

Mechanically Linked Polycarbonate

Charles-André Fustin,^{†,‡} Christian Bailly,^{*,†} Guy J. Clarkson,[§] Philippe De Groot,^{||}
Trent H. Galow,[⊥] David A. Leigh,^{*,⊥} Duncan Robertson,[∇]
Alexandra M. Z. Slawin,[¶] and Jenny K. Y. Wong[⊥]

Contribution from Unité de Physique et de Chimie des Hauts Polymères, Université catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium, Centre for Supramolecular and Macromolecular Chemistry, Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom, Chemicals, Research and Technology, Analytical Department, UCB, Anderlechtstraat 33, B-1620 Drogenboos, Belgium, School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom, ICI, The Wilton Centre, Wilton, Cleveland TS10 4RF, United Kingdom, and Department of Chemistry, University of St. Andrews, St. Andrews KY16 9ST, United Kingdom

Received November 7, 2002; E-mail: bailly@poly.ucl.ac.be, David.Leigh@ed.ac.uk

Abstract: The synthesis, by solid-state copolymerization, and characterization of the first polycatenanes based on a commercial polymer are reported. Various amounts of a benzylic amide [2]catenane, the corresponding macrocycle, and a rigid bisphenol fluorene derivative have been quantitatively and homogeneously incorporated into bisphenol A polycarbonate. The resulting copolymers were characterized by size exclusion chromatography coupled with viscosimetry, ¹H NMR, differential scanning calorimetry, and dynamic mechanical analysis. The unexpectedly small influence of [2]catenane incorporation on the glass transition temperature of the copolymers points to remarkable internal mobility of the catenane comonomer rings. A new relaxation linked to the flexible catenane units is also observed. The studies represent a detailed structural characterization of a polymer containing small amounts of mechanical linkages in its backbone and demonstrate that significant effects can be induced by doping conventional polymers with small percentages (2–6% of repeat units) of flexible catenanes.

Introduction

Given the high cost of introducing new chemical building blocks, it seems likely that future generations of commercial macromolecules will be derived from assembling existing cheap monomers in new ways, using novel types of polymer architectures to improve characteristics and provide “added value”. One type of architecture that is attracting interest^{1–4} is based upon incorporating mechanically interlocked rings, i.e. catenanes, into an otherwise covalently linked polymer backbone. By incorporating flexible—or even switchable—linkages, one might expect to induce significant changes in molecular level flexibility and degrees of freedom, generating unusual and potentially useful improvements in properties. However, no such

effects—nor even evidence for catenane ring mobility in the undissolved state—have been experimentally demonstrated in poly[2]catenane structures to date. The few examples reported^{5–13}

* To whom correspondence should be addressed. Fax: for C.B., +32-10-451593; for D.A.L., +44-131-6679085.

[†] Université catholique de Louvain.

[‡] Present address: Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany.

[§] University of Warwick.

^{||} UCB.

[⊥] The University of Edinburgh.

[∇] ICI.

[¶] University of St. Andrews.

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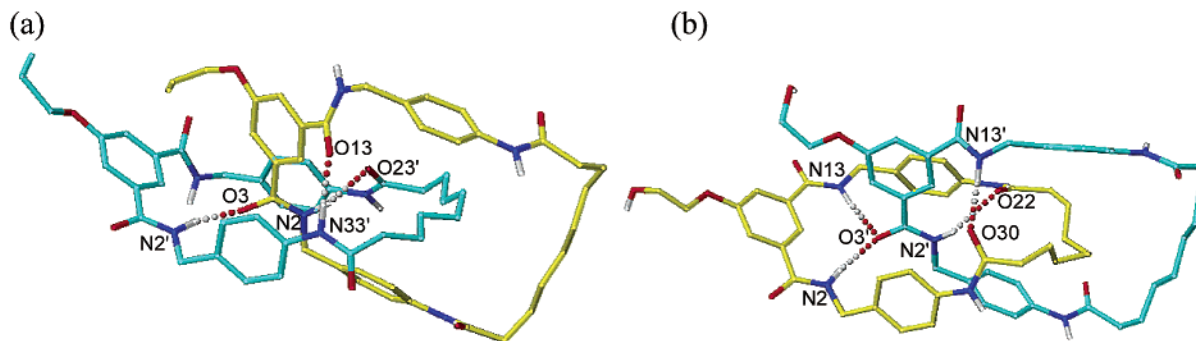


Figure 1. X-ray crystal structures of intramolecularly hydrogen bonded [2]catenane (a) **3** and (b) the bishydroxylated derivative of **3**. Crystals grown from slow infusion of water and methanol into solutions in dimethylformamide. For clarity the carbon atoms of one macrocycle are shown in yellow, the other light blue; oxygen atoms are depicted in red, nitrogen atoms dark blue, and selected hydrogen atoms white. Intramolecular hydrogen bond distances and angles (Å and deg): (a) N2H–O23', 2.29, 129.7; O3–HN2', 1.92, 160.1; O13–HN33', 1.89, 164.0. (b) N2H–O3', 2.15, 167.5; N13H–O3', 2.46, 171.4; O22–HN2', 2.53, 144.9; O30–HN13', 2.04, 166.3.

thus far in the literature have only been prepared in small quantities with broad molecular weight distributions and, consequently, little characterization of their structures or properties have been possible. Furthermore, the [2]catenane units typically make up 90–95% of the molecular weight of those copolymers (or they employ highly unusual comonomers), and the catenane linkages generally used cannot rotate, so they are probably not particularly suitable for making comparisons with conventional covalent backbone polymers in order to ascertain the role—if any—of the mechanical linkage on properties.

