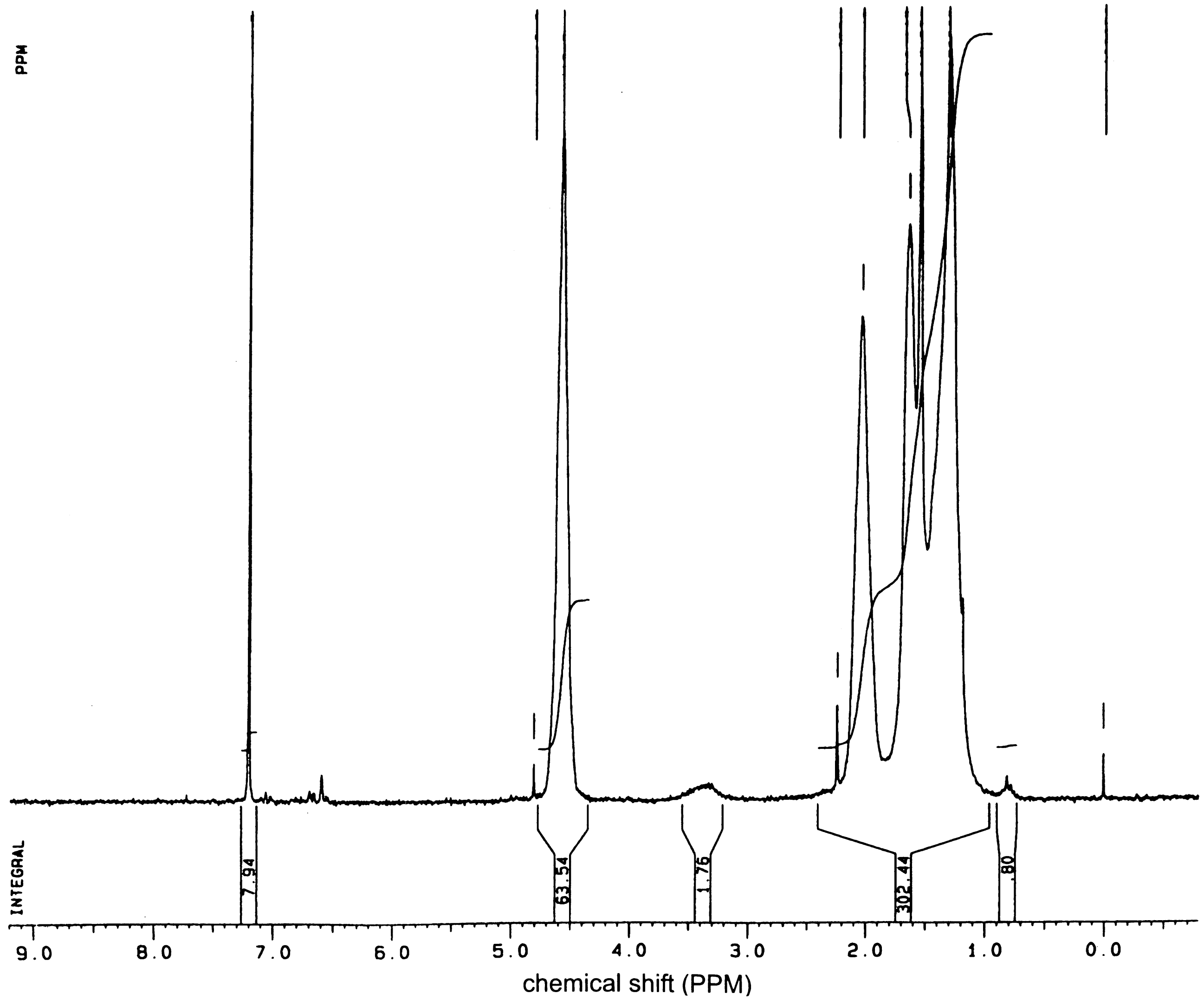

Fig. 1. ^1H NMR spectrum of the synthesized poly(cyclohexane carbonate) (PCHC), recorded in $CDCl_3$ (4.6 ppm = carbonate; 3.4 ppm = ether).

rate was 1 mm/min for the initial part of the stress–strain curve (used for the tensile modulus measurement) and 5 mm/min for the rest of the tensile test.

Finally, the rheological properties of PCHC were determined by dynamic mechanical analysis using a Rheometric Scientific RMS800 spectrometer, equipped with a 8 or 25 mm parallel plate system, at several temperatures between 100 and 170°C. Prior to the measurements the samples were carefully dried overnight at 80°C in vacuum.

