Effects of Polycarbonate Molecular Structure on the Miscibility with Other Polymers

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ABSTRACT: An exploratory investigation of the equilibrium phase behavior of binary blends of various polycarbonates with polystyrene (PS), poly(methyl methacrylate) (PMMA), bisphenol A polycarbonate (BPA-PC), and tetramethylbisphenol A polycarbonate (TMPC) is described. The variations in polycarbonate structure primarily involved substitutions onto the phenyl rings in two or four of the available positions and changing the connector group between the two phenyl rings, or both, of the bisphenol monomer. Polar connector groups promote favorable interactions with PMMA while ring substitution with methyl groups improves miscibility with PS. Other structural changes in the connector group or on the phenyl rings can act against the miscibility of polycarbonates with PMMA or PS. A wide range of polycarbonates was found to be miscible with BPA-PC and TMPC. The effect of PMMA and PS molecular weight on the miscibility of blends with selected polycarbonates was used to obtain more detailed information about their interactions. The use of this information to design useful polymer blends is discussed.

Introduction

The interactions of the polycarbonate based on bisphenol A (BPA-PC) with poly(methyl methacrylate) (PMMA) are, according to recent evidence,[1–10] almost favorable enough for this pair to form miscible blends when both components have molecular weights typical of useful polymers, whereas the interaction of BPA-PC with polystyrene (PS) is less favorable. However, tetramethylbisphenol A polycarbonate (TMPC) is well-known to be miscible with PS but immiscible with PMMA.[11–20] These facts indicate that methyl substitution on the phenyl rings of BPA-PC causes a major shift in its interactions with other polymers.

In this paper, we explore more broadly how the molecular structure of a series of new polycarbonates affects their miscibility with common polymers like PS, PMMA, BPA-PC, and TMPC for the purpose of obtaining information to guide molecular structural design for useful blends. To achieve this purpose, various new polycarbonates were prepared from systematically varied bisphenol monomers for blend screening. Most of the variation among the bisphenols involves ring substitutions in some or all of the four available positions or in the group connecting the phenyl ring. Many of the results obtained were qualitative in nature in order to limit the scope of the experimental program. The positive or negative observations of miscibility will nevertheless be useful for planning future in-depth, quantitative investigations.

Materials and Procedures

Most of the polymers used in this study are described in Tables I and II. Some of the polycarbonates were obtained from external sources while the remainder were synthesized in our laboratory. As-received bisphenol monomers (structures of the resulting polycarbonates are shown in Tables III–VI) were purified by a sublimation technique and then reacted with bis(trichloromethyl)carbonate,[21–23] triphosgene, to produce the polycarbonates using an interfacial polymerization technique.[24–27] The interfacial polymerizaton used a phase-transfer catalyst (triethylamine)[28,29] to transport salts from the aqueous phase into the organic phase (methylene chloride) where reaction with the soluble organic species occurs. The resulting polycarbonates dissolved in methylene chloride were precipitated with methanol.

Two of the polycarbonates, BPF-PC and BPS-PC (see Table I), proved to be insoluble in methylene chloride; thus, they precipitated during reaction. Because of this, they have lower molecular weights than the other polycarbonates. For example, the intrinsic viscosity of BPS-PC ($[\eta] = 0.16$ dL/g measured in *N,N*-dimethylformamide) is considerably lower than that of the commercial BPA-PC used here, Lexan 131-111, which has $[\eta] = 0.46$ dL/g in methylene chloride. The glass transition temperature of the BPF-PC synthesized here ($T_g = 102$ °C) is substantially lower than that reported in the literature ($T_g = 147$ °C).[24,25] Note that since BPF-PC appears to be insoluble with all conventional solvents,[24,25] molecular weight information could not be obtained. However, all other polycarbonates employed in this study have glass transition temperatures comparable to those reported in the literature (see Table I).

Most blend experiments were performed with a commercial poly(methyl methacrylate) from Rohm & Haas Co. with the designation Plexiglas V 811 which according to the supplier has $\bar{M}_w = 130\,000$ and $\bar{M}_n = 52\,900$. The polystyrene was supplied by Cosden Oil and Chemical Co. and designated as Cosden 550 with $\bar{M}_w = 330\,000$ and $\bar{M}_n = 100\,000$. In some cases, blends were made with the low molecular weight PS and PMMS standards listed in Table II. These polymers were purchased from Polymer Laboratories, Ltd., and are nearly monodisperse ($\bar{M}_w/\bar{M}_n = 1.03$–$1.18$).

Blend films were mainly prepared by solution casting from THF (tetrahydrofuran) into a Petri dish. Since TMF-PC is insoluble in THF, its blends with other polymers were prepared by solution casting from methylene chloride. The cast films were dried at 70 °C for 10 min in an air-circulating oven until most of the solvent had evaporated. Blends of BPS-PC with other polymers were precipitated from an NMP (*N*-methyl-2-pyrrolidinone) solution using methanol as the nonsolvent. The blend samples were further dried for 1 week in a vacuum oven at a temperature 20 °C higher than the T_g. Since BPF-PC appears to be insoluble with all conventional solvents, its blends with other polymers were prepared by melt mixing at 250 °C in a Mini-Max molder.

Glass transition temperatures of the polycarbonates and their blends were measured using a Perkin-Elmer DSC-7 at a scanning rate of 20 °C/min. The onset of the change in the heat capacity was defined as the T_g. Temperatures at which phase separation occurs on heating, i.e., LCST behavior, were determined in a manner designed to eliminate rate effects and to minimize artifacts caused by slow phase-separation kinetics.[2,30] Blend samples were annealed on a hot stage (Mettler, FP82 HT) equipped with a temperature controller (Mettler, FP80 HT) at various constant temperatures around the phase-separation temperature for certain time periods. The phase-separation tem-