Here we describe the synthesis and characterization of poly-[2]catenanes based on bisphenol A polycarbonate (PC). Bisphenol A PC has been commercially available since the 1960s and remains one of the most versatile and popular engineering resins in applications as diverse as toughened and bullet proof windows, safety helmets and shields, roofing panels, gears, bushings, automotive parts, tableware, food containers, medical instruments and appliances, heat and chemically resistant coatings, and telephone and electronic parts, etc. We incorporated [2]catenane linkages into the polycarbonate as 10–30% weight for weight (w/w), 2–6% by number of repeat units, by solid-state copolymerization. To build up our understanding of the role played by the mechanical bond, bisphenol A PC incorporating the corresponding uninterlocked macrocycle (10% (w/w)) or a rigid bulky comonomer, 4,4'-(9-fluorenylidene)-bisphenol (10% (w/w)), were prepared for property comparison with the catenane PC copolymer. The benzylic amide [2]-catenane^{14–16} comonomer **1** utilized in this study was synthesized on a large scale without the need for chromatography. Methylation of the secondary amide groups removed the possibility of intramolecular hydrogen bonding (which directs the assembly of the catenane) ensuring that the macrocyclic rings could be as mobile as possible in the mechanically linked polymer.¹⁷ The catenane contains two phenol groups and thus is suitable as a comonomer for the synthesis of polycarbonate copolymers. Solid-state polymerization (SSP) after solution

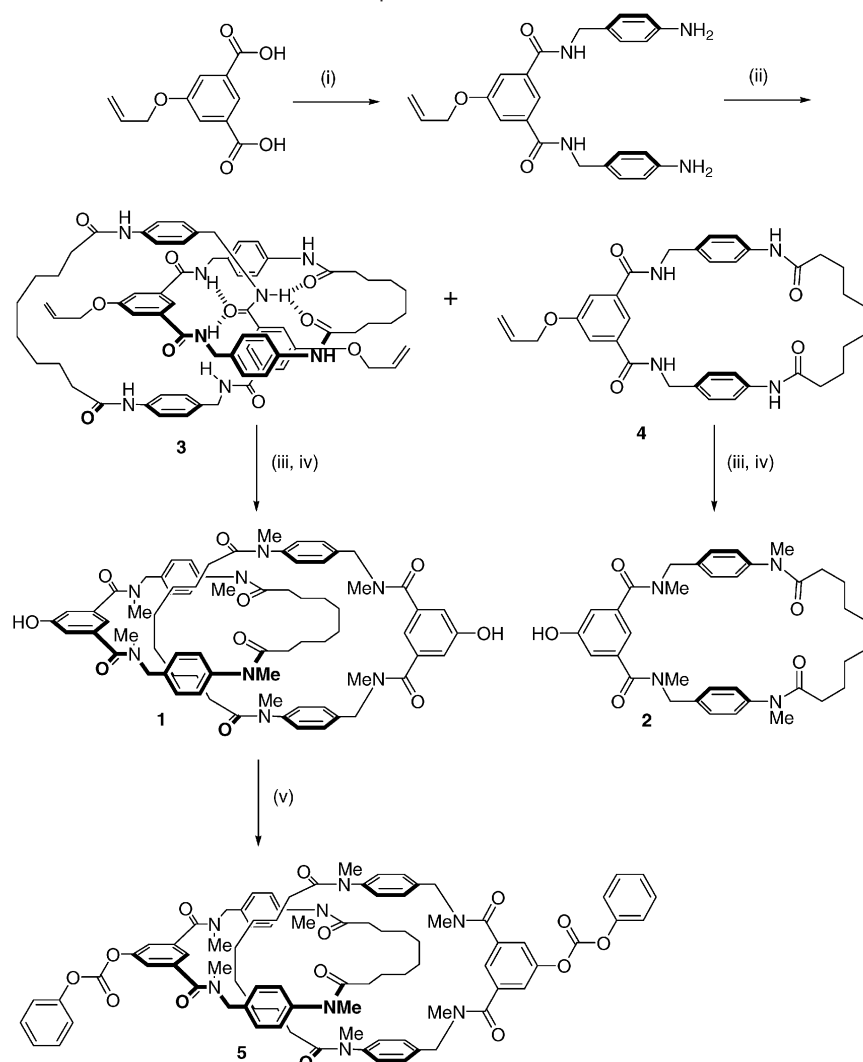
blending was used to incorporate the catenane into bisphenol A polycarbonate. Very few examples of solid-state copolymerization have been reported, and they all involve melt blending of the precursors as a first step.^{18–20} To our knowledge, this is the first example of a copolymerization performed in the solid state without first blending the components in the melt. The simple solution-based method developed offers the general advantage of not being limited by sample size. Moreover, using this technique the amount of catenane incorporated could easily be controlled and varied over a wide range to give a true picture of the effects of incorporating mechanical linkages into a material. Polycatenanes obtained in this way consist of bisphenol A polycarbonate segments of different statistical lengths separated by catenane units.

