Solution and Solid-State Properties of Mechanically Linked Polycarbonates

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ABSTRACT: Solution and solid-state properties of novel mechanically linked polycarbonate copolymers are reported and compared to corresponding properties of a reference copolymer with identical chemical composition but no mechanical linkages. The unperturbed dimensions of the catenane copolymers in solution are smaller than for bisphenol A polycarbonate homopolymer, presumably reflecting favorable specific interactions between bisphenol A and catenane units. A difference is observed between the mechanically linked and unlinked analogues, pointing to a specific effect of the mechanical linkage. Crystallinity measurements suggest a segmented composition for the copolymers, consistent with the solid-state synthesis. The melting point of the catenane copolymers is lower than that of the bisphenol A polycarbonate homopolymer because of a copolymer effect. The melting point of a mechanically linked copolymer is higher than of the unlinked analogue, presumably because of the additional mobility in the melt introduced by free macrocycle chain ends vs interlocked catenane units.

1. Introduction

Poly[2]catenanes, i.e., macromolecules containing mechanical linkages between some of the repeat units in the polymer backbone, have drawn an increasing amount of attention over the past few years.[1−12] Apart from the synthetic challenge, the interest in such architectures comes from the expected changes in molecular flexibility and degrees of freedom, generating unusual and potentially useful improvements of properties compared to classic covalently linked polymers. The higher degree of freedom gained by the polymer chains if flexible catenane linkages are used is expected to strongly influence chain dynamics and conformation, thus affecting thermal, rheological, mechanical, and solution properties. The few examples of poly[2]catenanes reported thus far in the literature have only been prepared in minute quantities, and consequently, little characterization of their properties has been possible.[1−11] Those copolymers were generally synthesized in solution from unusual comonomers or high fractions of [2]-catenane units (up to 90−95% of the molecular weight). Moreover, the catenane linkages used often did not permit rotation of the rings. Comparison with conventional covalent backbone polymers to ascertain the role of the mechanical linkage on properties was therefore not really possible.

To obtain "bulk" quantities of a mechanically linked analogue of a commercial polymer, and hence be able to fully characterize it as well as make comparisons with its covalent counterpart, we chose a different strategy. A benzylic amide [2]catenane was homogeneously and quantitatively incorporated into bisphenol A polycarbonate (PC) as 10−30% w/w (2−6% by number of repeat units) by solid-state copolymerization.[12] A bisphenol A polycarbonate copolymer incorporating the corresponding "free" macrocycle was also prepared as "unlinked" analogue to the catenane copolymers. The convenient synthesis, involving the solution blending of polycarbonate oligomers and catenane (or macrocycle) before a prolonged heating under vacuum, offers the advantage of not being limited by sample size. Moreover, the amount of incorporated catenane can easily be controlled and varied over a wide range. The validity of this synthetic method was proved by solution ^{1}H NMR and size exclusion chromatography (SEC). The effect of the catenane on glass transition and mechanical properties of polycarbonate copolymers was studied by differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA). It was found that the catenane has a small influence on the polymer T_g, which is suggestive of a rather high internal mobility/flexibility of the catenane. A new transition around −6 °C, associated with catenane ring or chain movements, was observed by DMA, which also showed that PC and catenane segments motions are not coupled, even in the catenane-rich blocks of the copolymer. In this paper, further characterization of catenane−polycarbonate copolymers is reported with an emphasis on solution and crystallization properties. A comparison is made with the properties of the "unlinked" analogue for one composition.

2. Results and Discussion

Catenane **1** or macrocycle **2** (Scheme 1) and polycarbonate oligomers were copolymerized by solid-state polymerization (SSP) after solution blending and crystallization of the blend. The reaction was performed