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Table I
Polycarbonates Used in This Study

polymer	abbrev	T_g		refractive index[b]	source
		measd	lit.[a]		
bisphenol A polycarbonate	BPA-PC[c]	149	150	1.590	General Electric Co. Lexan 131-111
bisphenol E polycarbonate	BPE-PC	130	130	1.594	synthesized
bisphenol F polycarbonate	BPF-PC[d]	102	145	1.608	synthesized
bisphenol S polycarbonate	BPS-PC[e]	195			synthesized
bisphenol Z polycarbonate	BPZ-PC	176	190	1.590	Mitsubishi Gas Chem.
norbonane polycarbonate	NBPC	232	207		Eastman Kodak
bisphenol AP polycarbonate	BPAP-PC	174	176	1.616	synthesized
bisphenol chlorol polycarbonate	BCPC	165	168	1.610	General Electric Co.
bisphenol AF polycarbonate	HFPC	171	172	1.539	synthesized
dimethylbisphenol A polycarbonate	DMPC	125	128	1.578	synthesized
dimethylbisphenol Z polycarbonate	DMZ-PC	140		1.547	synthesized
tetramethylbisphenol A polycarbonate	TMPC[f]	198	200	1.546	Bayer AG
tetramethylbisphenol F polycarbonate	TMF-PC[g]	178	181	1.565	synthesized
tetramethylbisphenol P polycarbonate	TMP-PC	184	196	1.562	synthesized
tetramethylbisphenol AF polycarbonate	TMHF-PC	205		1.471	synthesized
tetrabromobisphenol A polycarbonate	TBPC	248	265	1.615	synthesized
tetrachlorobisphenol A polycarbonate	TCPC	230	230	1.606	synthesized
3,4-bisphenol A polycarbonate	3,4 BPA-PC	108		1.590	synthesized
thiopolycarbonate	thio-PC	156			synthesized by M. W. Hellums[57]
tetramethylcyclobutane polycarbonate	TMCP-PC[h]	120			M. Aguilar-Vega[58]

[a] From ref 24 and 25. [b] Obtained by group contribution method. [c] $\bar{M}_w = 38\,000$ determined by light scattering in this laboratory. Molecular weight information provided by the supplier is $\bar{M}_w = 13\,000$, $\bar{M}_w = 34\,200$. [d] $T_m = 215$ °C. [e] Cast film is crystalline, $T_m = 233$ °C. [f] $\bar{M}_w = 33\,000$ determined by light scattering in this laboratory. [g] Cast film is crystalline, $T_m = 300$ °C. [h] Cast film is crystalline, $T_m = 246$ °C.

peratures reported here were determined by visual observations.

Results and Discussion

The bisphenols used for polycarbonate synthesis differed in terms of the nature of the unit connecting the two phenol rings or by substitutions onto these rings. The changes in the connector group structure primarily involved either size or polarity. Both may influence the interaction of the polycarbonate with other polymers by changing the balance of dispersive and polar interactions. In addition to the obvious direct interaction with the connector group itself, polar groups can affect the electronic structure of the rings and alter their interactions with other polymers.

Table II
Poly(methyl methacrylate) and Polystyrene Standards Used in This Study

	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
poly(methyl methacrylate)	1210	1.16
poly(methyl methacrylate)	2400	1.09
poly(methyl methacrylate)	4250	1.07
poly(methyl methacrylate)	10550	1.11
poly(methyl methacrylate)	20300	1.11
poly(methyl methacrylate)	33500	1.07
polystyrene	580	1.18
polystyrene	680	1.16
polystyrene	980	1.13
polystyrene	2950	1.05
polystyrene	9200	1.03
polystyrene	17500	1.04

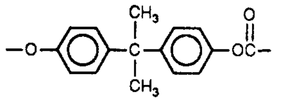
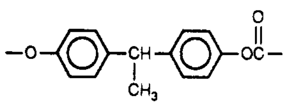
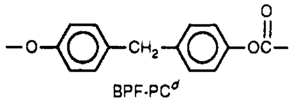
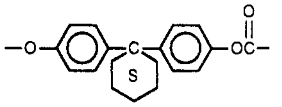
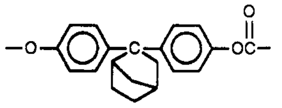
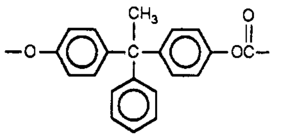
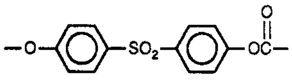
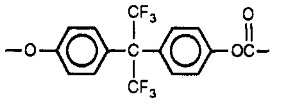
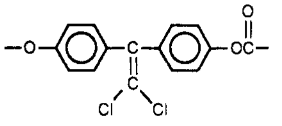
As listed in Table III, the connector groups were changed systematically from that of BPA-PC which has an isopropylidene connector group.

The electronic rearrangement caused by ring substitution may affect interaction with other polymers. For example, BPA-PC is not miscible with polystyrene, but adding four methyl groups on the rings of the bisphenol A unit causes miscibility of TMPC with polystyrene.[11-20] To explore this issue, systematic variations in ring substitution were examined as illustrated in Table IV. As seen in Table V, tetramethyl substitution can be combined with a number of different connector groups to learn more about the nature of interactions responsible for blend phase behavior. Figure 6 shows the structure of three other polycarbonates, i.e., the isomer of BPA-PC (3,4-BPA-PC), thio-PC, and the aliphatic polycarbonate (2,2,4,4-tetramethylcyclobutane polycarbonate), that were included in this investigation.

Blends of all these polycarbonates with PS, PMMA, BPA-PC, or TMPC were examined for miscibility using visual observations and T_g behavior. Blends having a single T_g were annealed for at least 1 day in a vacuum oven at a temperature 20 °C higher than the T_g predicted by the Fox equation. Transparent blends with a single T_g were classified directly as miscible except when the two polymers had similar glass transitions and refractive indices. Blends having two T_gs were directly classified as immiscible including the transparent pairs like BPA-PC/PS and BPZ-PC/PS. If the T_gs of the two polymers were too close to resolve by DSC, miscibility was judged by visual observation. Note that the blends of TMPC/TMF-PC and TMPC/BPS-PC show a single T_g but are not transparent because of crystallinity. These blends were heated above the melting temperature and miscibility was judged by their clarity. The results are summarized in Tables III–VI.

Blends of PMMA with Polycarbonates. We have reported extensively on blends of commercial bisphenol A polycarbonate with commercial poly(methyl methacrylate) materials that contain a small amount of a comonomer for heat stability. These blends are not miscible but appear to be right on the edge of being so.[2,4,10] Elimination of one methyl group from the isopropylidene connector group leads to BPE-PC (see Table III) which is also not miscible with commercial PMMA. As listed in Table III, blends of this PMMA with other polycarbanates having larger hydrocarbon connectors, i.e., BPZ-PC, NBPC, and BPAP-AP, are also immiscible. However, polar connector groups have the effect of increasing miscibility with PMMA. BCPC and HFPC are miscible with PMMA at all compositions.[4,31] BCPC blends show LCST behavior, whereas HFPC blends do not phase separate prior to decomposition. As discussed in a previous paper,[4] the