Results and Discussion

Catenane Monomer Synthesis. The *per*-methylated benzylic amide [2]catenane **1** and macrocycle **2** were prepared according to Scheme 1. 5-Allyloxyisophthalic acid was coupled²¹ to **2** equiv of 4-aminobenzylamine (hydroxybenzotriazole (HOBt), dicyclohexylcarbodiimide (DCC), tetrahydrofuran (THF), 16 h, 78%) and the resulting bisamine condensed with sebacyl chloride (MeCN/CH₂Cl₂, Et₃N, 12 h) to give the *O*-allyl-protected secondary amide [2]catenane **3** and macrocycle **4** in 22 and 26% yields, respectively. The X-ray crystal structure of **3**, together with a bishydroxylated derivative showing a similar inter-macrocycle hydrogen bonding motif, is shown in Figure 1. The X-ray crystal structure of **4**, illustrating that the cavity in the macrocycle does not collapse even when it is not threaded, is shown for comparison in Figure 2. The strong intercomponent hydrogen bonding seen in the crystal structure of **3**, and also in the ¹H NMR spectra in CDCl₃, led us to derivatize the secondary amide groups in order to “switch off” the inter-ring hydrogen bonding and increase the mobility of the catenane rings. Methylation of the amide groups (MeI, NaH, dimethyl sulfoxide (DMSO)/THF, 91% catenane; 95% macrocycle) and catalytic de-*O*-allylation²² (Pd(OAc)₂, Ph₃P, HCO₂H, Et₃N, EtOH, 80%

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Scheme 1. Synthesis of Comonomers **1** and **2** and Model Compound **5**^a

^a (i) $\text{NH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$, HOBT, DCC, THF, 16 h, 78%; (ii) $\text{ClOC}(\text{CH}_2)_8\text{COCl}$, $\text{MeCN}/\text{CH}_2\text{Cl}_2$, Et_3N , 12 h, 22% **3**, 26% **4**; (iii) MeI, NaH, DMSO/THF, 91% catenane, 95% macrocycle; (iv) $\text{Pd}(\text{OAc})_2$, Ph_3P , HCO_2H , Et_3N , EtOH, 80% **1**; 84% **2**; (v) phenyl chloroformate, Et_3N , CH_2Cl_2 , 17 h, 83%.

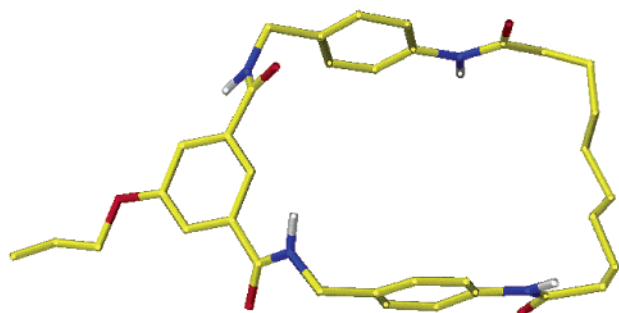


Figure 2. X-ray crystal structure of secondary amide macrocycle **4**. Crystals grown from slow infusion of water into a solution of **4** in ethanol.

catenane; 84% macrocycle) gave the octa-*N*-methylbisphenol [2]catenane **1** and tetra-*N*-methyl-phenol macrocycle **2**. X-ray crystal structures of both the *O*-allyl-protected and deprotected [2]catenane **1** are shown in Figure 3. The X-ray structures of the *N*-methylated catenanes are significant different from each other (one has both macrocycles encapsulating the alkyl chain of the other ring; the other has one macrocycle wrapped around

a benzylic group of the other macrocycle) and also very different from the structure of the intramolecularly hydrogen bonded secondary amide catenane (Figure 1). The lack of any identifiable recognition elements—not even aromatic stacking interactions—between the macrocycles in the crystal structures in the *N*-methylated catenanes encouraged us that they really should behave like nonadhering mechanical linkages when incorporated into a polymer backbone.

Polymer Synthesis. Polycarbonate oligomers were obtained by melt polycondensation of bisphenol A with a slight excess of diphenyl carbonate in the presence of basic catalysts ($\text{Bu}_4\text{NOH}/\text{NaOH}$). Size exclusion chromatography (SEC) was used to characterize the molecular weight distribution of the oligomers ($M_w = 2200$; $M_n = 1300$). Differential scanning calorimetry (DSC) was performed on the crystallized oligomers to yield a glass transition temperature of 89 °C and a melting point of 205 °C. ^1H NMR was used to determine the ratio between phenyl ($\delta = 7.47, 7.45, 7.43$ ppm) and phenol ($\delta = 7.11, 7.09$ ppm; $\delta = 6.71, 6.69$ ppm) chain ends, giving phenol:phenyl = 0.67, confirming that the most abundant chain ends were of the phenyl type. Since catenane **1** bears phenol functions, oligomers with phenyl-rich chain ends were used to balance