3. Results and discussion

3.1. Synthesis of poly(cyclohexane carbonate) (PCHC) and molecular characterization

Using zinc glutarate and $[Zn(2,6\text{-difluorophenoxide})_2]_2(THF)_2$ as catalysts, several attempts were undertaken to synthesize poly(cyclohexane carbonate) from CO_2 and cyclohexene oxide, using a total polymerization time of 48 h, at 80°C and 50 bars CO_2. No solvent was applied. In accordance with literature data, the use of the difluorophenoxide based catalyst resulted in the highest yield of the white polymer. Using this catalyst, the polymerization was repeated several times in order to prepare a stock of poly(cyclohexane carbonate), which after mixing of all batches allowed for the molecular, thermal and a limited mechanical characterization of this aliphatic PCHC. A typical turnover number of 1239 g polymer/g zinc and a typical turnover frequency of 25.8 g polymer/g zinc h were achieved.

During one batch the polymerization actually started in the presence of catalyst during the addition of the cyclohexene oxide monomer and before the reactor was pressurized with CO_2. After this undesired polymerization, resulting in the formation of ether bonds, the reactor was fully pressurized with CO_2 and the copolymerization of carbon dioxide with cyclohexene oxide was allowed to proceed. A ^1H NMR analysis indicated that the obtained

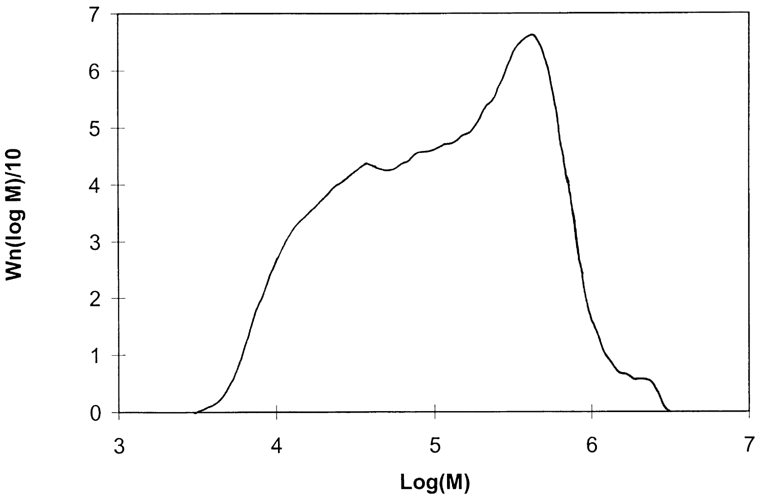

Fig. 2. Absolute Molecular Weight Distribution of PCHC, determined by SEC-DV in THF.

polymer indeed contained a significant mole percentage of ether bonds. This particular polymerization run, with a total cyclohexene oxide consumption of 69.6 mol% (determined by ^{1}H NMR), resulted in 75.4 mol% carbonate linkages and 24.6 mol% ether linkages. The polymer was dissolved in methylene chloride and reprecipitated with methanol several times. This treatment reduced the mole percentage of ether linkages in the polymer to merely a few mole%, as shown by the ^{1}H NMR spectrum in Fig. 1. In this spectrum the aliphatic carbonate absorption is present at 4.6 ppm, and the aliphatic ether absorption is present at 3.4 ppm. Integration learns that, after the reprecipitations, the polymer contains 97.3 mol% carbonate and 2.7 mol% ether linkages. This result strongly indicates that the originally obtained polymer was a mixture of polycarbonate and polyether, rather than a copolymer containing both ether and carbonate linkages. The batch with the remaining 2.7 mol% ether linkages was mixed with all other PCHC batches, which had less than 1 mol% ether linkages.

^{13}C NMR was used to determine the stereoregularity of the polymer. The two ^{13}C resonances at 153.7 and 153.1 ppm (spectrum not shown here) correlate with those of polymers made from previous zinc phenoxide systems [6,7].

A Size Exclusion Chromatography analysis of the mixed PCHC batches with on line measurement of the intrinsic viscosity of the eluents (SEC-DV) showed that the molecular weight distribution was extremely broad ($M_w/M_n = 6.0$), and that the absolute M_n and M_w were 42,000 and 252,000 g/mol, respectively. The molecular weight distribution is given in Fig. 2. The reason why a kind of multi-modal distribution is observed is not understood at the moment. It is possible that the presence of more than one active catalytic species play a role here. Another possibility is a biphasic polymerization mixture, with a 1,2-cyclohexene oxide-rich and a CO_2-rich phase, which may also result in a broadening of the molecular weight distribution, provided that the catalyst is present in both phases. It is obvious that more fundamental work is required to elucidate this point,

