

Topological effects on blend miscibility

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Abstract: Thermodynamics of mixing is shown to be quite sensitive to changes in the topology of blend components. Cyclic bisphenol A carbonate oligomers are miscible with a wider range of polystyrene [PS] molecular weights than are chemically equivalent linear oligomers. The Flory–Huggins mean-field theory predicts the shape of phase boundaries quite well for linear PS/linear polycarbonate [PC] blends as well as for linear PS/cyclic PC blends. However, the interaction parameter is strongly dependent upon topology with $\chi_{PS_L/PC_C} < \chi_{PS_L/PC_L}$. This result is explained in terms of a topological repulsion between rings which is expected to be quite general.

Introduction

The objective of the present work is to investigate the influence of topology on the thermodynamics of mixing. While the equilibrium thermodynamic properties of blends of linear polymers continue to be the subject of great commercial and academic interest,¹⁻⁴ the effect of topological variations in blend components has only recently been considered.⁵⁻⁶

The effect of topological variations in blend components will be addressed in the present work by comparing the miscibility of bisphenol A carbonate cyclic oligomers [BPACY] as well as that of equivalent linear oligomers with a series of narrow molecular weight distribution polystyrenes. The synthesis of BPACY as well as their ring opening polymerization to form high molecular weight polycarbonate has recently been reported by Brunelle et. al.⁷⁻⁹ The determination of the critical polystyrene molecular weight for complete miscibility allowed the Flory-Huggins χ parameter for linear carbonate oligomer/polystyrene blends as well as cyclic carbonate oligomer/polystyrene blends to be determined.

Experimental

The synthesis and characterization of the BPACY as well as their linear analogues, have been described in detail elsewhere.⁷⁻¹⁰ The synthesis scheme is outlined in Figure 1 and the characterization data are collected in Table 1. Two different end groups were utilized in the case of the linear oligomers: diphenyl carbonate and grouped oligomers (PCLN) and di-(4-isopropyl) phenyl carbonate end capped oligomers [IPLN].

TABLE 1. Cyclic and linear carbonate oligomers

	T_g (°C)	Density (g/cc)	M_n (NMR)	M_n (LC)	M_w	M_z
BPACY	147	1.197 ± 0.001		1144	1529	2228
BPACY-HF	146	1.196		1493	1987	2783
BPACY-LF	136	1.197		876	997	1140
PCLN	82	1.214	1501	1558	2074	2716
PCLN-LF	70	1.215	1350	1195	1367	1518
IPLN	73	1.183	1406	1012	2182	3106
IPLN-LF	70	1.181	1518	1193	1803	2050