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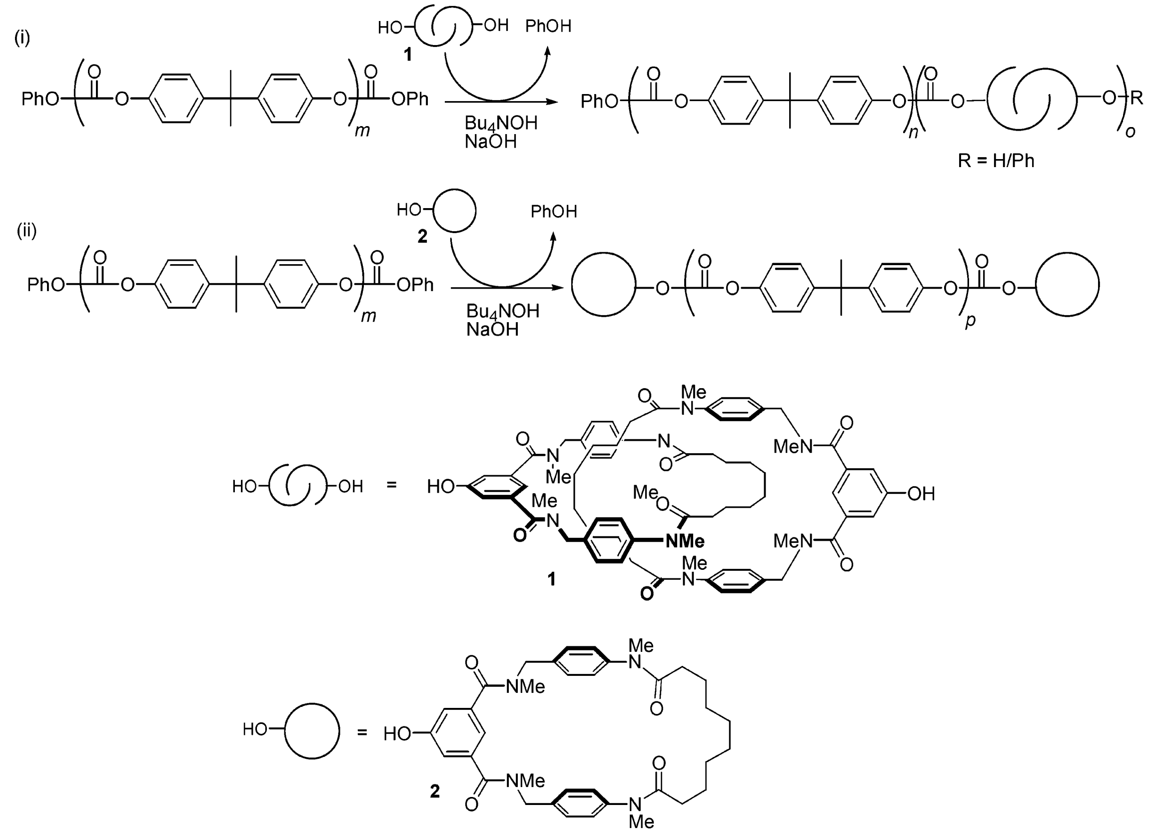
Scheme 1. Synthesis of Bisphenol A Polycarbonate Copolymers with (i) Catenane 1 and (ii) Macrocycle 2



under vacuum (approximately 6 × 10^{-2} mbar) by applying an increasing temperature program from 190 to 215 °C for about 28 h total. The detailed syntheses of the monomers and of the copolymers as well as proof that the catenanes have been homogeneously and quantitatively incorporated have been published elsewhere.[12]

Solution Properties. Intrinsic viscosity measurements coupled to SEC were performed on the copolymers and polycarbonate standards used as references. Using the measured intrinsic viscosity for PC and corresponding Mark–Houwink–Sakurada coefficients found in the literature[13] ($[\eta] = KM^{\alpha}$ with $\alpha = 0.80$, $K = 0.0119$ mL/g), a universal calibration curve ($[\eta]M = f$(elution time)) was obtained. Retention times were converted into molecular weights by applying this PC-based universal calibration to the copolymers. The viscosity laws are presented in Figure 1, and the absolute molecular weights calculated from this polycarbonate-based universal calibration are summarized in Table 1. The exponent of the viscosity law decreases with increasing catenane concentration, going from $\alpha = 0.80$ for pure PC to $\alpha = 0.55$ for 30% w/w catenane, almost the value in θ conditions (Figure 1). Catenane presence strongly affects polymer–solvent interactions in dichloromethane. This is qualitatively confirmed by the increasing difficulty to solubilize copolymers with increasing catenane concentration, the 30% copolymer requiring at least 2 days under vigorous stirring. Viscosities for a given molecular weight, and hence hydrodynamic volumes, are smaller for the copolymers as compared to PC and decrease with increasing catenane concentration, in agreement with reduced excluded-volume effects.