Table III
Effects of Polycarbonate Connector Group on Miscibility with Polystyrene, Poly(methyl methacrylate), Bisphenol A Polycarbonate, and Tetramethylbisphenol A Polycarbonate

polycarbonate	PMMA	PS	BPA-PC	TMPC
 BPA-PC	immiscible (opaque),[a] 2 T_g	immiscible (clear),[b] 2 T_g		miscible (clear), 1 T_g, $T_c > T_d$[c]
 BPE-PC	immiscible (cloudy), 2 T_g (overlapped)	immiscible (cloudy), 2 T_g (overlapped)	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c > T_d$
 BPF-PC[d]	miscible (clear),[e] 1 T_g, $T_c > T_d$	immiscible (cloudy), T_gs nearly equal	miscible (clear),[e] 1 T_g, $T_c > T_d$	miscible (clear),[f] 1 T_g, $T_c > T_d$
 BPZ-PC	immiscible (cloudy), 2 T_g	immiscible (clear),[b] 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c < T_d$[e]
 NBPC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c < T_d$
 BPAP-PC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g (overlapped)	miscible (clear), 1 T_g, $T_c > T_d$
 BPS-PC[d]	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$
 HFPC	miscible (clear), 1 T_g, $T_c > T_d$	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g (overlapped)	immiscible (cloudy), 2 T_g (overlapped)
 BCPC	miscible (clear), 1 T_g, $T_c < T_d$	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c > T_d$

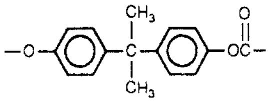
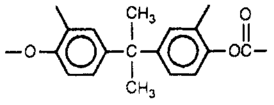
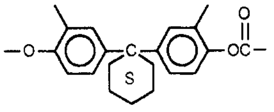
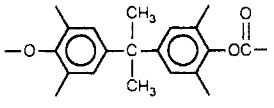
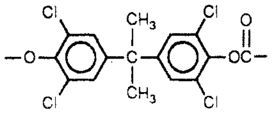
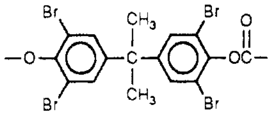
[a] Results shown are for annealed sample. Hot cast (70 °C) film of blend is clear and has a single T_g; however, this is not equilibrium state. [b] Blend films are clear, but refractive indices are very similar (n_{PS} = 1.590). [c] $T_c > T_d$ indicates that blends do not phase separate prior to decomposition. [d] Note that BPF-PC and BPS-PC have low molecular weight. [e] Blends are clear at melt mixing temperature (250 °C). [f] $T_c < T_d$ indicates that blends undergo phase separation prior to decomposition.

main factors affecting the interaction with PMMA appear to be the electronegativity of these polar connector groups themselves and the rearrangement they cause in the electronic charge distribution within the phenyl rings.

The blends of DMPC, TMPC, TBPC, and TCPC with PMMA are also immiscible. This indicates that the phenyl ring substitutions with methyl or halogen groups do not lead to interactions that are favorable for miscibility with PMMA. With tetramethyl substitution on the phenyl rings, making the connector group smaller (TMF-PC), larger (TMP-PC), or more polar (TMF-PC) than the isopropylidene unit does not lead to miscibility with PMMA evidently because the unfavorable effects of tetramethyl substitution seem to overwhelm the effects of other changes even when they may be favorable.

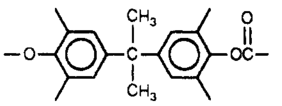
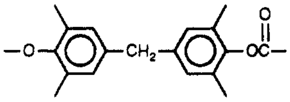
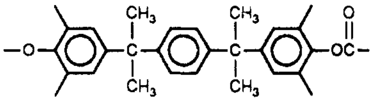
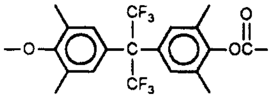
Blends of PS with Polycarbonates. It is well-known that blends of BPA-PC and PS are immiscible, but they are effectively transparent because of the similar refractive indices of the two pure materials. The results of this study of the miscibility of various polycarbonates with PS are listed in Tables III–VI. Making the connector group smaller (BPE-PC), larger (BPZ-PC, NBPC), or more polar (BCPC, HFPC) does not improve miscibility with PS. However, ring substitution with methyl groups can lead to interactions favorable for miscibility with PS as seen for TMPC.[11-20] However, dimethyl substitution is not sufficient since DMPC is immiscible with PS. This issue will be explored more fully later. Halogen substitution on the phenyl ring instead of methyl groups (TBPC, TCPC) is also unfavorable for miscibility. With tetramethyl substitution, making the connector group smaller (TMF-PC), larger (TMP-PC), or more polar (TMHF-PC) is unfavorable for miscibility with PS.

Table IV
Effects of Polycarbonate Ring Substitution on Miscibility with Polystyrene, Poly(methyl methacrylate), Bisphenol A Polycarbonate, and Tetramethylbisphenol A Polycarbonate

polycarbonate	PMMA	PS	BPA-PC	TMPC
 BPA-PC	immiscible (opaque),[a] 2 T_g	immiscible (clear),[b] 2 T_g		miscible (clear), 1 T_g, $T_c > T_d$[c]
 DMPC	immiscible (cloudy), 2 T_g (overlapped)	immiscible (cloudy), 2 T_g (overlapped)	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c > T_d$
 DMZ-PC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c > T_d$
 TMPC	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c < T_d$[d]	miscible (clear), 1 T_g, $T_c > T_d$	
 TCPC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g
 TBPC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g

[a] Results shown are for annealed sample. Hot cast (70 °C) film of blend is clear and has a single T_g; however, this is not equilibrium state. [b] Blend films are clear, but refractive indices are very similar ($n_{PS} = 1.590$). [c] $T_c > T_d$ indicates that blends do not phase separate prior to decomposition. [d] $T_c < T_d$ indicates that blends undergo phase separation prior to decomposition.

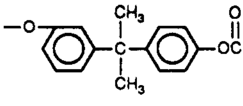
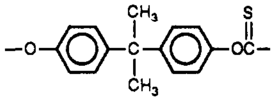
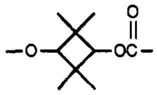
Table V
Effects of Polycarbonate Connector Group with Tetramethyl Ring Substitution on Miscibility with Polystyrene, Poly(methyl methacrylate), Bisphenol A Polycarbonate, and Tetramethylbisphenol A Polycarbonate

polycarbonate	PMMA	PS	BPA-PC	TMPC
 TMPC	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c < T_d$[a]	miscible (clear), 1 T_g, $T_c > T_d$[b]	
 TMF-PC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$	miscible (clear), 1 T_g, $T_c > T_d$
 TMP-PC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	miscible (clear), 1 T_g, $T_c > T_d$
 TMHF-PC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), T_gs nearly equal

[a] $T_c < T_d$ indicates that blends undergo phase separation prior to decomposition. [b] $T_c > T_d$ indicates that blends do not phase separate prior to decomposition.