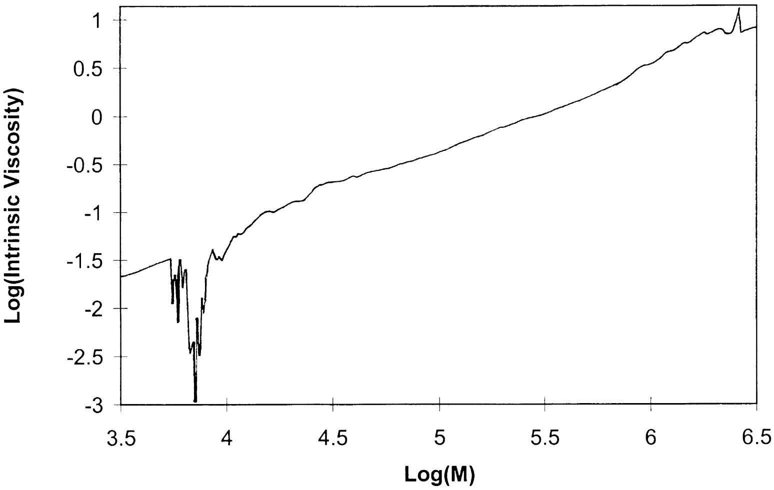

Fig. 3. Mark–Houwink plot of PCHC, constructed with the SEC-DV data obtained in THF.

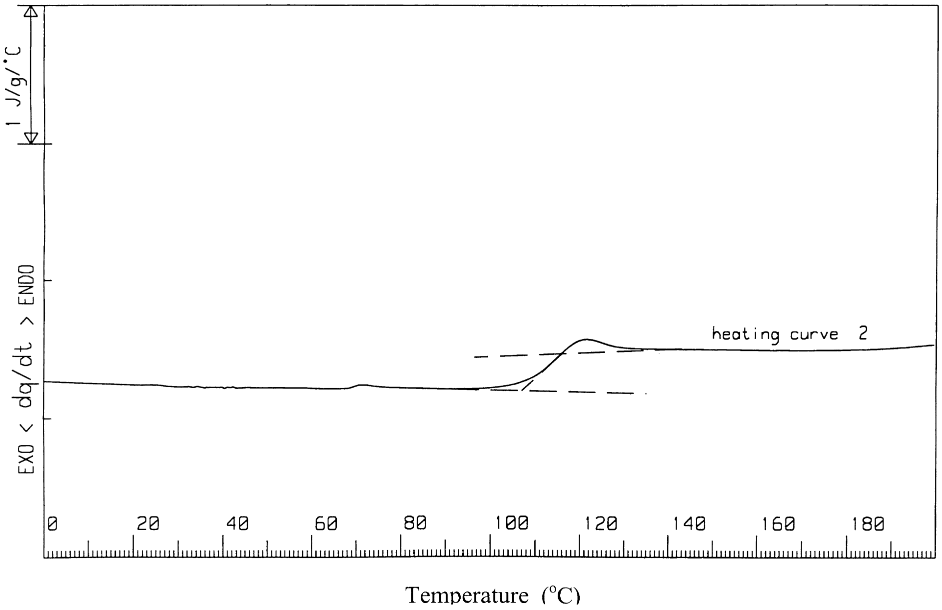

Fig. 4. DSC thermogram of PCHC, containing 2.7 mol% ether linkages and 97.3 mol% carbonate linkages (heating rate 10°C/min).

but this falls beyond the scope of the present paper. We want to emphasize here that thus far the reported molecular weight distributions of PCHC, synthesized from cyclohexene oxide and carbon dioxide, are very broad. For example Darensbourg and Holtcamp [6] report M_w/M_n values between 2.5 and 11.9 for a system using a (2,6-diphenylphenoxide)$_2$Zn (diethyl ether)$_2$ catalyst (with M_w ranging from 17,000 to 213,000 g/mol), and Super et al. [8] report for a system using a CO_2 soluble fluoroalkyl-Zinc catalyst M_w/M_n values ranging from 2.4 to 27, with $9{,}800 < M_w < 299{,}000$ g/mol. Remarkably, Mang et al. [12] showed recently that, even in a biphasic polymerization medium consisting of a cyclohexene oxide-rich and a carbon dioxide-rich phase, narrow molecular weight distributions are obtained if CO_2 and 1,2-cyclohexene oxide are copolymerized in supercritical carbon dioxide, using a CO_2-soluble chromium fluorinated porphyrin catalyst. They obtained strong indications that in their system the catalyst was predominantly present in the cyclohexene oxide-rich phase, which indeed might result in a narrowing of the molar mass distribution. The disadvantage of Mang's catalyst, however, is that even after 18 h of polymerization at 95–110°C the M_n values are usually far below 10,000 g/mol, which is by far not enough to obtain