FIGURE 1. Synthesis of Cyclic and Linear Oligomers

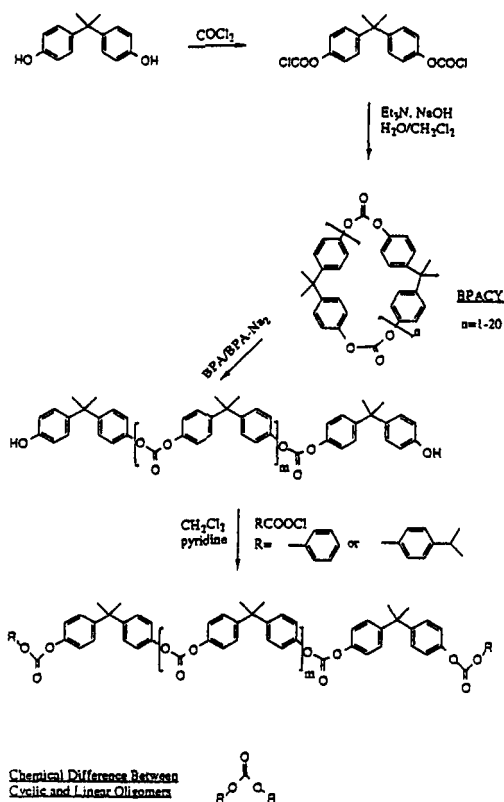
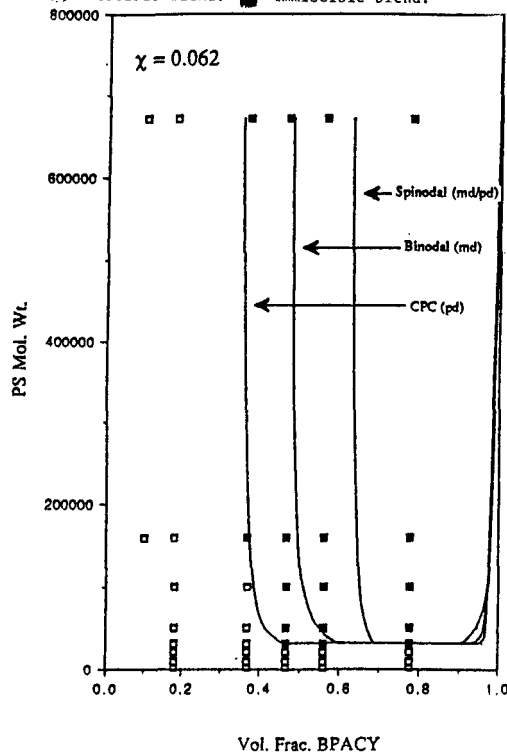


FIGURE 2. Miscibility of polystyrenes of various molecular weights vs composition of BPACY. □ Miscible blend. ■ Immiscible blend.



The T_g 's of the cyclic oligomers are significantly higher than those of linear oligomers of similar molecular weight. This phenomenon has been observed in several other ring systems and has been explained in terms of the lower configurational entropy of glasses of ring polymers relative to that of linears.¹¹ Although T_g usually increases with decreasing molecular weight for ring systems, the slight reduction in T_g for BPACY-LF can be explained in terms of a large increase in intramolecular stiffness for the smaller rings.¹⁷

Blends of cyclic and linear bisphenol A carbonate oligomers with various chemically dissimilar linear polymers were prepared via solution casting. Blend components were dissolved in hot *o*-dichlorobenzene [0.01 wt% Ultraxon 626, GE Spec. Chem., added as anti-oxidant] and cast onto a glass petri dish which had been treated with chlorotrimethylsilane. Films were cast at 165°C in order to prevent crystallization of the carbonate oligomers. Films were dried under vacuum [slight N_2 purge] at temperatures between 130°C and 160°C, depending upon T_g 's of components, for at least three days. Thermal gravimetric analysis [Perkin-Elmer TGA-7] confirmed complete removal of casting solvent. Blend T_g 's were determined using a Perkin-Elmer DSC-7 at a heating rate of 20°C/min. All samples were held at 200°C for 5 min. in the DSC and quenched prior to analysis. Thermodynamic equilibrium was assumed to have been reached during this 5 min. hold at 200°C. The one phase/two phase boundary was then determined from the T_g measurements. Miscibility (i.e., a composition in the one phase region) was judged based on the appearance of a single T_g . Blends containing BPACY were analyzed by GPC to ensure that no polymerization occurred during thermal treatment.

Results and Discussion

The observation of a miscibility gap in terms of polystyrene molecular weight enables the determination of the Flory-Huggins χ parameter which will be discussed later. Therefore, in order to more completely describe the miscibility of BPACY with polystyrene, blends of BPACY and polystyrenes of molecular weights between 1.5K and 670K, of varying composition, were prepared and analyzed by DSC.

BPACY are miscible at all compositions with polystyrenes of molecular weight less than 20.4K. Phase separation occurs at BPACY compositions greater than 40 wt% for blends with PS(31.5K). Similar behavior is observed for blends of BPACY with PS(51K) and PS(100K). Blends of BPACY with PS(160K) as well as PS(670K) phase separate at compositions greater than 20 wt% BPACY. These results are summarized in Figure 2.