Blends of BPA-PC with Other Polycarbonates. Bisphenol A polycarbonate is miscible with a wide range of other polycarbonates. As seen in Table III, it is miscible with all the polycarbonates without ring substitutions that have hydrocarbon connector groups with the exception of BPAP-PC. The latter has a phenyl ring replacing a methyl group in the standard isopropylidene connector. On the other hand, BPA-PC is immiscible with all the polycarbonates having polar connector groups ($-SO_2-$ or $>C(CF_3)_2$) except for bischloral polycarbonate with which it is miscible.[32] It is iportant to note that the chloral connector is less electronegative and causes less electronic

Table VI
Effects of Polycarbonate Structure on Miscibility with Polystyrene, Poly(methyl methacrylate), Bisphenol A Polycarbonate, and Tetramethylbisphenol A Polycarbonate

polycarbonate	PMMA	PS	BPA-PC	TMPC
 3,4-BPA-PC	immiscible (cloudy), T_gs nearly equal	immiscible (clear),[a] T_gs nearly equal	miscible (clear), 1 T_g, $T_c > T_d$[b]	miscible (clear), 1 T_g, $T_c > T_d$
 thio-PC	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g	immiscible (cloudy), T_gs nearly equal	miscible (clear), 1 T_g, $T_c > T_d$
 TMCB-PC	immiscible (cloudy), 2 T_g (overlapped)	immiscible (cloudy), 2 T_g (overlapped)	immiscible (cloudy), 2 T_g	immiscible (cloudy), 2 T_g

[a] Blend films are clear, but refractive indices are very similar (n_{PS} = 1.590). [b] $T_c > T_d$ indicates that blends do not phase separate prior to decomposition.

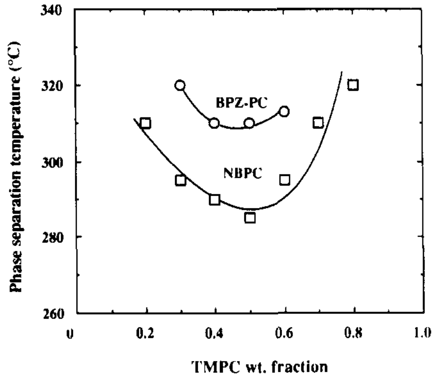


Figure 1. Phase-separation temperatures for binary blends of TMPC with BPZ-PC and with NBPC.

rearrangement in adjacent phenyl rings than does the >C-$(CF_3)_2$ connector group.[4] It is likely that the $-SO_2-$ connector is more like $>C(CF_3)_2$ than chloral in this regard. As seen in Table IV, BPA-PC is miscible with polycarbonates having either one (DMPC, DMZ-PC) or two (TMPC) methyl groups per phenyl ring and either isopropylidene (DMPC, TMPC) or cyclohexyl (DMZ-PC) connectors. However, tetrachloro or tetrabromo substitution on the rings of bisphenol A leads to polycarbonates that are not miscible with BPA-PC. Table V compares the miscibility of BPA-PC with other polycarbonates having tetramethyl substitution onto the bisphenol monomer. As noted earlier, BPA-PC is miscible with TMPC and it is seen here that replacing the isopropylidene with the smaller $-CH_2-$ connector preserves this miscibility. However, BPA-PC is not miscible with TMP-PC where there is an added phenylene isopropylidene unit in the bisphenol or with TMHF-PC where the polar $>C(CF_3)_2$ replaces the nonpolar, hydrocarbon isopropylidene connector.

In summary, bisphenol A polycarbonate is miscible with a wide range of other polycarbonates having aliphatic hydrocarbon connector groups in the bisphenol. Incorporation of aromatic or strong polar connectors seems to cause immisibility with BPA-PC. Miscibility with BPA-PC is apparently not changed by ring methyl substitution; however, ring halogen substitution leads to immiscibility.

Blends of TMPC with Other Polycarbonates. The polycarbonate based on tetramethybisphenol A is miscible at some temperature with every polycarbonate shown in Tables III–V except three, each of which has more than two halogens per repeat unit.

TMPC is miscible with BPZ-PC and NBPC, both of which contain large hydrocarbon connectors. It is interesting to note that TMPC blends with BPA-PC do not phase separate prior to decomposition,[33-36] whereas TMPC blends with these polycarbonates having large connectors, i.e., BPZ-PC or NBPC, show LCST behavior. As shown in Figure 1, the blends of TMPC with BPZ-PC have a higher LCST than those of TMPC with NBPC. From these results, it is apparent that bulky or large hydrocarbon connectors tend toward less favorable interactions with TMPC.

It is interesting to note that while TMPC blends with DMZ-PC are miscible and do not phase separate prior to thermal decomposition, TMPC blends with BPZ-PC do show phase separation at about 310 °C. TMPC is miscible with the tetramethyl-substituted TMF-PC which has a small $-CH_2-$ connector and with TMP-PC which has a large phenylene isopropylidene connector, and these blends do not phase separate prior to thermal decomposition. These results suggest that methyl substitution on the phenyl rings tends to lead to more favorable interactions with TMPC.

The polycarbonates having the polar $-SO_2-$ and chloral connectors are both miscible with TMPC. However, HFPC with the $>C(CF_3)_2$ connector is not miscible with TMPC. Addition of four methyls to the former, i.e., TMHF-PC, does not produce miscibility with TMPC. As stated earlier, methyl substitution onto the phenyl rings seems to promote more favorable interactions with TMPC. The failure of tetramethyl substitution to induce miscibility suggests that the interaction of the unit containing $>C(CF_3)_2$ with TMPC is too unfavorable to salvage in this way.

The results shown in Table IV clearly indicate that substitution of halogens onto the bisphenol rings does not favor miscibility with TMPC, as was also the case for BPA-PC.

Blends Involving Other Polycarbonates. The polycarbonate 3,4-BPA-PC, a structural isomer of BPA-PC, does not form miscible blends with PMMA as shown in Table VI. Cast films of blends of 3,4-BPA-PC with PS were transparent and exhibited an apparent single T_g. However, the refractive indices of PS and 3,4-BPA-PC calculated by a group contribution method are quite similar ($n_{PS} \approx n_{3,4\text{-BPA-PC}} \approx 1.590$), and the T_gs of the two polymers are too close to resolve by DSC. Alternatively, the phase

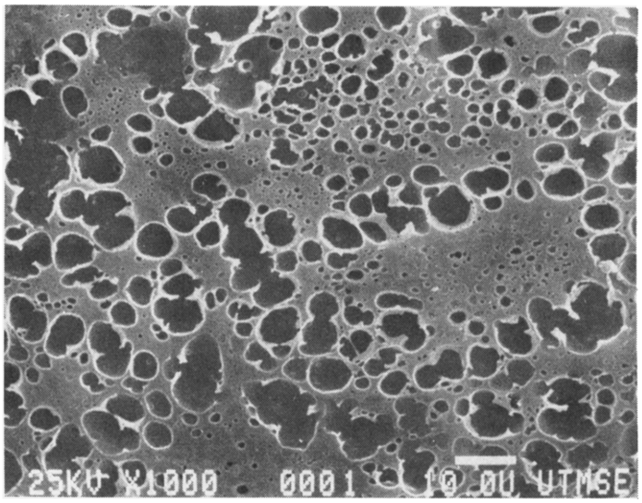


Figure 2. SEM photomicrograph of a 70/30 blend of 3,4-BPA-PC with PS after extraction with cyclohexane. The blend sample was prepared by solvent casting from THF.