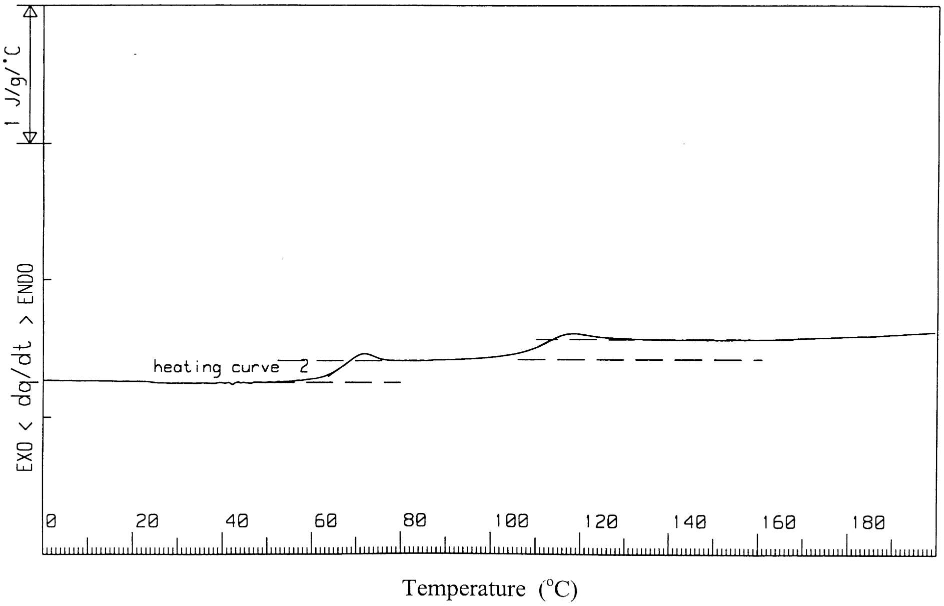

Fig. 5. DSC thermogram of PCHC containing 24.6 mol% ether linkages and 75.4 mol% carbonate linkages (heating rate 10°C/min).

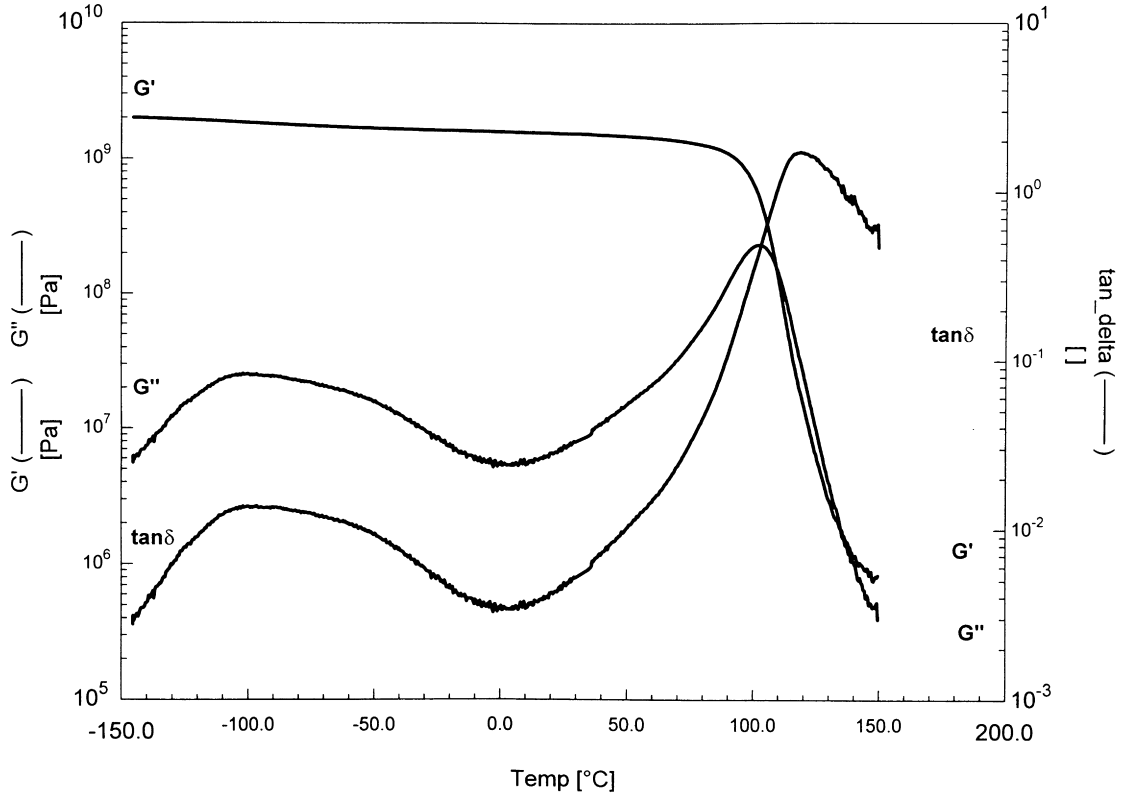

Fig. 6. Dynamic Mechanical Analysis of PCHC (torsional load, 1 Hz, heating rate 3°C/min). Upper curve = G′; Middle curve = G″; Lower curve = tan δ.

