Blends containing tetramethyl bisphenol-A polycarbonate: 2. Aliphatic polyesters

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The phase behaviour for blends of tetramethyl bisphenol-A polycarbonate, MPC, and poly(2,6 dimethyl-1, 4 phenylene oxide), PPO, with various aliphatic polyesters was examined using differential scanning calorimetry and optical indications of phase separation on heating, i.e. lower critical solution temperature, *LCST*, behaviour. MPC was found to be miscible with aliphatic polyesters characterized by a ratio of aliphatic carbons to ester groups in the repeat unit, CH_2/COO, larger than 4 and up to at least 10. Interaction parameters deduced from polyester melting point depression were all negative and showed a minimum within this range of polyester molecular structures. MPC was found to be immiscible with the aliphatic polyesters having a CH_2/COO equal to 3 and 4 as well as with selected polyesters with branched and saturated cyclic units in their structure. An exploratory study shows that PPO is apparently not fully miscible with any aliphatic polyester. The phase behaviour of blends containing MPC and poly(ε-caprolactone), PCL, was found to be affected by the solvent used to cast the blends.

(Keywords: polycarbonate blends; polyesters; solution properties)

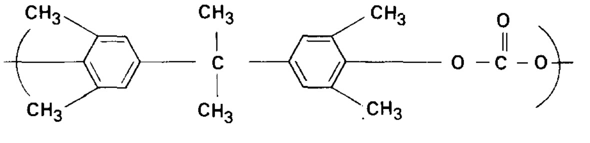
INTRODUCTION

The purpose of this series of papers has been to examine the phase behaviour of blends of tetramethyl bisphenol-A polycarbonate, MPC, with a variety of other polymers and a series of aliphatic polyesters is the focus of this paper. We have recently reported results showing that several polymers[1–7], including bisphenol-A polycarbonate, form completely miscible blends with all linear aliphatic polyesters whose ratio of aliphatic carbons per ester groups, i.e. CH_2/COO, fall within a given range specific to each of these polymers. Bisphenol-A polycarbonate was reported[1] to form fully miscible blends with polyesters having CH_2/COO ratios in the range of two to five, while only partially miscible blends resulted for $CH_2/COO = 7$; other ratios not mentioned were not studied. Thus, the objective of this work was to learn whether MPC is miscible with any of the aliphatic polyesters and, if so, to compare the range of CH_2/COO ratios over which this occurs with that for bisphenol-A polycarbonate since it is structurally similar to MPC except for the four methyl groups on the rings of the repeat unit of the latter. Portions of the MPC repeat unit are identical with the repeat unit of poly(phenylene oxide), PPO, so a cursory study of PPO–polyester blends was made for gaining further insight about interaction mechanisms.

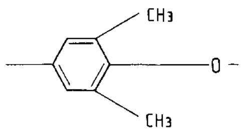
The techniques used include observations of glass transition behaviour and clarity of the blends in the melt state to ascertain blend miscibility and the depression of polyester melting points to obtain estimates of interaction parameters.

MATERIALS AND PROCEDURES

The tetramethyl bisphenol-A polycarbonate, MPC, used in this study was supplied by Bayer AG through the courtesy of Drs V. Serini and L. Bottenbruch. This polymer has a high glass transition temperature, 193.5°C and is usually amorphous; however, it was found to undergo solvent and thermally induced crystallization when cast from tetrahydrofuran, THF, or toluene[8].



The poly(phenylene oxide), PPO, was supplied by the General Electric Co. The material as received had a small amount of crystallinity and exhibited a glass transition temperature of 214°C.



The aliphatic polyesters described in *Table 1* include one branched polyester and a polyester containing a saturated cyclic unit in its structure in addition to the linear polyesters which were the primary focus of the study. The numerical value included as part of the code for many of the polyesters refers to the CH_2/COO ratio for the polyester repeat structure.