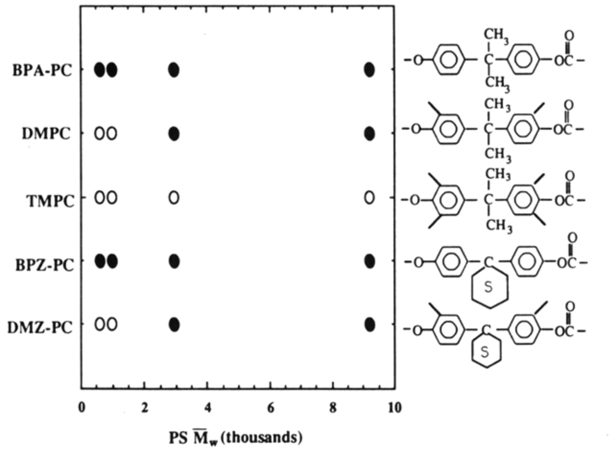


Figure 3. Phase behavior of polycarbonate blends with PS having various molecular weights: (○) miscible, (●) immiscible. The results for BPA-PC and BPZ-PC are from Callaghan.[10]

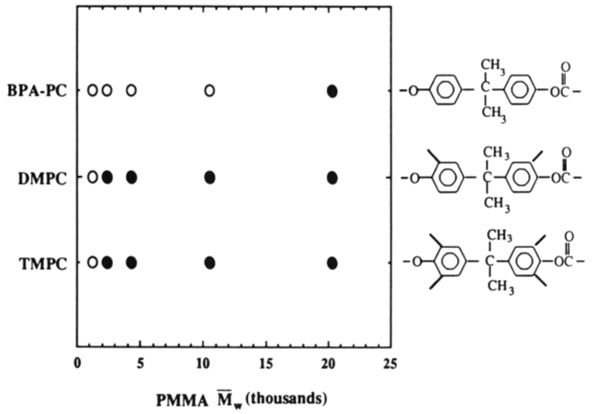


Figure 4. Phase behavior of polycarbonate blends with PMMA having various molecular weights: (○) miscible, (●) immiscible. The results for BPA-PC are from Callaghan.[10]

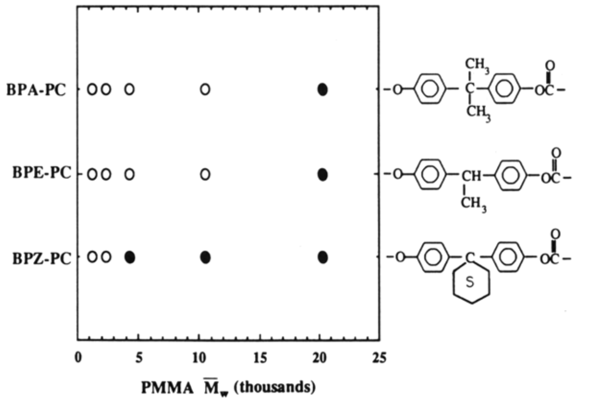


Figure 5. Phase behavior of polycarbonate blends with PMMA having various molecular weights: (○) miscible, (●) immiscible.

structure of the 30/70 PS/3,4-BPA-PC blend was examined by SEM (scanning electron microscopy). The blends were exposed to cyclohexane at 40 °C for 2 min which would dissolve any dispersed polystyrene phase. The etched sample was dried in a vacuum oven for several hours at room temperature, and then the surface was gold–palladium coated using a Pelco sputter coater prior to viewing in the electron microscope. Figure 2 shows the phase morphology observed by using a JEOL 35 C SEM operated at 25 kV. This result suggests that 3,4-BPA-PC blends are immiscible with PS. The blends of 3,4-BPA-PC with BPA-PC and TMPC are miscible and do not phase separate prior to thermal decomposition.

Thio-PC, which has the structure shown in Table VI, does not form miscible blends with PMMA, PS, and BPA-PC while miscible blends with TMPC are formed that do not phase separate prior to thermal decomposition. The aliphatic polycarbonate (TMCB-PC, 2,2,4,4-tetramethylcyclobutane polycarbonate) does not form miscible blends with PMMA, PS, BPA-PC, or TMPC.

Molecular Weight Effects. Kambour et al.[5] recently described a potentially useful method by which semiquantative information about interaction energies can be determined by lowering the molecular weight of one or both polymers until the mixture becomes miscible. This method is only applicable when the interaction energy is relatively small and positive. Such pairs form immiscible blends when the molecular weights are high. However, as the molecular weight of one or both components is lowered, the combinatorial entropy term becomes more and more important and eventually miscibility may occur. According to the Flory–Huggins theory, a UCST phase boundary occurs when

$$B \le \frac{RT_c}{2}\left(\frac{1}{\tilde{V}_1^{1/2}}+\frac{1}{\tilde{V}_2^{1/2}}\right)^2 \qquad (1)$$

where B is the interaction energy density between the two components, T_c is the experimentally determined critical temperature, and $\tilde{V}_i$ is the molar volume of component i. Since the molar volume is proportional to molecular weight, 1 indicates that lowering the molecular weight of one or both components can eventually result in a miscible blend. We applied this approach for a more thorough examination about interactions of certain polycarbonates with PMMA and PS since the latter two materials are readily available over a wide range of molecular weights. It is important to note that these PMMA materials are homopolymers and, thus, are not as stable against unzipping as the commercial material used earlier. Blends of the selected polycarbonates with PMMA or with PS having various molecular weights were prepared by solution casting from THF at 70 °C. The miscibility of the blends was judged by T_g behavior and visual observations. The results shown in Figures 3–5 can be interpreted as an isothermal plane defined by the drying condition of 140 °C.