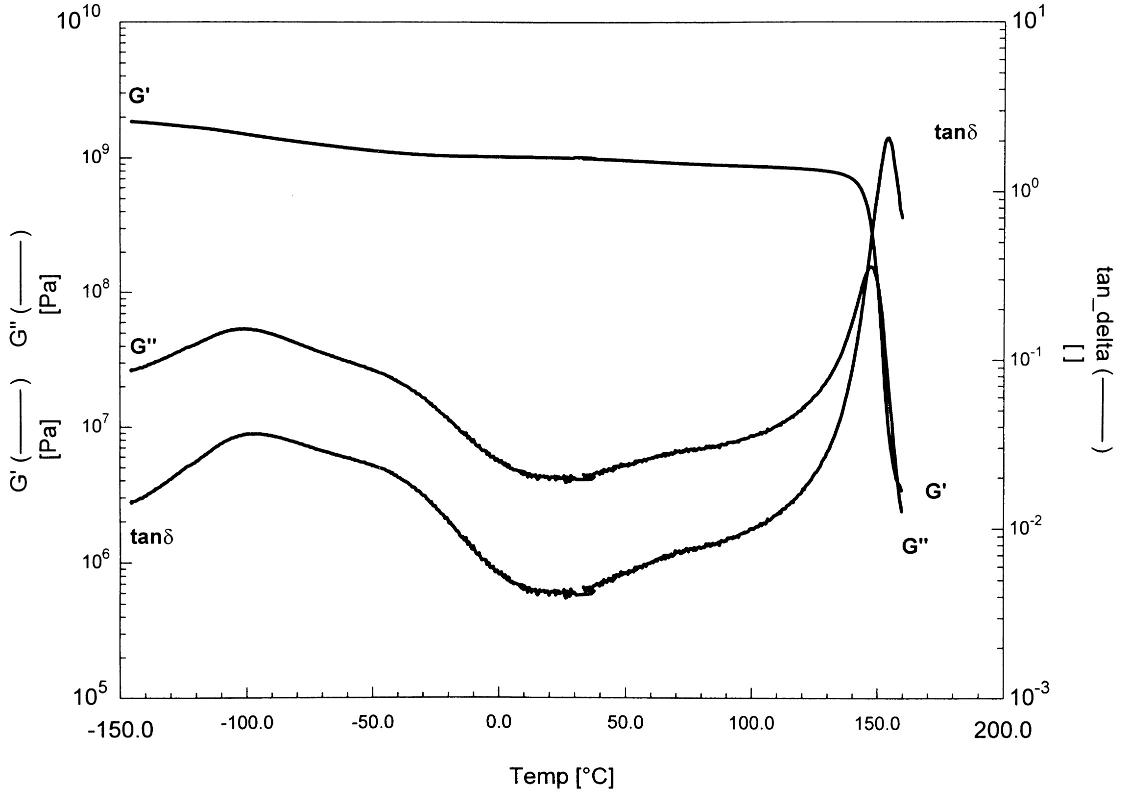

Fig. 7. Dynamic Mechanical Analysis of bisphenol-A PC (torsional load, 1 Hz, heating rate 3°C/min). Upper curve = G′; Middle curve = G″; Lower curve = tan δ.