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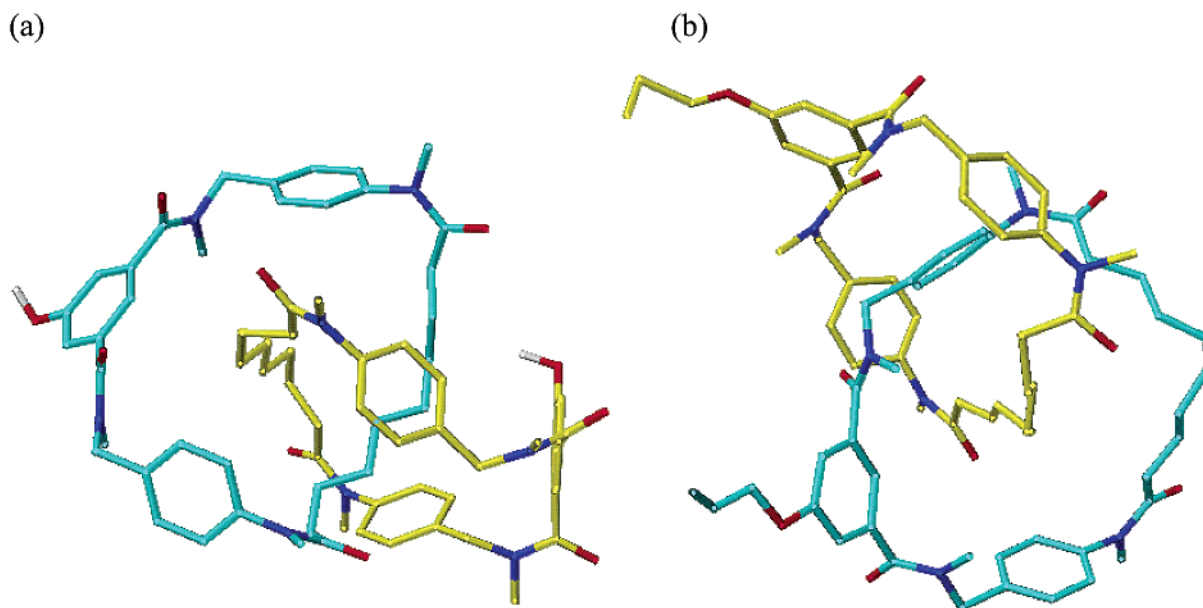
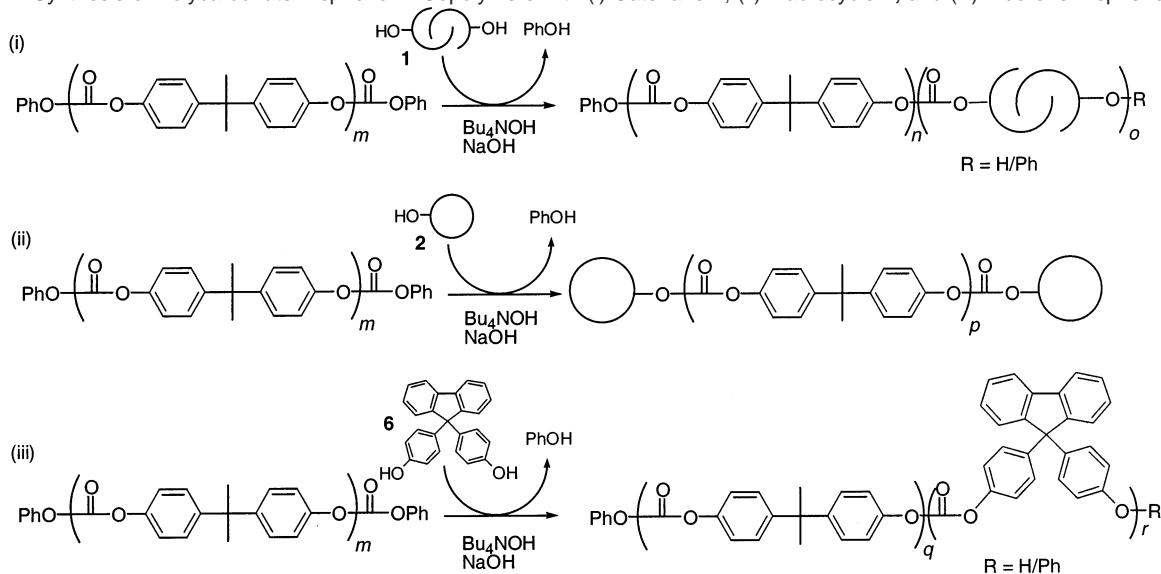


Figure 3. X-ray crystal structures of octa-*N*-methyl [2]catenane (a) **1** and (b) the bis-*O*-allyl derivative of **1**. Crystals grown from slow infusion of water into solutions in dimethylformamide.

Scheme 2. Synthesis of Polycarbonate Bisphenol A Copolymers with (i) Catenane **1**, (ii) Macrocycle **2**, and (iii) Fluorene Bisphenol **6**



the chain end stoichiometry and enable molecular weight build-up of the copolymers.

A 10, 20, or 30% (w/w) amount of catenane **1** or 10% (w/w) of macrocycle **2** (Scheme 2) and polycarbonate oligomers were copolymerized by solid-state polymerization (SSP) after solution blending. The reaction was performed under vacuum (approximately 6×10^{-2} mbar) by applying an increasing temperature program from 190 to 215 °C for approximately 28 h total (details included as Supporting Information). We confirmed that this program does not lead to loss of catenane monomer from the mixture by evaporation/sublimation by a variety of methods. Since solid-state polymerization requires crystalline precursors,^{23–24} we crystallized the blend under acetone vapors prior to SSP. In this case, crystallinity of the blends offers an

important advantage: upon crystallization, most defects—including catenane and chain ends—are rejected in the amorphous phase. Catenanes and chain ends are therefore in close proximity and can react together more easily. Furthermore, the reaction conditions are much milder than melt polycondensation, thus minimizing the chance of catenane degradation.