The T_g -composition behavior of phase separated systems reveals that when phase separation occurs one phase is essentially pure BPACY while the composition of the PS rich phase is dependent on the overall blend composition. In all cases the polystyrene rich phase contains more BPACY at higher contents of BPACY in the blend. For example, the T_g of the PS rich phase in a 50/50 blend of BPACY/PS(31.5K) is lower than that of the PS rich phase of a 80/20 blend. The significance of this will be discussed later.

Similar results were obtained for blends of BPACY-HF with the various molecular weight polystyrenes. As expected the critical polystyrene molecular weight for miscibility is lower for this higher molecular weight fraction of cyclic oligomers. BPACY-HF are miscible at all compositions with PS(4K) but form immiscible blends with PS(10K) at compositions between 20 and 80 vol% BPACY-HF. The low molecular weight fraction of cyclic oligomers, BPACY-LF, were found to be miscible with PS(20.4K) at all compositions and immiscible with PS(51K) for BPACY-LF compositions greater than 50 wt%.

The miscibilities of bisphenol A carbonate linear oligomers, PCLN, PCLN-LF, IPLN and IPLN-LF with various molecular weight polystyrenes were also characterized in order to complete the investigation of the topological effects on miscibility. The critical polystyrene molecular weight data for miscibility for all oligomers investigated is summarized in Table 2.

TABLE 2. Critical polystyrene molecular weights for miscibility and calculated interaction parameters.

	<u>Miscible</u>	<u>Immiscible</u>	$\chi_{PSL/PCC}$ or $\chi_{PSL/PCL}$
BPACY	PS 20.4 K	PS 31.5 K	$0.057 < \chi_{PSL/PCC} < 0.062$
BPACY-LF	PS 20.4 K	PS 51 K	$0.076 < \chi_{PSL/PCC} < 0.087$
BPACY-HF	PS 4 K	PS 10 K	$0.074 < \chi_{PSL/PCC} < 0.076$
PCLN		PS 1.475 K	$0.13 < \chi_{PSL/PCL}$
PCLN-LF	PS 1.475 K	PS 2.5 K	$0.13 < \chi_{PSL/PCL} < 0.16$
IPLN		PS 1.475 K	$0.12 < \chi_{PSL/PCL}$
IPLN-LF	PS 1.475 K	PS 2.5 K	$0.11 < \chi_{PSL/PCL} < 0.14$

Determination of Flory-Huggins χ Parameter

Qualitatively, the cyclic carbonate oligomers are significantly more miscible with polystyrene than are the equivalent linear oligomers. The critical polystyrene molecular weight for the highest molecular weight cyclic fraction, BPACY-HF ($M_w = 1987$), is between 4K and 10K while that for both the lower molecular weight linear fractions PCLN-LF ($M_w = 1367$) and IPLN-LF ($M_w = 1803$) is between 1.5K and 2.5K. Application of Flory-Huggins solution theory enables a more quantitative evaluation of the topological effects on the thermodynamics of mixing.

In order to analyze the data accurately, polydispersity in the oligomers must be taken into account. Polydispersity affects the phase diagram by removing the coincidence between the binodal and the cloud point curve.

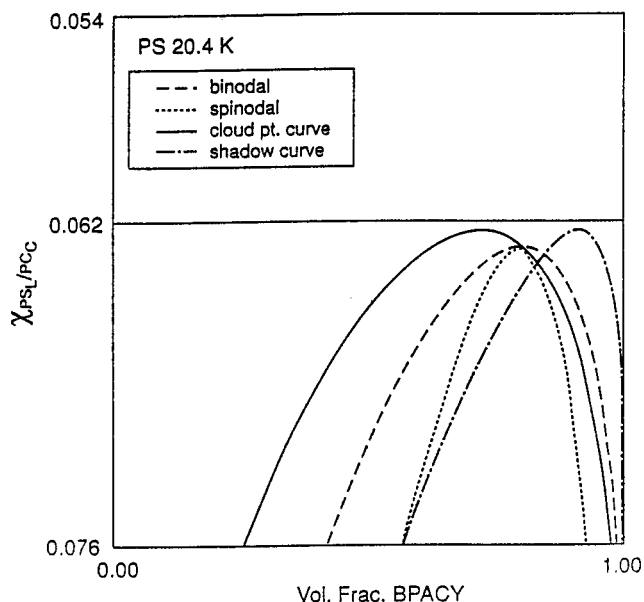
Thus, there exist three separate curves representing:

1. The locus of cloud points [Cloud Point Curve].
2. The locus of incipient phases coexisting with corresponding principle phases [Shadow Curve.]
3. The locus of coexisting phases as temperature [i.e. χ] is changed [Coexistence Curve].

Biosym software provides algorithms for the determination of these curves as well as spinodals employing methods described by others previously.¹²⁻¹⁷

The calculated phase boundary for BPACY/PS(20.4K) blends is shown in Figure 3. The effects of polydispersity are quite dramatic. The cloud point curve for the pseudo-binary is skewed relative to the binodal calculated assuming monodisperse components. In addition the critical point has shifted down the right branch of the spinodal toward higher BPACY compositions. Note also the shift in the shadow curve relative to the cloud point curve. The spinodal for the pseudo-binary case is coincident with that for the monodisperse case since the weight average degree of polymerization of BPACY was used for monodisperse calculations.

FIGURE 3. Phase diagram for polystyrene of 20,400 molecular weight with BPACY, showing effects of polydispersity.


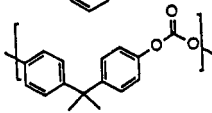
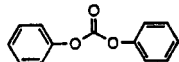
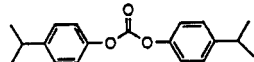


The compositions at the binodals [assuming both components are monodisperse], spinodals and cloud point curves for a particular value of the interaction parameter were obtained via calculations of this type for the range of polystyrene molecular weights studied. The results for $\chi_{PSL}/P_{CC} = 0.062$ are summarized in Figure 2. In all cases, the Flory-Huggins cloud point curves calculated using an interaction parameter estimated from critical molecular weight data represent the experimental phase boundaries very well. The calculated spinodals and monodisperse binodals are far too narrow. With proper consideration of polydispersity, the mean-field Flory-Huggins theory predicts the shape of the phase boundary quite well for both cyclic/linear blends as well as linear/linear blends. These results also demonstrate the errors involved in interpreting partial miscibility in terms of spinodal criteria as is often done in the literature due to the difficulty in calculating binodals and cloud point curves.

The calculation of the pseudo-binary phase boundaries also yields an explanation for the dependence of the composition of the polystyrene rich phase on the overall blend composition. In truly binary systems [i.e. monodisperse] with a composition independent χ , a horizontal tie line can be drawn connecting two points on the binodal. These two points represent equilibrium phase compositions at a particular value of the interaction parameter [or temperature]. Further, these two compositions are coupled; when one represents the principal phase the other represents the incipient phase and vice versa. In contrast, a simple horizontal tie line cannot be drawn if either of the components are polydisperse since, as discussed above, the binodal can no longer be represented as a simple two dimensional curve. Instead, it is essential to realize that coupled to the cloud point curve, representing the locus of principal phases is the shadow curve representing the locus of incipient phases. These curves are generally not coincident when the components are polydisperse.

As noted in Figure 1 the chemical difference between a linear oligomer and a cyclic due to the presence of end-groups is only the addition of a di-aryl carbonate. We have attempted to keep the end-groups as chemically similar to bisphenol A carbonate as possible and further, have investigated two different end-groups. The chemical nature of the end-groups relative to polystyrene and bisphenol A polycarbonate can be interpreted in terms of their solubility parameters [see Table 3]. The solubility parameter for diphenyl carbonate is higher than that for both polystyrene and polycarbonate. Therefore, we would expect the presence of this end-group to result in slightly decreased miscibility. Diisopropylphenyl carbonate has a solubility parameter which lies between that of polycarbonate and polystyrene, in this case we would expect the presence of end-group to make the linear oligomer slightly more miscible with polystyrene than a cyclic. In any case, χ_{PSL}/P_{CL} was not found to depend strongly on the nature of the end-group [see Table 2] and more importantly the difference between χ_{PSL}/P_{CL} is far too large to be due to the chemical nature of the end-group.