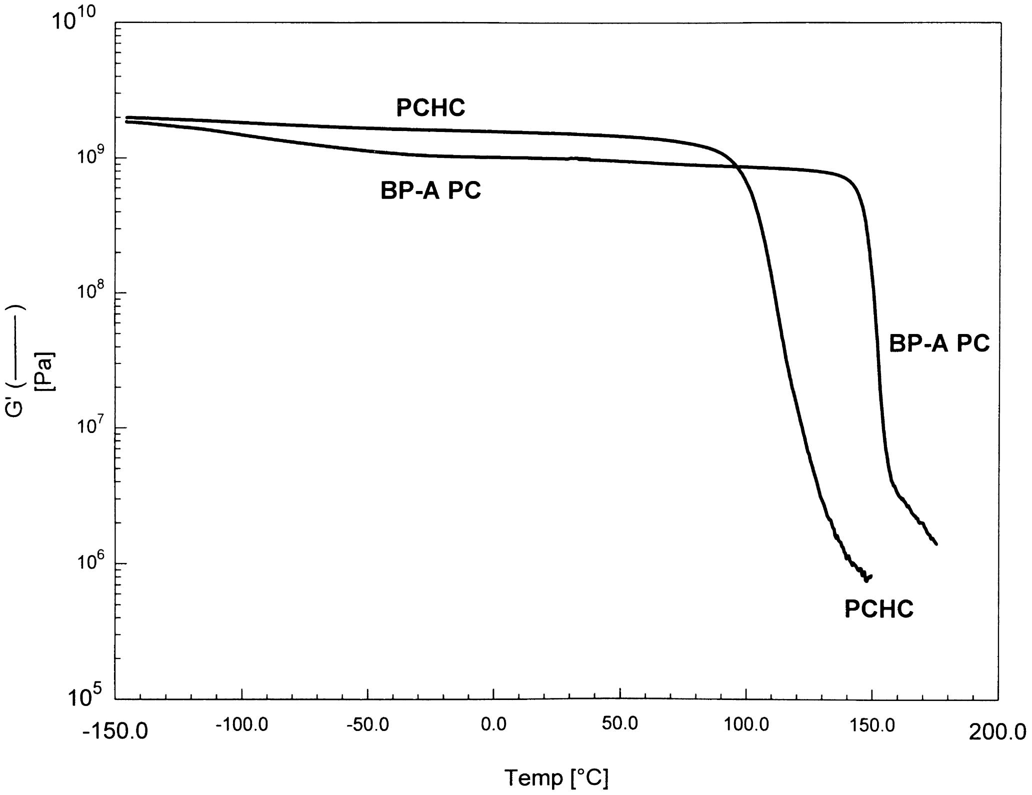

Fig. 8. Comparison of G′ of PCHC (upper curve with lowest T_g) and bisphenol-A PC (lower curve with highest T_g), as derived from Figs. 6 and 7.

satisfactory physical properties (see further). As a possible explanation for the low molar masses Mang et al. [12] mention that the polymerization temperature was fairly close to the ceiling temperature of the polymer.

Fig. 3 shows the Mark–Houwink plot, constructed from the SEC-DV data. Apart from some scattering in the low molecular weight region, this Mark–Houwink plot is quite linear, pointing to a linear character of the synthesized poly(cyclohexane carbonate). If the polymer would have a strongly branched character, then a deviation to lower viscosity values for the higher values of log(M) would have been observed in the Mark–Houwink plot.

The average intrinsic viscosity, as determined by the SEC-DV measurement, amounted to 0.82 dl/g.

3.2. Differential scanning calorimetry analysis

The polymer containing 2.7 mol% ether linkages (see above) was submitted to a DSC analysis. The DSC thermogram is given in Fig. 4. This thermogram shows two baseline shifts. The T_g at 114.9°C, ascribed to poly(cyclohexane carbonate), is very close to the value of 116°C reported by Beckman. A small baseline shift is observed around 69°C. This T_g value is very close to the value of ca. 64°C, reported for high molecular weight poly(cyclohexene oxide) (M_n ca. 17,000 g/mol), heated at a rate of 10°C/min [13]. The T_g of the polyether is more clearly visible in a DSC thermogram of a mixture of poly(cyclohexane carbonate) and poly (cyclohexene oxide) with a higher polyether content (see Fig. 5). This thermogram shows a T_g at 64.9°C and a T_g at 110.2°C. This value for the polycarbonate T_g is lower than the earlier mentioned 114.9°C for the polymer containing merely traces of polyether. This phenomenon points to partial miscibility of poly(cyclohexane carbonate) and poly(cyclohexene oxide). The observed T_g of ca. 115°C is significantly lower than that of the classical bisphenol-A polycarbonate (149°C).

Table 1
Tensile properties of compression molded and machined testbars of PCHC and BP-A PC. Average values, with highest recorded value between parentheses (σ = stress at yield or at break)

	σ_{yield} (MPa)	σ_{break} (MPa)	Strain at break (%)	Tensile modulus (MPa)
PCHC	43 ± 2 (45)	42 ± 2 (44)	1.7 ± 0.6 (2.3)	3600 ± 100 (3700)
BP-A PC	59 ± 3 (62)	47 ± 4 (51)	40 ± 35 (75)	2400 ± 400 (2800)

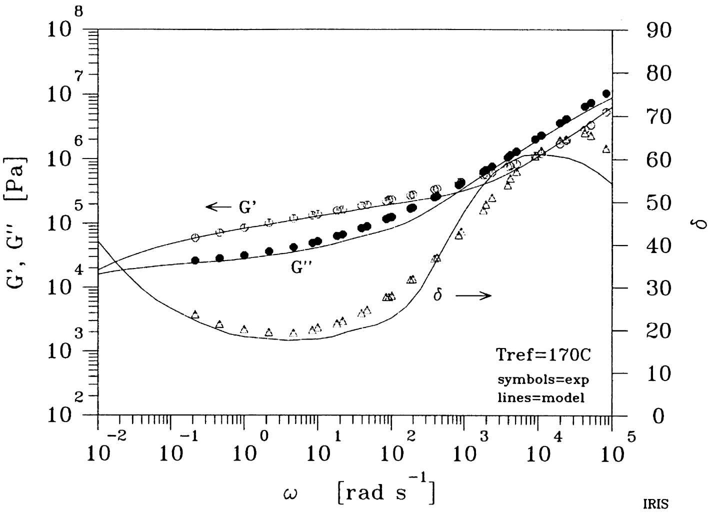

Fig. 9. Master curves of the storage and the loss modulus and of the phase angle as a function of the angular frequency at a reference temperature of 170°C. Symbols depict experimental data, drawn lines have been obtained by model calculations (Parameters used in Wasserman/Graessley model: $G_N^0 = 300$ kPa; JG $= 0.100 \times 10^1$; ME $= 0.139 \times 10^5$; MC $= 0.279 \times 10^5$; ETAK $= 0.200 \times 10^{-11}$; $A = 0.338 \times 10^1$; Tstar $= 0.300 \times 10^{-3}$; Beta $= 0.850 \times 10^0$).