Quantitative Monomer Incorporation. SEC was used to check that all the catenane monomer had been incorporated into the polymer. Samples coming out of SSP are highly crystalline and are often difficult to solubilize. Therefore, crystallinity was first eliminated by a quick heating–cooling cycle before dissolution in dichloromethane. Figure 4 shows SEC chromatograms of the oligomer blend containing 20% (w/w) catenane and of copolymers containing 10 and 20% (w/w) of catenane. The catenane monomer peak (around 25.3 min) completely disappears after polymerization. We know that the catenane has sufficient thermal stability to survive polymerization (from DSC

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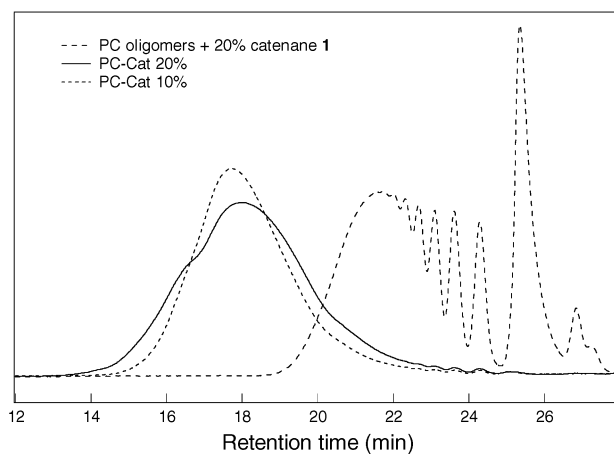


Figure 4. SEC (CH_2Cl_2) of the PC oligomers–catenane **1** blend and of copolymers containing 10 and 20% (w/w) catenane **1**.

Table 1. Molecular Weights and Polydispersity of Copolymers Containing 10, 20, and 30% (w/w) of Catenane **1**, 10% (w/w) of Macrocycle **2**, and 10% (w/w) of Fluorene **6** Obtained by SEC Viscosity in CH_2Cl_2

	M_w	M_n	PDI
PC-cat. at 10%	40 100	15 900	2.5
PC-cat. at 20%	41 400	9 900	4.2
PC-cat. at 30%	38 900	8 100	4.8
PC-Mac 10%	18 000	6 500	2.8
PC-fluorene 10%	11 500 ^a	4 700 ^a	2.4

^a Molecular weight expressed in polycarbonate equivalent.

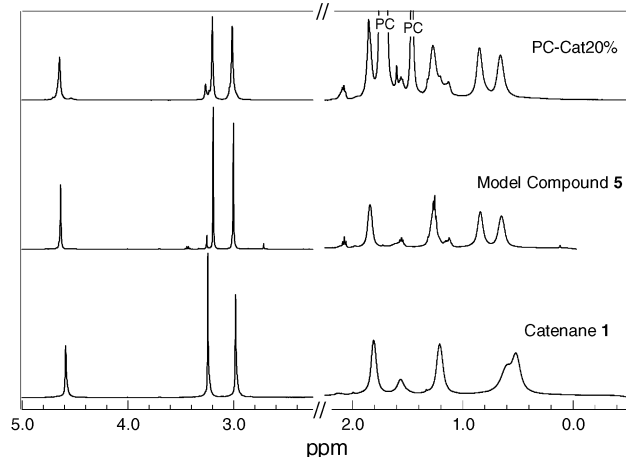


Figure 5. Aliphatic proton region of ^1H NMR spectra of **1** of PC copolymer containing 20% (w/w) catenane **1** and of the model compound **5** in tetrachloroethane- d_2 at 105 °C.

studies and see also the discussion of the NMR spectra below), and, since it could not escape from the reacting mixture by evaporation and since the total sample was injected in the SEC columns, all the catenane must be incorporated and no free catenane remains after SSP. By use of a polycarbonate-based universal calibration (see below), absolute molecular weights of the different copolymers were calculated (Table 1).

High-temperature (105 °C) ^1H NMR spectra in tetrachloroethane of the catenane **1** and the copolymer containing 20% (w/w) catenane are shown in Figure 5. The ^1H NMR spectra recorded at elevated temperatures to ensure any dynamic effects in the molecule, including spinning of the macrocyclic rings and rotamerization of the tertiary amide groups, were fast on the NMR time scale. For clarity, only the aliphatic region is