Table 1. Molecular Weights and Polydispersity of a PC Homopolymer and Copolymers Containing 10, 20, and 30% w/w Catenane 1 and 10% w/w Macrocycle 2 Obtained by SEC–Viscosity in CH_2Cl_2

	M_w (kg/mol)	M_n (kg/mol)	PDI
PC	33	13	2.5
PC-Cat 10%	40	16	2.5
PC-Cat 20%	41	9.9	4.1
PC-Cat 30%	39	8.1	4.8
PC-Mac 10%	18	6.5	2.8

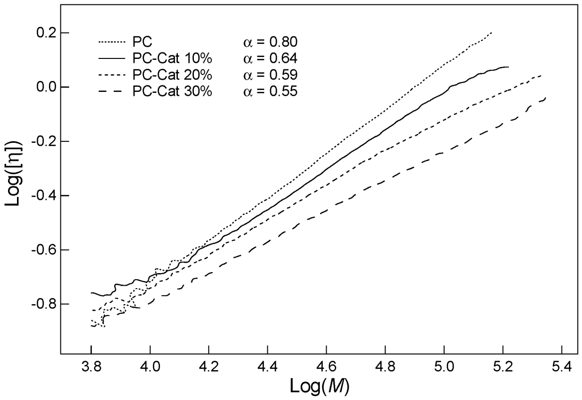


Figure 1. Viscosity laws of PC and copolymers containing 10, 20, and 30% w/w catenane **1** obtained from viscosimetry–SEC coupling.

Figure 2 presents intrinsic viscosity results for the copolymers containing 10% catenane **1** and 10% macrocycle **2** (the monofunctional macrocycle is exclusively incorporated as chain ends). As expected, because of identical average composition, Mark–Houwink exponents are almost identical, 0.64 and 0.66, respectively, but intrinsic viscosity for a given molecular weight is lower for the macrocycle copolymer than for the cat-

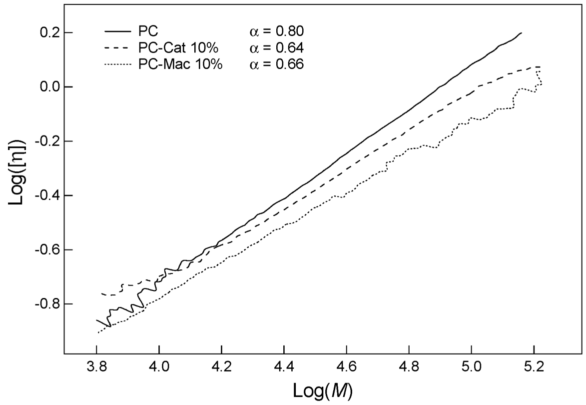


Figure 2. Viscosity laws of PC and copolymers containing 10% w/w catenane **1** and macrocycle **2** obtained from viscosimetry−SEC coupling.

enane copolymer, indicating a smaller hydrodynamic volume. This discrepancy points to a specific effect of the mechanical linkage on chain conformation.

To understand the short- or long-range nature of the observed effects, we have decided to calculate the unperturbed mean-square radius of gyration of the copolymers from the viscosity data. We have used the analysis of Maeda et al.,[14] who have modified a bead−string model by Yamakawa[15] and applied it to relatively low molecular weight polycarbonate to determine unperturbed dimensions. This method has also been successfully applied to random copolymers.[16] This approach has been preferred over the well-known Stockmayer−Fixman extrapolation[17] because the latter is known to yield inaccurate results for the strongly interacting polycarbonate−dichloromethane system.[13,14] On the other hand, the Yamakawa model modified by Maeda et al. is consistent with small-angle neutron scattering results.[14] Yamakawa considers a wormlike chain of persistence length q and composed of N beads of diameter d. Maeda et al. use the following relations:

$$(M^2/[\eta])^{1/3} = A + BM^{1/2} \tag{1}$$

where

$$A = A_0\Phi_0^{-1/3}M_L \tag{2}$$

and

$$B = B_0\Phi_0^{-1/3}(6\langle S^2\rangle_0/M)^{-1/2} \tag{3}$$

Φ_0 is the Flory viscosity constant (2.87×10^{23} mol^{-1}), and M_L is the molar mass per unit contour length. A_0 and B_0 are function of q and d. B_0 being very close to 1 for semiflexible chains such as PC,[13] the slope of $(M^2/[\eta])^{1/3}$ vs $M^{1/2}$ will directly yield $\langle S^2\rangle_0/M$, the unperturbed mean-square radius of gyration per unit molar mass. Figure 3 presents such plots for PC and for copolymers containing 10, 20, and 30% catenane and 10% macrocycle. For a good solvent system, which is the case for PC in dichloromethane, the relationship shows a downward curvature at high molecular weight and should only be used in the low molecular weight linear portion where excluded-volume effects are small. In a less good solvent, which is the case for all copolymers, the relationship is perfectly linear. The mean-square radii of gyration per unit mass calculated from these values are given in Table 2. The unperturbed radius of gyration per unit mass gradually decreases with increasing catenane concentration. Again, the macrocycle end-capped copolymer shows a different behavior from that of the corresponding 10% catenane copolymer. The smaller radius of gyration for the copolymers has been confirmed by light scattering measurements although the results are not quantitative in the absence of dn/dc values for the copolymers. Under the naive assumption that $\langle S^2\rangle_0/M$ contributions of copolymer segments are additive, the observed decrease with increasing catenane concentration is unexpected: the "contribution" of catenane segments is found to be negative. However, it is well-known that no truly θ conditions exist for copolymers.[18] Calculation of unperturbed dimensions from measurements in non-θ solvents, as described above, only eliminates excluded-volume effects. It does not remove the effects of specific monomer−monomer interactions, which will persist even in θ solvent. This can be inferred from the Stockmayer equation developed for copolymer solutions:[19]

$$\chi_{1C} = \phi_A\chi_{1A} + \phi_B\chi_{1B} - \phi_A\phi_B\chi_{AB} \tag{4}$$

where ϕ_A and ϕ_B are the volume fractions of A and of B in the copolymer, χ_{1A}, χ_{1B}, and χ_{1C} are the interaction parameters for the homopolymers and copolymer in the same solvent, and χ_{AB} is the parameter characterizing the A−B interactions. Since our viscosity measurements have shown that dichloromethane is almost a θ solvent for the 30% copolymer, χ_{1C} must be closed to 0.5 in that case. On the other hand, dichloromethane is a very good solvent for bisphenol A PC and probably also for the catenane carbonate homopolymer (which we could not synthesize by our method), and therefore χ_{1A} and χ_{1B} are much lower than 0.5. Indeed, the solubility parameter of catenane carbonate units has been compared to the one found for bisphenol A carbonate units using the tables published by Hoy.[20] The calculated mismatch does not exceed 0.1 [cal/cm^3]$^{1/2}$. For χ_{1C} to be close to 0.5, χ_{AB} must be strongly negative according to eq 4, and therefore favorable specific interactions between catenane and bisphenol A segments must exist.

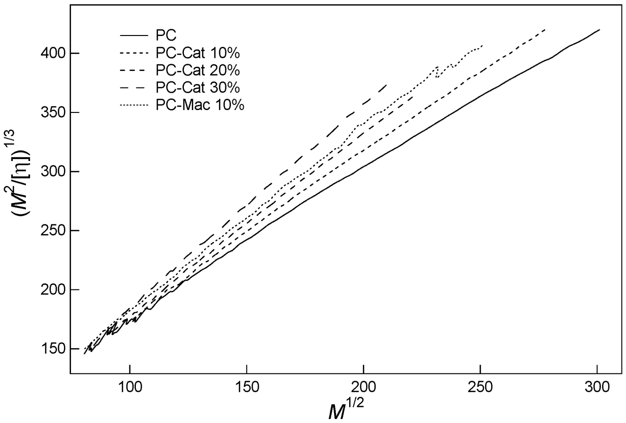


Figure 3. Plots of $(M^2/[\eta])^{1/3}$ vs $M^{1/2}$ derived from viscosimetry results for a PC homopolymer and the catenane and macrocycle copolymers.