3.3. Mechanical properties and dynamic mechanical analysis of PCHC and BP-A PC, and rubbery plateau modulus and average molar mass between entanglements of PCHC

In Figs. 6 and 7 the results of the Dynamic Mechanical Thermal Analysis of poly(cyclohexane carbonate) and bisphenol-A polycarbonate are given. In accordance with its lower T_g PCHC shows a significant loss of stiffness at a much lower temperature than BP-A PC. In agreement with its very broad molecular weight distribution PCHC shows a relatively broad tan delta peak. Since the DMTA was performed on a mix of several PCHC batches, including the one containing 2.7 mol% poly(cyclohexene oxide), the T_g of the polyether is not visible anymore in the DMTA plot. Below its T_g, the torsional modulus of the aliphatic PCHC is significantly higher than that of the BP-A PC. This is illustrated in Fig. 8, and discussed in more detail further on.

Before giving our comments on the stress–strain measurements on different testbars of PCHC and BP-A PC, we emphasize that the tensile properties of polymeric materials may be inferior if compression moulded and machined testbars are used compared to injection molded testbars, because the latter may be anisotropic. However, the aim of this test is to obtain a qualitative comparison of the tensile properties of both polycarbonates.

The results of the tensile tests have been summarized in Table 1. Given are the average values obtained for several testbars (five for PCHC and six for BP-A PC) and the highest recorded values. The data clearly show the brittle behavior of PCHC, in contrast to the (known) ductile behavior of BP-A PC.

Table 1 shows that the yield stress and the stress at break of PCHC are significantly lower than the corresponding values of BP-A PC. The difference in strain at break is dramatic. Whereas the tough BP-A PC, with a typical M_w between 20,000 and 25,000 g/mol, gives elongations at break in this test of up to ca. 80%, the bars of the poly (cyclohexane carbonate) already break at a strain of a few %, which is in the same order of magnitude as the strain at break of e.g. polystyrene, being a brittle polymer. Obviously, the PCHC is extremely brittle, in spite of the relatively high values of M_n and, especially, M_w (42 kg/mol, respectively 252 kg/mol). We will come to a possible explanation for this brittleness further on.

A closer examination of the DMTA curves of Figs. 6–8 learns that, like BP-A PC, the PCHC exhibits a γ-relaxation peak around −110°C. A striking difference, however, is that BP-A PC, as known, looses a significant amount of stiffness on passing the γ-transition upon heating, whereas in the case of PCHC the decrease in stiffness is very limited, and in fact is hardly perceptible. Although we do not have an explanation for this difference at the moment, it implies that BP-A PC gains mobility in the chain on a sub-segment level in the temperature region between T_γ and T_g, which has been postulated to result in a good ability to absorb energy in an impact test, and thus in good toughness. Obviously PCHC lacks this significant raise in energy absorbance power upon passing T_γ, which might explain the brittleness of this polymer compared to BP-A PC. The relation between the existence of a low temperature transition and toughness is not entirely clear, and contradictory papers have appeared in the literature over the past years. Without having the intention to be complete, we here summarize a few papers on this subject, thereby showing the discrepancy. The high toughness of BP-A PC has been related to the low-temperature mechanical loss process, which indeed is very pronounced in BP-A PC [14–16], but on the other hand Boyer [17] already in the late 1960s showed, by examining eight different types of polymers, that a low temperature loss peak is neither a necessary nor a sufficient condition to guarantee good toughness at room temperature. Boyer e.g. showed that poly(2,6-dimethylphenylene oxide), which is a very tough polymer at room temperature, does not exhibit a pronounced loss peak below room temperature. BP-A PC, which is also extremely tough at room temperature, does exhibit a pronounced loss peak below room temperature, for which in (main) chain motion is mentioned as the source.

Furthermore, Boyer shows that poly(cyclohexylmethacrylate) exhibits a pronounced low temperature transition at −80°C, but at room temperature this polymer is extremely brittle. For this polymer the source of the low temperature loss peak is ascribed to motions in the side group, more specifically to chair–chair transitions of the cyclohexyl ring [18,19]. Boyer writes, and refers to a communication with Heijboer, that motion in a side group of a polymer chain may not contribute to the impact strength of that polymer. In PCHC the cyclohexyl ring should in fact be regarded as a side group. So, the contribution of possible chair–chair transitions to the ability to absorb energy may be limited (or virtually nil) for the same reason given for poly(cyclohexylmethacrylate). On the other hand, if cyclohexylgroups are incorporated into the main chain, as e.g. in poly(1,4-cyclohexylenedimethylene terephthalate) [20], then the chair–chair transitions take place in the main chain, and large-amplitude molecular motions occur at room temperature, resulting in very tough polyesters exhibiting strong low temperature transitions.