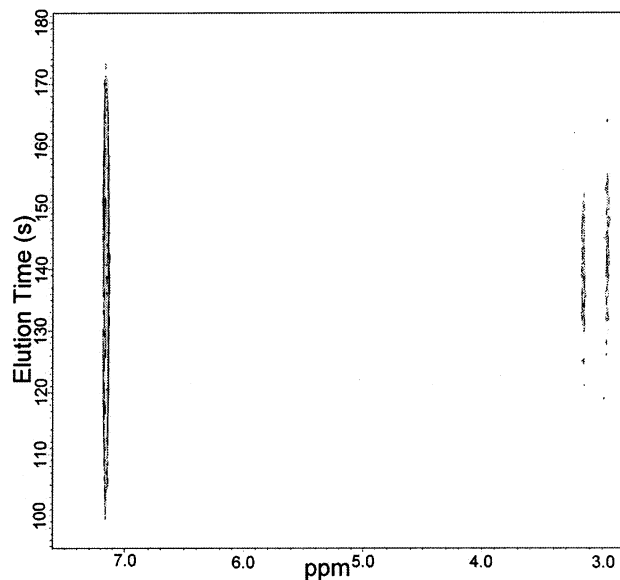


Figure 6. Contour plot, ^1H NMR coupled to SEC, of the intensity of PC and catenane signals according to elution time for PC copolymer containing 20% (w/w) catenane **1**.

shown (the aromatic region is dominated by the bisphenol A carbonate units). The spectra of the catenane monomer and the copolymer are different in several respects; for example, the broad signals observed around 0.5 ppm in the case of the catenane are replaced by well-resolved peaks at 0.86 and 0.67 ppm in the copolymer. To understand these changes, we synthesized (**1**, phenyl chloroformate, Et_3N , CH_2Cl_2 , 17 h, 83%) the phenol carbonate model compound **5** which mimics the repeat unit of the catenane upon incorporation into polycarbonate. The ^1H NMR spectrum of **5** (Figure 5) is almost identical to the spectrum of the copolymer, proving that catenane **1** has indeed been incorporated into polycarbonate as a comonomer.

Homogeneity and Linearity of the Copolymer. A shoulder is clearly visible on the left-hand side (high MW) of the 20% copolymer chromatogram presented in Figure 4. This shoulder is observed for copolymers containing 20 and 30% catenane but not for the 10% copolymer and provides evidence of some degree of heterogeneity in the polymerization process. Three possible origins of heterogeneity can be considered in such a reaction: (i) a composition heterogeneity of the copolymer across the molecular weight distribution, i.e., a change in average catenane concentration as a function of the polymer chain length, (ii) the presence of branched chains which are known to broaden molecular weight distributions and sometimes arise upon melt polymerization of polycarbonate,²⁵ or (iii) heterogeneities in the polymerization kinetics due, for example, to local differences in the diffusion kinetics of volatile reaction products (i.e. phenol).

SEC coupled to ^1H NMR was performed to check for homogeneity of the catenane concentration across the molecular weight distribution. Figure 6 shows a contour plot, in the elution region of the copolymer, summarizing the results. The peaks corresponding to the catenane methyl groups (~ 3 ppm, the most intense signal of the catenane) are approximately centered, with respect to the elution time scale, around the same time as the

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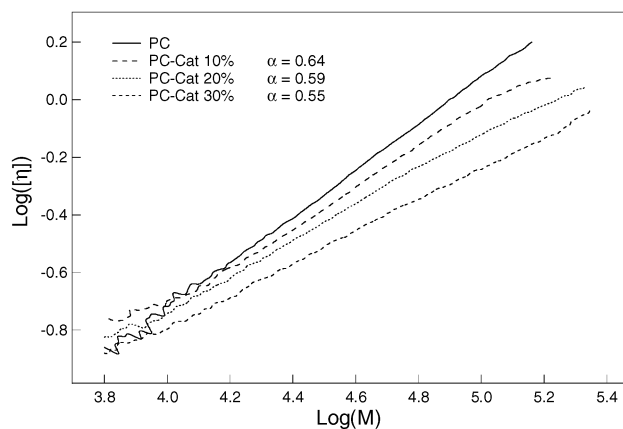


Figure 7. Viscosity laws of PC and copolymers containing 10, 20, and 30% (w/w) catenane **1** obtained from viscosimetry–SEC coupling.

7.1 ppm peak corresponding to the phenyl rings of the polycarbonate. The catenane signals are only visible in the central part of the copolymer distribution and not over the whole elution range because the copolymer concentration is too low at the tails of the distribution. Since the catenane and polycarbonate peaks are centered at the same position, it is reasonable to conclude that the catenane is homogeneously distributed throughout and that the shoulder observed on the chromatograms is not linked to a composition change.

Closer inspection of the ^1H NMR spectra of the copolymer reveals the presence of small peaks at 3.26, 2.09, 1.56, and 1.13 ppm (Figure 5) associated with macrocycle **2**. The macrocycle is not present in its free form since there is no corresponding peak on the chromatograms (Figure 4), so it must be present as macrocycle end-capping, probably produced by a thermal ring opening–ring closure mechanism (we have, indeed, observed that a small amount of macrocycle is produced when catenane **1** is heated for several hours at 215 °C under vacuum). Alternatively, the macrocycle could also be produced by exchange reactions between catenane amide groups and carbonate moieties. It is known that during melt blending of polycarbonate with polyamide, exchange reactions can occur to give ester and carbamate groups.^{26,27} The same reaction could occur in the present system, which would cause one catenane ring to open. In this case, the polymer would end up with a chain end-capped by one macrocycle and another chain containing a branching point. No direct evidence of the branching point can be obtained from the ^1H NMR spectra in Figure 5, but the chemical shifts for the opened macrocycle would probably be very similar to the closed one. The amount of macrocycle present as endgroups is typically $\sim 13\%$ by integration.