Films containing different proportions of MPC and the polyester of interest were cast from methylene chloride or toluene solutions; whereas, to cast films of PPO and polyester, trichloroethylene was used. In general, the solutions had a total solids content in the range of 2 to 5% by weight. After most of the solvent was removed at room temperature, the samples were placed in a vacuum oven for 3 days at 80°C when $MeCl_2$ was used as the solvent or

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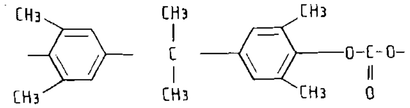
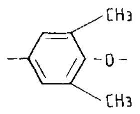
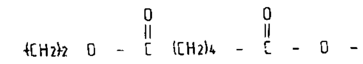
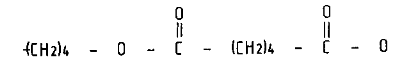
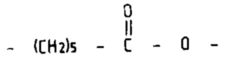
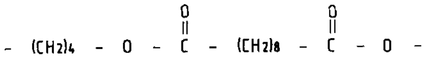
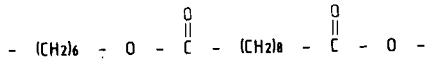
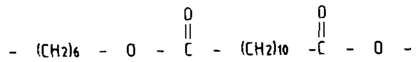
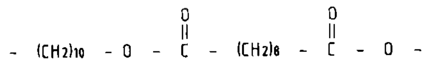
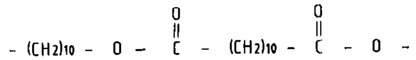
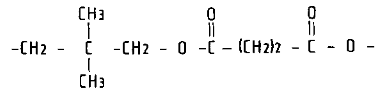
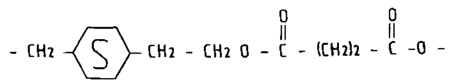
Table 1 Polymers used in this study

Abbreviation	Polymer	Structure	Density	Molecular weight information	T_g (°C)	T_m (°C)	ΔH_{2u} (cal/g)	Source
MPC	Tetramethyl bisphenol-A polycarbonate		1.0824[a]	$\eta_{rel} = 1.29$[b]	193.5[a]	≃280[a]	—	Bayer AG
PPO	Poly(2,6-Dimethyl-1,4-phenylene oxide)		1.071[k]	$\bar{M}_n = 22\,600$ $\bar{M}_w = 34\,000$ $\bar{M}_z = 57\,200$	214[a]	248[a]	—	General Electric Co.
PEA 3	Poly(ethylene adipate)	 $-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-$	1.21[c]	$\bar{M}_v = 1500$[c]	−47[a]	49.7[a]	29.2[d]	Scientific Polymer Products
PBA 4	Poly(1,4-butylene adipate)	 $-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O$	1.12[c]	$\bar{M}_v = 2500$[c]	−68[a]	57.3[a]	30.5[c]	Scientific Polymer Products
PCL 5	Poly(ε-caprolactone)	 $-(CH_2)_5-\overset{\overset{O}{\|}}{C}-O-$	1.095[c]	$\bar{M}_n = 15\,500$[c] $\bar{M}_v = 40\,500$ $\bar{M}_w = 46\,700$	−68[a]	58.2[a]	34.6[e]	Union Carbide PCL 700
PBS 6	Poly(butylene sebacate)	 $-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-$	1.136	$\bar{M}_v = 2500$	−62	64.8	37.0	(i)
PHS 7	Poly(hexamethylene sebacate)	 $-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-$	1.03[c]	$\bar{M}_w = 16\,500$[c]	−60[f]	69.4[a]	38.5[g]	Scientific Polymer Products
PHD 8	Poly(hexamethylene decamethylene dicarboxylate)	 $-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-O-$	1.08[g]	$\bar{M}_n = 3200$[j]	—	61.3	39.2	The C.P. Hall Company
PDS 9	Poly(decamethylene sebacate)	 $-(CH_2)_{10}-O-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-O-$	1.15[h]	$\bar{M}_v = 5200$[h]	−58	73.7[a]	39.9[d]	(i)
PDEDE 10 or P-10	Poly(decamethylene decamethylene dicarboxylate)	 $-(CH_2)_{10}-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-O-$	1.10[g]	$\bar{M}_v = 5300$[h]	—	79.4[a]	41.0	(i)
PDPS	Poly(2,2-dimethyl-1,3-propylene succinate)	 $-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-$	1.17[c]	1000[c]	−17[a]	—	—	Scientific Polymer Products
PCDS	Poly(1,4-cyclohexane dimethylene succinate)		1.16[c]	6000[c]	−1	122.6[a]	—	Scientific Polymer Products