Table 2. Unperturbed Mean-Square Radius of Gyration per Unit Molar Mass Determined by the Maeda Method[14]

	$\langle S^2\rangle_0/M$ (cm^2 mol/g)		$\langle S^2\rangle_0/M$ (cm^2 mol/g)
PC	2.2×10^{-17}	PC-Cat 30%	1.3×10^{-17}
PC-Cat 10%	2.0×10^{-17}	PC-Mac 10%	1.6×10^{-17}
PC-Cat 20%	1.6×10^{-17}		

Table 3. Melting Temperature, Heat of Fusion, and Corrected Crystallinity for Bisphenol A Polycarbonate Homopolymer and Copolymers Containing 10, 20, and 30% w/w Catenane 1 and 10% w/w Macrocycle 2 Obtained by DSC

	T_m (°C)	ΔH_m (J/g)	corrected crystallinity (%)
PC	255	46	34
PC-Cat 10%	247	30	25
PC-Cat 20%	245	23	21
PC-Cat 30%	239	21	22
PC-Mac 10%	239	29	24

A suggestive observation from Table 2 is that the unperturbed radius of gyration per unit mass for the 10% w/w macrocycle copolymer is lower than for the 10% w/w catenane copolymer. At the same concentration, macrocycle interactions with bisphenol A PC segments are therefore stronger as compared to catenane interactions. This can be rationalized by comparing the interlocked catenane rings with the free macrocycles from the standpoint of interactions with closest neighbors and clearly points to a specific effect of mechanical linkage.

Solid-State Properties. DSC has been used to determine the influence of catenane incorporation on the crystallization properties of polycarbonate copolymers. The melting temperature and the enthalpy of fusion (ΔH_m) of the copolymers have been measured right after SSP and compared to those of a pure polycarbonate prepared by SSP following the same temperature program. The crystallinity of the samples has been calculated on the basis of a heat of fusion of 133.8 J/g for pure PC crystal.[21] The crystallinity values for the copolymers have been corrected by the weight fraction of PC units to yield a value expressing the crystallinity of the crystallizable fraction, i.e., segments of pure PC. The results are reported in Table 3. The "corrected" crystallinity drops by about 10% compared to that of pure PC for the copolymer containing 10% catenane and stays almost constant at higher catenane concentration. It is important to note that the PC homopolymer has significantly lower molecular weight than the copolymers. This probably explains most of the discrepancy between homo- and copolymers crystallinity since low molecular weight favors high crystallinity. The crystallinity of the copolymer containing 10% macrocycle is very similar to the 10% catenane copolymer. The constant "corrected" crystallinity suggests that the copolymer chains are composed of pure bisphenol A PC crystallizable segments separated by uncrystallizable segments of random bisphenol A and catenane copolymer where the catenane concentration is higher than the average value. This picture is consistent with the idea that SSP occurs mainly in the amorphous phase[22,23] and thus concentrates the catenane comonomers on segments originally confined to the amorphous phase. When the overall catenane concentration increases, the local concentration in the uncrystallizable segments increases, but the segments of pure PC are not modified and hence the corrected crystallinity does not change either. The melting temperature systematically decreases when the catenane concentration increases. (MW and polydispersity differences between the samples do not seem to affect this trend.) This can be rationalized by two complementary arguments. It is indeed known from Flory's theory of the thermodynamic melting point depression by diluents that the melting point of a copolymer is affected by specific interactions with the comonomer.[24] This is consistent with the favorable interaction parameter deduced from the solution data (see above). It is also logical that the presence of a comonomer in the amorphous phase can modify the interfacial energy of the crystalline lamellar fold plane and hence affect the melting point through the Thompson–Gibbs equation:

$$T_m = T_m^0\left(1 - \frac{2\sigma_e}{l_c \Delta H_m^0}\right) \tag{5}$$

with T_m the measured melting point, T_m^0 the thermodynamic melting point, σ_e the lamellar fold plane interfacial energy, l_c the lamellar thickness, and ΔH_m^0 the bulk melting enthalpy.