Since the presence of macrocycles in the copolymers points to the possibility of chain branching, intrinsic viscosity measurements coupled to SEC were performed to clarify the situation. Figure 7 shows the evolution of intrinsic viscosity $[\eta]$ vs molecular weight for the three catenane copolymers and a bisphenol A polycarbonate (PC) standard used as a reference. A universal calibration curve ($[\eta]M = f(\text{elution time})$) was built using the measured intrinsic viscosity for PC and corresponding

Table 2. Measured Glass Transition Temperatures for Pure PC and Different Copolymers Compared to a Calculated T_g Using Equation 5 and Considering the Copolymers as Pure PC

	T_g^a (°C)	
	measd	calcd
PC1 ^b	149	148
PC2 ^c	132	135
PC-cat. 10%	150	150
PC-cat. 20%	150	150
PC-cat. 30%	149	150
PC-Mac 10%	131	143
PC-fluorene 10%	149	137

^a T_g measured upon heating after crystallinity has been removed by a first heating–cooling cycle. ^b $M_w = 30\,700$. ^c $M_w = 10\,400$.

Mark–Houwink–Sakurada coefficients found in the literature²⁸ ($[\eta] = KM^\alpha$ with $\alpha = 0.8$, $K = 0.0119$ mL/g). This PC-based universal calibration was applied to the copolymers to convert retention times into molecular weights. An important observation is the linearity of the viscosity law in log–log scale for the copolymers over the molecular weight range where the viscosity signal is sufficiently linear (except perhaps for a small inflection around 70 000 for the 20% copolymer). This confirms the compositional homogeneity determined by the SEC NMR coupled experiments. Moreover, a constant power viscosity law precludes branching over the measured molecular weight range. The concentration of branched chains has to be vanishingly small at the low end of the measured range,²⁹ and their presence at the high end of the range should therefore become visible by a slope reduction on the log–log scale. The shoulder observed in the SEC chromatograms (Figure 4) is therefore most likely linked to heterogeneity in polymerization kinetics, yielding different populations of molecular weight distributions. The small inflection observed for the 20% copolymer may be indicative of a small amount of branching.

Solid-State Properties. Differential scanning calorimetry was used to determine the influence of catenane incorporation on the glass transition temperature of the polycarbonate copolymers. Table 2 shows the T_g values obtained for various copolymers and pure PC. These values are compared to a calculated T_g assimilating the copolymers to pure PC of the same molecular weight using the equation³⁰

$$T_g = 155 - 2.1 \times 10^5/M_w \quad (5)$$

whose validity has been verified for available PC standards. Molecular weights given in Table 1 were used for these calculations. By this method the effect of catenane or macrocycle incorporation on copolymer T_g can be estimated without the perturbing influence of molecular weight. T_g values of copolymers containing catenane units are identical to those of pure bisphenol A PC at the same molecular weight, even at a catenane concentration as high as 30% (w/w). Although the exact equality is something of a coincidence, the main conclusion is that the catenane comonomer mobility is comparable to that of bisphenol A carbonate units, which in turn is very suggestive of remarkable

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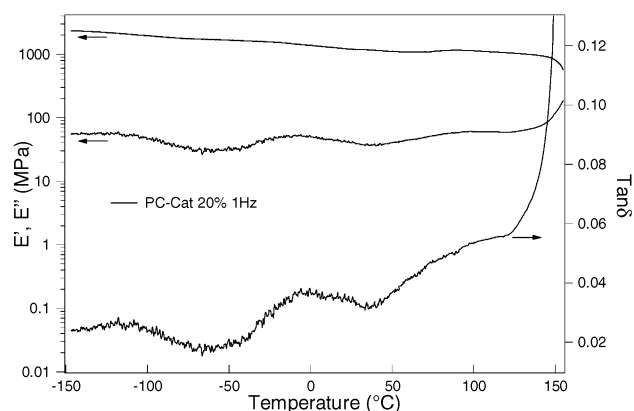


Figure 8. DMA spectra of the PC copolymer containing 20% (w/w) catenane **1**.

ring flexibility and mobility in the melt. For comparison, a PC copolymer containing 10% (w/w) of a very rigid monomer, fluorene bisphenol **6**, was prepared following the same procedure as that described for the catenane and macrocycle copolymers. In this case, the T_g increase vs pure PC is very large, about 12 °C.

The situation is very different for the copolymer containing 10% (w/w) macrocycle **2**. In this case T_g drops by about 12 °C vs pure PC at the same molecular weight, which is probably linked to the free volume increase resulting from the presence of macrocycle at the chain ends. The macrocycles are rather large, and it is known that chain ends have a strong impact on free volume and hence on T_g .³¹ From the copolymer M_n (Table 1), we calculate that about half of the chain ends in the polymer are macrocycles and half “ordinary” (i.e. phenyl carbonate and bisphenol A monocarbonate). By combining this information with eq 5 (and taking $M_w \approx 2.5M_n$ as a reasonable approximation for bisphenol A PC), we can roughly estimate the relative effect of macrocycle chain ends compared to ordinary (phenol/phenyl) ones on T_g . The calculation shows that macrocycles reduce T_g about 2.6 times more than standard chain ends at the same molar concentration.