As described in previous sections, the placement of four methyl groups on the bisphenol A unit causes miscibility of TMPC with PS; on the other hand, the interaction of PMMA with BPA-PC is more favorable for miscibility

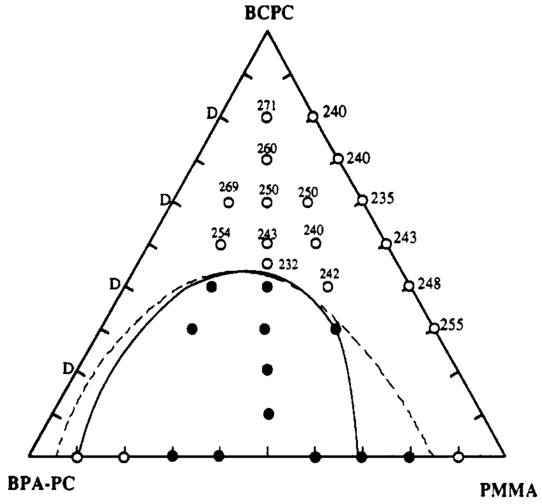


Figure 6. Isothermal ternary phase diagram for blends of BPA-PC, BCPC, and PMMA after annealing at 140 °C: (○) clear, (●) opaque. Numbers indicate temperatures (in °C) at which each composition phase separates on heating. "D" denotes that these miscible blends to not phase separate prior to thermal decomposition. The points for the BPA-PC/PMMA binary are the results after annealing homogeneous blends for 80 h at 140 °C as reported by Nishimoto et al.[2] Owing to the slow phase separation of this pair, longer annealing may lead to phase separation of some blends denoted here by open points.

than that with TMPC. To systematically explore this issue, blends of selected polycarbonates with PMMA or with PS having various molecular weights were examined. These polycarbonates are assumed to be similar in molecular weight to commercial BPA-PC. Figure 3 shows the effect of varying PS molecular weight on its miscibility with BPA-PC, BPZ-PC, DMPC, DMZ-PC, and TMPC. The blends of TMPC with PS are always miscible, while DMPC and DMZ-PC form miscible blends when the PS molecular weight ($\bar{M}_w$) is equal to 1100 or less. Polystyrene having the lowest molecular weight ($\bar{M}_w = 680$) does not form miscible blends with BPA-PC and BPZ-PC. These results further indicate that phenyl ring substitution with methyl groups is favorable for miscibility with PS, while replacing the isopropylidene connector with a large aliphatic connector does not improve miscibility. Figure 4 shows the miscibility of BPA-PC, DMPC, and TMPC with PMMA of various molecular weights. The interactions of PMMA with these polycarbonates become more unfavorable for miscibility as methyl groups are substituted on the phenyl rings.

Figure 5 examines the effects of changes in the size of hydrocarbon connector groups on the miscibility with PMMA by blending of BPE-PC, BPA-PC, and BPZ-PC with PMMA having different molecular weights. As shown, BPA-PC and BPE-PC form miscible blends with PMMA when its molecular weight is equal to 11 700 or less while these materials are immiscible with PMMA of molecular weight 22 500 or higher. The blends with BPZ-PC are only miscible when the PMMA molecular weight is equal to 2600 or less. These results indicate that a connector group larger than an isopropylidene is not favorable for interaction with PMMA, while on this scale of discrimination no trend for improved interaction for a smaller connector group can be seen. It should be noted that the resolution of this technique depends on how closely spaced the molecular weights of the PMMA standards are.

The relatively low molecular weight BPF-PC forms miscible blends with PMMA, BPA-PC, and TMPC but not with PS during melt mixing at ~250 °C. BPS-PC only forms miscible blends with TMPC. As seen above, when the interaction energy has small positive values, blends that may be immiscible for typical high molecular weight components may become miscible upon lowering the molecular weight of one or both components. Because of this effect, BPF-PC and BPS-PC having higher molecular weights should be synthesized by other techniques and the phase behavior of their blends reevaluated.

Ternary Blends. It has been repeatedly suggested in the literature[33,37-44] that mixtures of two immiscible polymers can be homogenized by adding a third component that is miscible with both. Since BCPC is miscible with PMMA and BPA-PC but the latter two are not miscible with each other, at commercially useful molecular weights, we examined these ternary blends to determine the extent of homogenization that can be achieved. Figure 6 is an isothermal phase map (drying or annealing temperature of 140 °C) showing which ternary compositions are miscible or not. The phase-separation temperatures of the miscible compositions are also shown.

The binary interaction energies (B_{ij}) for each pair of the ternary system can, in principle, be extracted from the type of phase boundary shown in Figure 6. A spinodal analysis based on the Flory–Huggins theory was used here for simplicity. From the phase stability condition, the ternary spinodal curve has to satisfy[44-46]

$$g_{11} > 0 \tag{2}$$

$$\det \begin{vmatrix} g_{11} & g_{12} \\ g_{12} & g_{22} \end{vmatrix} = 0 \tag{3}$$

where g is the free energy per unit volume $g_{ij} = g_{[ij]} - g_{[ir]} - g_{[jr]} + g_{[rr]}$, and $g_{[ij]} = (\partial g/\partial\phi_i\partial\phi_j)$ with each volume fraction treated as independent. In terms of the Flory–Huggins theory, the indicated derivatives are given by

$$g_{11} = RT\left(\frac{1}{V_1\phi_1} + \frac{1}{V_3\phi_3}\right) - 2B_{13} \tag{4}$$

$$g_{12} = (B_{12} - B_{13} - B_{23}) + RT\left(\frac{1}{V_3\phi_3}\right) \tag{5}$$

$$g_{22} = RT\left(\frac{1}{V_2\phi_2} + \frac{1}{V_3\phi_3}\right) - 2B_{23} \tag{6}$$

The condition given in eq 2 indicates that ternary blends having immiscible pairs cannot be homogenized unless combinatorial entropy terms overcome the unfavorable energetic terms of the immiscible pairs. The phase boundary of the BPA-PC/PMMA binary pair was determined by using the Flory–Huggins interaction energy for this pair which has been estimated to be 0.05 cal/cm^3 from the experimental phase boundary at 140 °C for blends of TMPC/BPA-PC copolymers with SMMA copolymers.[47] Binary interaction energies for the BCPC/BPA-PC and BCPC/PMMA pairs were obtained by a trial and error fitting of the ternary Flory–Huggins spinodal condition to the experimental miscibility map shown in Figure 6. The molecular weight information for the BCPC has been reported previously.[4] The solid line in Figure 6 is the best fit that could be obtained using this simple model which yielded the values $B_{\mathrm{BCPC/BPA\text{-}PC}} = -0.11$ cal/cm^3 and $B_{\mathrm{BCPC/PMMA}} = -0.06$ cal/cm^3. Note that ΔP^* (the bare interaction energy from the Sanchez–Lacombe theory[45,48-50] for the BCPC/PMMA pair obtained from the phase diagram for BCPC/PMMA blends is -0.08 cal/cm^3.[4]