Table 3 Solubility parameters of polymers and end-groups.

	δ (cal/cc) ^{1/2}
	9.0 ^A
	10.4 ^A
	11.5 ^B
	10.1 ^B

^A Van Krevelen, D.W.; *Properties of Polymers*, Elsevier: New York, 1976.
^B Estimated by group contribution methods given by Van Krevelen, [see above].

Summary

The thermodynamics of mixing have been shown to be quite sensitive to changes in the topology of blend components. Cyclic bisphenol A carbonate cyclic oligomers are miscible with a wider range of polystyrene molecular weights than are chemically equivalent linear oligomers. The Flory-Huggins mean field theory predicts the shape of phase boundaries quite well for linear polystyrene/linear polycarbonate blends as well as for linear polystyrene/cyclic polycarbonate blends. However, the interaction parameter was determined to be strongly dependent upon topology with $\chi_{\text{PSL/PCC}} < \chi_{\text{PSL/PCL}}$. This result has been explained in terms of a topological repulsion between ring polymers which is expected to be quite general.⁽¹⁸⁾

References

1. L.A. Utracki, *Polymer Alloys and Blends: Thermodynamics and Rheology*, Hanser, New York (1989).
2. K. Solc, Ed., *Polymer Compatability and Incompatibility: Principles and Practices*, MMI, New York (1982).
3. D.R. Paul and S. Newman, Eds., *Polymer Blends*, Vol. 1 & 2, Academic Press, New York (1978).
4. O. Olabisi, L.M. Robeson and M.T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York (1979).
5. M.M. Santore, C.C. Han and G.B. McKenna, *Macromolecules* **25**, 3416 (1992).
6. G. Hadziioannou, P.M. Cotts, G. ten Brinke, C. Han, P. Lutz, C. Strazielle, P. Rempp and A.J. Kovacs, *Macromolecules* **20**, 493 (1987).
7. D.J. Brunelle, E.P. Bowden and T.G. Shannon, *J. Amer. Chem. Soc.* **117**, 2399 (1990).
8. D.J. Brunelle and T.G. Shannon, *Macromolecules* **24**, 3035 (1991).
9. D.J. Brunelle, Ed., *Ring Opening Polymerization* Ch. 11, Hanser Verlag, Munich.
10. D.J. Brunelle, personal communication.
11. A.J.-M. Yang and E.A. Di Marzio, *Macromolecules* **24**, 6012 [and references therein] (1991).
12. R. Koningsveld and A.J. Staverman, *J. Polym. Sci. A-2* **6**, 305 (1968).
13. R. Koningsveld and A.J. Staverman, *J. Polym. Sci. A-2* **6**, 325 (1968).
14. R. Koningsveld and A. J. Staverman, *J. Polym. Sci. A-2* **6**, 349 (1968).
15. R. Koningsveld and L.A. Kleintjens, *J. Polym. Sci. Polym. Symp.* **61**, 221 (1977).
16. K. Solc, *Macromolecules* **3**, 665 (1970).
17. For details see: (a) *Polymer User Guide Pt. 2*, version R-5.0, San Diego: Biosym Technologies (1992); (b) C. Qian, S.J. Mumby and B.E. Eichinger, *Polymer Preprints* **31** (2), 691 (1990); (c) S.J. Mumby, P.B. Sher and B.E. Eichinger, *Polymer* in press.
18. W.L. Nachlis, J.T. Bendler, R.P. Kambour and W.J. MacKnight, *Macromolecules* in press.