To further investigate the influence of the catenane on polymer properties, dynamic mechanical analysis (DMA) was performed on thin films ($\sim 40 \mu\text{m}$) of the copolymer containing 20% (w/w) catenane **1**. The DMA spectrum recorded at 1 Hz is shown in Figure 8. Three transitions are clearly visible around -100 , -6 , and $+80$ °C. The first and third peaks, usually called γ and β transitions, are well-known transitions characteristic of pure polycarbonate segments associated with cooperative motions of several repeat units of PC³² and defects or constraints in the film,³³ respectively. The peak at -6 °C, however, is not observed in a DMA spectrum of pure polycarbonate and can be linked to motions related to catenanes. The γ transition of the PC is unchanged, and the DMA spectrum in Figure 8 is virtually a superposition of a PC spectrum with a new transition at -6 °C. This is the signature of noncoupled or weakly coupled segmental motions as demonstrated on studies on different PC copolymers.^{32,34} In other words, the incorporation of catenane into PC does not distinctively alter the inherent segmental

motions of the polycarbonate. This is understandable for the long, pure PC blocks but somewhat surprising for the catenane-rich blocks of the copolymer. While we cannot assign a precise motion to this new transition, the temperature where the transition occurs and the fact that the related motion is not coupled to the motion of PC segments both suggest that the motion is linked to a relatively large amplitude rearrangement of part of the catenane, such as a conformational change of the alkyl chains or (partial) rotation of the rings. Further work to elucidate the details of this process is ongoing.

Conclusions

The synthesis of [2]catenane-containing polycarbonates, the first mechanically linked analogues of a commercial polymer, has been achieved by solid-state copolymerization. This convenient method, involving solution blending of the comonomers, crystallization of the blend, and prolonged heating under vacuum, has been shown to quantitatively incorporate the catenane into bisphenol A polycarbonate. The catenane comonomer is homogeneously distributed across the molecular weight distribution (intermolecular homogeneity), but heterogeneity of polymerization kinetics probably occurs at high catenane content. The unexpectedly small influence of the catenane on T_g is suggestive of considerable internal mobility/flexibility of the catenane, certainly when compared to the strong influence of very rigid comonomers such as fluorene bisphenol. DMA on a copolymer thin film shows a new transition around -6 °C linked to catenane ring or chain movements. Remarkably, the motions of the PC and catenane segments are not coupled, even in the catenane-rich blocks of the copolymer. Overall the studies reveal some of the first examples of the effects on structure and properties of incorporating mechanical linkages into a polymer backbone.

Experimental Section

Measurements. Thermal analyses were performed on a Perkin-Elmer DSC 7 at a heating rate of 10 °C/min. ¹H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer, using 1,1,2,2-tetrachloroethane-*d*₂ as solvent and as internal standard at a temperature of 105 °C or on a Bruker Avance 400 MHz spectrometer using other solvents and temperatures. Size exclusion chromatography was carried out on a Waters system equipped with a Waters 410 differential refractometer and three (100, 1000, and 10000 Å pore sizes) 5 μm PLgel columns from Polymer Laboratories. Dichloromethane was used as solvent, and the flow rate was set to 1 mL/min. Before solubilization all SSP samples were dried under vacuum at 70 °C for 24 h and then heated at 280 °C for 1 min under dry nitrogen and quickly cooled to room temperature to obtain amorphous samples. On-line viscosimetric measurements were performed on a Waters Alliance GPCV 2000 system equipped with the same three columns and using the same conditions as for SEC. The on-line SEC/NMR system consisted of a JEOL Eclipse 500 MHz instrument as the detector and a Polymer Laboratories PLgel 5 μm mixed-D SEC column. Deuteriochloroform was used as the mobile phase (and internal lock) and was pumped (Gilson 305) at a flow rate of 0.7 mL/min. A commercially available flow cell (JEOL UK) was employed as the NMR observation cell. A typical sample of 200 μL (approximately 5% (w/v)) was injected onto the column. A 45° pulse angle and a repetition time of 0.3 s was used for the NMR data acquisition. Each spectrum obtained consisted of four scans of NMR data per increment, each spectrum consisting of 32K data points over a spectral width of 5000 Hz. DMA experiments were performed on a DMA 2980 from TA instruments used in tensile mode at a frequency of 1 Hz. Temperature was ramped from -140 to

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160 °C at a heating rate of 3 °C/min. Samples were prepared by spreading a 5% (w/w) copolymer solution in dichloromethane onto a glass slide. The samples were left for 4 h at room temperature for the solvent to evaporate, and the resulting films were held for a further 12 h at 50 °C under vacuum to remove remaining solvent and moisture. Typical sample size was 15 mm × 6 mm × 40 μm.

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Supporting Information Available: Synthetic details of all compounds (catenanes, model compound, PC oligomers and

copolymers) and X-ray crystallographic details of catenane **1** (and *bis-O*-allyl-protected **1**), catenane **3** (and *bis-O*-hydroxyethyl **3**), and macrocycle **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data for each structure (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-197295 (catenane **1**), CCDC-197294 (*bis-O*-allyl derivative of **1**), CCDC-197296 (catenane **3**), CCDC-197293 (*bis-O*-hydroxyethyl derivative of **3**), and CCDC-197297 (macrocycle **4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: Int. code + (1223)336-033. E-mail: teched@chemcryst.cam.ac.uk).

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