The location of the miscibility region along the BPA-PC/PMMA binary leg, as predicted by the Flory–Huggins theory, is skewed in the wrong direction. A better representation of the observations for this pair is given by the equation of state theory of Sanchez–Lacombe. The phase boundary for the BPA-PC/PMMA pair was determined using the spinodal condition of the lattice fluid theory using $\Delta P^* = 0.03$ cal/cm^3 obtained from the experimental phase-separation temperature for PMMA blends with a low molecular weight BPA-PC.[2,4] The results of this calculation are represented by the points where the dashed line intersects the BPA-PC/PMMA binary leg. The dashed line is the best fit, obtained by trial and error, of the Flory–Huggins ternary spinodal condition to the experimental miscibility map which forces the curve to go through the BPA-PC/PMMA binary points predicted by the equation of state theory and assumes $B_{\mathrm{BCPC/PMMA}} \approx \Delta P^*_{\mathrm{BCPC/PMMA}} \approx -0.08$ cal/cm^3. The interaction energy for the BCPC/BPA-PC pair obtained from the curve-fitting process is $B_{\mathrm{BCPC/BPA\text{-}PC}} = -0.2$ cal/cm^3. In general, the LCST-driven phase-separation temperatures increase as the BCPC content in the ternary mixture increases, consistent with the fact that the interactions of BCPC with BPA-PC or with PMMA are more favorable than those of the BPA-PC/PMMA pair.[4,30,31]

Summary

The results presented here offer some directions for control of polymer blend phase behavior through molecular structure design. We have mainly focused on the extent of miscibility of PS, PMMA, BPA-PC, and TMPC with a series of polycarbonates. The interactions between the polycarbonate and other monomer units can be manipulated by changing the group connecting the bisphenol rings or by substitution onto these rings. Polar connector groups promote favorable interactions with PMMA while ring substitution with methyl groups improves interactions with PS. However, other structural changes in the connector group or phenyl ring substitution can act against polycarbonate miscibility with PMMA or PS. BPA-PC shows favorable interactions with other polycarbonates having a range of aliphatic connector groups including those having methyl groups on the phenyl rings. TMPC forms miscible blends with PS and various polycarbonates. Small aliphatic connector groups and methyl ring substitution in the polycarbonate tend to favor miscibility with TMPC. By varying the molecular weight of PMMA or PS more detailed information about their interaction with selected polycarbonates was obtained. These results indicate that the interaction parameters for binary pairs such as BPA-PC/PMMA, BPE-PC/PMMA, DMPC/PS, and DMZ-PC/PS are relatively small and positive. As a result, these pairs might be candidates for formation of miscible blends by appropriate incorporation of a comonomer[3,4,16,47,51,52] or by adding a third polymer to the blend.

It useful to summarize here a few examples of how such qualitative information can be useful as a guide in the design of copolymer systems for enhanced blend interaction or phase behavior. As described in Table III, HFPC is miscible with PMMA but immiscible with BPA-PC. However, the blends of BCPC with PMMA or with BPA-PC are miscible. Copolymers of BPA-PC containing small amounts of HFPC were found to be quite effective for increasing the LCST of blends with PMMA.[4] According to the copolymer model,[53-56] the interaction between PMMA and a copolymer of BPA-PC will become more favorable for miscibility as HFPC units are incorporated due to favorable intermolecular interaction between HFPC and PMMA and the intramolecular repulsion between BPA-PC and HFPC. However, copolymers of BPA-PC and BCPC would not be assisted by the intramolecular repulsion effect because the favorable interaction between BPA-PC and BCPC would act against miscibility with PMMA. As indicated in the previous section, certain ternary blends of PMMA/BPA-PC/BCPC form homogeneous, stable mixtures. Polystyrene forms miscible blends with TMPC, but they phase separate on heating at temperatures that are relatively low which limits melt processibility. The addition of comonomer units to either polymer can be an effective way of raising the phase-separation temperature. Styrene copolymers with modest amounts of methyl methacrylate tend to serve this function[51,52] even though PMMA is not miscible with TMPC. Acrylonitrile is an even more effective comonomer for this purpose;[16,51] likewise, TMPC copolymers with BPA-PC serve a similar role.[47]

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References and Notes

(1) Chiou, J. S.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1459.

(2) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Polymer* **1991**, *32*, 272.

(3) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Polymer* **1991**, *32*, 1274.

(4) Kim, C. K.; Paul, D. R. Miscibility of PMMA Blends with Halogen Containing Polycarbonates and Copolymers. *Polymer*, submitted.

(5) Kambour, R. P.; Gundlach, P. E.; Wang, I. C. W.; White, D. M.; Yeager, G. M. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (2), 140.

(6) Kyu, T.; Saldanha, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (2), 124.

(7) Saldanha, J. M.; Kyu, T. *Macromolecules* **1987**, *20*, 2840.

(8) Kyu, T.; Saldanha, J. M. *Macromolecules* **1988**, *21*, 1021.

(9) Kyu, T.; Saldanha, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 33.

(10) Callaghan, T. A. Ph.D. Dissertation, University of Texas at Austin, Austin, TX, 1992.

(11) Shaw, M. T. *J. Appl. Polym. Sci.* **1974**, *18*, 449.

(12) Casper, R.; Morbitzer, L. *Makromol. Chem.* **1977**, *58/59*, 1.

(13) Humme, G.; Rohr, H.; Serini, V. *Makromol. Chem.* **1977**, *58/59*, 85.

(14) Yee, A. F.; Maxwell, M. A. *J. Macromol. Sci., Phys.* **1980**, *17*, 543.

(15) Wisniewsky, C.; Marin, G.; Monge, P. *Eur. Polym. J.* **1984**, *No. 7*, 691.

(16) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *Polymer* **1986**, *27*, 1789.

(17) Yang, H.; O'Reilly, J. M. *Mater. Res. Soc. Symp. Proc.* **1987**, *79*, 129.

(18) Brereton, M. G.; Fisher, E. W.; Herkt-Maetzky, C. *J. Chem. Phys.* **1987**, *10*, 6144.

(19) Guo, W.; Higgins, J. S. *Polymer* **1990**, *31*, 699.

(20) Kim, C. K.; Paul, D. R. Interaction Parameters for Blends Containing Polycarbonates. Part I. Tetramethyl Bisphenol-A Polycarbonates/Polystyrene. *Polymer*, to be published.

(21) Technical Information Bulletin No. AL-176, Aldrich Chemical Co., Inc.

(22) Eckert, H.; Forster, B. *Angew. Chem.* **1987**, *99*, 922.