The relaxation strength of the low temperature transition is much lower in the case of PCHC, which indicates that either the main chain of PCHC is much less flexible, or the subsegmental motions are limited to side group movements, in analogy with poly(cyclohexylmethacrylate).

More important than the presence of a low temperature relaxation mechanism, the entanglement density of polymers is thought to play a determining role in toughness of polymers by affecting the balance between shear yielding (tough) and craze formation (brittle) (see e.g. Refs. [21–24]). E.g. polystyrene, having a relatively low entanglement density, and accordingly a high average molecular weight between two adjacent entanglements, M_e, of ca. 19,000 g/mol [25], is brittle, whereas, e.g. poly(2,6-dimethylphenylene oxide) with $M_e = 3000$–4000 g/mol and BP-A PC with $M_e = 1800$ g/mol [25] both have a high entanglement density, and consequently are extremely tough at room temperature.

According to the method of Wu [26,27], the average molecular weight between two adjacent entanglements (M_e) can be estimated by determining the plateau modulus (G_N^0) in the melt state with dynamic mechanical analysis. The relation between plateau modulus and M_e is given by the following relation: $M_e = \rho RT/G_N^0$, with $\rho =$ density of the polymer at the temperature T at which G_N^0 is measured, and R is the gas constant.

Fig. 9 shows master curves of the storage and loss modulus and of the phase angle as a function of the angular frequency at a reference temperature of 170°C. The symbols depict the experimental results. A minimum of the phase angle in the rubbery plateau is found between 1 and 10 rad/s. Since the storage modulus shows a steady decrease with decreasing frequency, no reliable value of the plateau modulus can be extracted although it is clearly lower than the value of about 2 MPa reported for BP-A PC.

In order to get a more quantitative indication of the plateau modulus the model of Wasserman and Graessley [28] was used to predict the linear viscoelastic properties of the PCHC melt from its molar mass distribution, as determined with size exclusion chromatography. The properties were calculated assuming a BSW type relaxation time spectrum for the terminal regime (below 1 rad/s) and a power law for the transition regime (above 1 rad/s). Since no relaxation parameters were available for PCHC, these were fitted for the best description of the experimental results. The results of the model calculations have been depicted in Fig. 9 with solid lines. Most attention was paid to a good description of the rubbery region. The plateau modulus G_N^0 proved to be the most important parameter in this regime. A value of 300 ± 50 kPa was found to give the best descriptive model predictions. Using a melt density of 1.135 g/mol, this is equivalent to an entanglement molar mass M_e of about 15 kg/mol, which is clearly much higher than the value of 1800 g/mol reported for BP-A PC [25], and which approaches the M_e of polystyrene, being a brittle polymer. These results further substantiate that PCHC is indeed a much less flexible polymer than BP-A PC and therefore expected to be more brittle.

Now, the low recorded values of the elongation at break, typical for brittle polymers with a low entanglement density, can be understood. Probably a significant part of the molecular weight distribution has a molecular weight below M_e, which prevents this part of the polymer from forming efficient entanglements, resulting in brittle behavior.

In agreement with the higher torsional modulus observed in the DMTA test, the tensile modulus of the aliphatic PCHC is significantly higher than that of the classical aromatic BP-A PC. The high stiffness can be attributed to the low magnitude of the γ-relaxation of PCHC.

4. Conclusions

The T_g of the aliphatic poly(cyclohexyl carbonate) (ca. 115°C) is some 35°C lower than the T_g of the ‘classical’ bisphenol-A polycarbonate, being ca. 150°C. It is obvious that this limits the high temperature applications for the PCHC, since the Heat Distortion Temperature of PCHC will be some 35°C lower as well.

The tensile properties, like yield stress, stress at break and elongation at break, of the PCHC are inferior to the corresponding properties of the classical BP-A PC. The low elongation at break, in spite of a reasonably high molecular weight, implies that PCHC is a brittle polymer, although a low temperature relaxation is present, which is quite often related to toughness. The T_γ transition, however, is thought to correspond to chair–chair transitions of the cyclohexyl ring, which is merely present as a side group and accordingly cannot contribute to toughness.

The relatively low amplitude of the observed γ-relaxation of the PCHC at -110°C, which in addition seems to be related to side group motions, causes a high room temperature stiffness. The relatively low rubbery plateau modulus in the melt, implying a low entanglement density, seems to be responsible for the brittleness of PCHC, even for high molecular weight material.

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