An interesting observation is the significantly lower melting point of the 10% macrocycle copolymer compared to the corresponding catenane copolymer. This effect cannot be due to a "copolymer" effect since the comonomer concentrations are identical. By reference to eq 5, we can argue that the bulk melting enthalpy and crystal fold surface energy should be similar for the catenane and macrocycle copolymers at the same level of incorporation. Despite the lack of data in the literature about l_c for polycarbonate, we can reasonably guess that l_c should also be similar for the catenane and macrocycle since the solid-state copolymerization was performed more than 100 deg below T_m^0, in a region were the dependence of l_c on ΔT is probably rather flat. Therefore, the difference of 8 °C between the measured melting points (Table 3) is presumably due to a difference in thermodynamic melting point. This clearly points to an entropic origin for the difference since $T_m^0 = \Delta H/\Delta S$, the ratio of melting enthalpy and entropy. The higher melting entropy for the macrocycle end-capped copolymer in the melt is most probably due to the increased mobility and concentration of the chain ends. We have indeed shown that the presence of macrocycle chain ends decreases T_g about 2.6 times more than "normal" phenyl carbonate chain ends do at the same molar concentration.[12] Macrocycle chain ends therefore clearly increase the mobility of the polycarbonate copolymer. The catenane comonomer, on the other hand, has little effect on T_g of the copolymer and can be considered "neutral" from the standpoint of mobility.[12] Even if we had catenane and macrocycle copolymers at exactly the same molecular weight, we would still presumably have a lower melting point for the macrocycle copolymer because of this mobility effect. The difference would almost certainly disappear if the macrocycles were included in the chain.

3. Conclusion

Solution and crystallization properties of novel mechanically linked co-polycarbonates and unlinked analogues have been determined. In solution, the presence of the catenane comonomer strongly modifies the interactions of the copolymer with dichloromethane, leading to almost θ conditions at 30% w/w catenane concentration. The unperturbed dimensions of the copolymers have been determined from viscosity measurements and have been shown to decrease with increasing catenane concentration. Strong favorable specific interactions between catenane and bisphenol A carbonate segments, which should induce shrinkage of the polymer coil, are suggested to explain the decrease of the unperturbed radius of gyration. A clear difference is observed between the unperturbed radii of gyration per unit mass of a 10% catenane copolymer and the mechanically unlinked analogue (macrocycle end-capped copolymer), pointing to a specific effect of the mechanical linkage. Crystallinity measurements suggest that the copolymers are not truly random but composed of crystallizable (pure bisphenol A PC) and uncrystallizable (catenane comonomer-rich) segments. As the overall comonomer concentration increases, the catenane accumulates in the uncrystallizable segments, leaving the crystallizable segments unaffected. This picture is consistent with the SSP synthesis. A decrease in melting point of the catenane copolymer is observed vs the bisphenol A polycarbonate homopolymer. This is mainly due to a "copolymer effect". On the other hand, a macrocycle end-capped copolymer has lower melting point than the mechanically linked equivalent, at identical comonomer concentration. This cannot be explained by a copolymer effect and probably points toward mechanical linkage effect, i.e., the additional entropy in the melt brought about by the free macrocycle chain ends vs interlocked catenanes.

4. Experimental Section

Measurements. Thermal analysis was performed on a Perkin-Elmer DSC 7 at a heating rate of 10 °C/min. SEC experiments were carried out on a Waters system equipped with a Waters 410 differential refractometer, a multiangle light scattering detector Dawn DSP from Wyatt Technology, and three (100, 1000, and 10 000 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 have been performed on a Waters Alliance GPCV 2000 system equipped with the same three columns used in SEC and used under the same conditions.

Solvents and Reagents. All the solvents used were commercial HPLC grade. All other chemicals were purchased from Aldrich or Acros and used as received.

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