(23) Daly, W. H.; Poche, D. *Tetrahedron Lett.* **1988**, *29* (10), 5859.

(24) Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. Polycarbonates. *Mark–Bikales–Overberger–Menges: Encyclopedia of Polymer Science and Engineering* 2nd ed.; John Wiley and Sons, Inc.: New York, 1988, Vol. 11, p 648.

(25) Schnell, M. *Chemistry and Physics of Polycarbonates*; Interscience: New York, 1963; p 33.

(26) Schnell, H.; Bottenbruch, L. (Farbenfabriken Bayer AG). U.S. Patent 3,530,094, Dec 1, 1966.

(27) Sikdar, S. K. (General Electric Co.). U.S. Patent 4,360,659, May 6, 1981.

(28) Vernaleken, H. In *Interfacial Synthesis*; Millich, F., Carraher, C. E., Jr., Eds.; Marcel Dekker Inc.: New York, 1977; Vol. 11, p 65.
(29) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis, Principles and Techniques*; Academic Press: New York, 1978.
(30) Maruta, J.; Ougizawa, T.; Inoue, T. *Polymer* **1988**, *29*, 2056.
(31) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci.* **1987**, *33*, 2935.
(32) Factor, A.; Orlando, C. M. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 579.
(33) Landry, C. J. T.; Yang, H.; Machell, J. S. *Polymer* **1991**, *32*, 44.
(34) Hellmann, E. H.; Hellmann, G. P.; Rennie, A. R. *Colloid Polym. Sci.* **1991**, *269*, 343.
(35) Kim, C. K.; Aguilar-Vega, M.; Paul, D. R. Dynamic Mechanical Behavior of Blends and Random Copolymers of Bisphenol-A Polycarbonate and Tetramethyl Bisphenol Polycarbonate and Their Relationship with Gas Transport Properties. *J. Polym. Sci., Polym. Phys. Ed.* to be published.
(36) Fischer, E. W.; Hellmann, G. P.; Spiess, H. W.; Hörtch, F. J.; Ecarius, U.; Wehrle, M. *Makromol. Chem. Suppl.* **1985**, *12*, 198.
(37) Kwei, T. K.; Frisch, H. L.; Radigan, W.; Vogel, S. *Macromolecules* **1977**, *10*, 157.
(38) Wang, Y. Y.; Chen, S. A. *Polym. Eng. Sci.* **1981**, *21*, 47.
(39) Rigby, D.; Lin, J. L.; Roe, R. J. *Macromolecules* **1985**, *18*, 2269.
(40) Shah, V.; Keitz, J. D.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1986**, *32*, 3863.
(41) Equizabal, J. I.; Irvin, J. J.; Cotazar, M.; Guzman, G. M. *J. Appl. Polym. Sci.* **1986**, *32*, 5945.
(42) Goh, S. H.; Siow, K. S.; Yap, K. S. *Thermochim. Acta* **1986**, *105*, 191.
(43) Christiansen, W. H.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1987**, *34*, 537.
(44) Brannock, G. R.; Paul, D. R. *Macromolecules* **1990**, *23*, 5240.
(45) Sanchez, I.C. Polymer Phase Separation. *Encyclopedia of Physical Science and Technology*; Meyers, R. A., Ed.; Academic Press: New York, 1987; Vol. XI, p 1.
(46) Sanchez, I. C. *Macromolecules* **1991**, *24*, 908.
(47) Kim, C. K.; Paul, D. R. Interaction Parameters for Blends Containing Polycarbonates. Part III. Polycarbonate Copolymers/Styrene-based Copolymers. *Polymer*, submitted.
(48) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(49) Sanchez, I. C.; Lacombe, R. H. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 71.
(50) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(51) Kim, C. K.; Paul, D. R. Interaction Parameters for Blends Containing Polycarbonates. Part II. Tetramethyl Bisphenol-A Polycarbonates/styrene Copolymers. *Polymer*, to be published.
(52) Min, K. E.; Paul, D. R. *Macromolecules* **1987**, *20*, 2828.
(53) Paul, D. R.; Barlow, J. W.; Keskkula, H. Polymer Blends. *Mark–Bikales–Overberger–Menges: Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1988; Vol. 12, p 399.
(54) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(55) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(56) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(57) Hellums, M. W. Ph.D. Dissertation, University of Texas at Austin, Austin, TX, 1990.
(58) Aguilar-Vega, M.; Paul, D. R. Gas Transport Properties of Poly(2,2,4,4-tetramethyl cyclobutane carbonate), to be published.

Registry No. PS, 9003-53-6; PMMA, 9011-14-7; (BPA)(PC) (copolymer), 25037-45-0; (BPA)(PC) (SRU), 24936-68-3; TMPC (copolymer), 52684-16-9; TMPC (SRU), 38797-88-5; (BPE)(PC) (copolymer), 27815-48-1; (BPE)(PC) (SRU), 28774-91-6; (BPF)(PC) (copolymer), 29832-46-0; (BPF)(PC) (SRU), 28935-53-7; (BPZ)(PC) (copolymer), 26471-16-9; (BPZ)(PC) (SRU), 25135-52-8; NBPC (copolymer), 26007-14-7; NBPC (SRU), 24979-94-0; (BPAP)(PC) (copolymer), 29250-91-7; (BPAP)(PC) (SRU), 26985-42-2; (BPS)(PC) (copolymer), 30231-71-1; (BPS)(PC) (SRU), 28930-33-8; HFPC (copolymer), 31563-79-8; HFPC (SRU), 32291-26-2; BCPC (copolymer), 29057-43-0; BCPC (SRU), 31546-39-1; DMPC (copolymer), 26570-63-8; DMPC (SRU), 26500-24-3; (DMZ)(PC) (copolymer), 30142-62-2; (DMZ)(PC) (SRU), 29468-33-5; TCPC (copolymer), 26814-08-4; TCPC (SRU), 26913-25-7; TBPC (copolymer), 27815-51-6; TBPC (SRU), 28774-93-8; (TMF)(PC) (copolymer), 52757-25-2; (TMF)(PC) (SRU), 38797-89-6; (TMP)(PC) (copolymer), 52684-31-8; (TMP)(PC) (SRU), 38245-65-7; (TMHF)(PC) (copolymer), 126724-74-1; (TMHF)(PC) (SRU), 125431-72-3; (3,4-BPA)(PC) (copolymer), 131561-09-6; (3,4-BPA)(PC) (SRU), 132516-43-9; (BPA)(thio-PC) (copolymer), 120411-62-3; (BPA)(thio-PC) (SRU), 32200-44-5; (TMCB)(PC) (copolymer), 25548-96-3; (TMCB)(PC) (SRU), 25722-32-1.