[a] Determined experimentally in this study
[b] Bayer AG
[c] Ref. 20
[d] Ref. 21
[e] Ref. 22
[f] Ref. 23
[g] Estimated value
[h] Experimental value from this laboratory
[i] Synthesized by E. M. Woo
[j] The C. P. Hall Company
[k] Ref. 24

110°C when the solvent used was toluene. The PPO blends were placed in a forced air oven at 75°C for 3 days.

All samples were examined by differential scanning calorimetry using a cyclic heating and cooling procedure between the limits of −63°C and 317°C at a heating rate of 20°C/min and a cooling rate of 320°C/min. All transition behaviours were recorded after the first cycle. In some cases the polyester crystallinity was further limited by quenching to −103°C in the d.s.c. using liquid nitrogen. The melting points for the miscible blends were determined using a slightly different procedure. The samples were first heated at 10°C/min between −63°C and 317°C and then immediately cooled at 10°C/min within the same temperature range. The melting points were recorded in a subsequent heating at 10°C/min.

Visual observations of blend clarity were made while heating on a hot plate device following a procedure described previously[9].

DETERMINATION OF PHASE BEHAVIOUR

MPC blends

The phase behaviour observed for solution cast blends of MPC in some cases depended on the solvent used so several solvents were tried and considerable care exercised to ensure that the equilibrium state of miscibility could be determined. This 'solvent effect' has been observed for other blend systems[10–12] and has been explained by Robard *et al.*[13] in terms of the difference in the two polymer–solvent interaction parameters, $\Delta\chi = |\chi_{12} - \chi_{13}|$, where 1 = solvent while 2 and 3 represent the two polymers. In the following, we give details about the results from different casting procedures so the reader may know the basis for our conclusions.

Blends of MPC and PCL (see *Table 1* for polyester code) were especially influenced by the solvent used to cast the films. Although toluene induces crystallization of MPC[8], we found it more suitable for obtaining well-blended mixtures of MPC with PCL. As seen in *Figure 1*, a single, composition dependent glass transition is observed for blends cast from toluene. The arrow indicates the existence of a broad transition whose onset was difficult to locate precisely due to the superposition of PCL crystallization and melting. However, two glass transitions were detected for blends cast from $MeCl_2$ that were rich in MPC.

According to the analysis of Robard *et al.*[13], phase separation by the 'solvent effect' is less likely to occur during casting when the solvent has about the same affinity for each of the two polymers, i.e. $\Delta\chi$ is small. For the pair MPC and PCL, our experimental observations suggest that $\Delta\chi$ is smaller for toluene than for $MeCl_2$.

On the other hand, no phase separation seemed to occur when blends of MPC with PBS 6 or PHS 7 were cast from $MeCl_2$. *Figure 2* shows single glass transitions for these blends. As we will show later, the polymer–polymer interaction parameter is more negative for blends of MPC with these two polyesters than for PCL and apparently this outweighs the 'solvent effect'. In contrast, we were not able to obtain blends having a single T_g (see *Figure 3*) for blends of MPC with PBA 4 or with PEA 3, no matter what solvent was used.

For MPC/PBA 4 blends, the results shown are those obtained when $MeCl_2$ was used as solvent. A blend containing about 60% of MPC was repeated using toluene and no significant changes in the glass transition temperatures were observed. For MPC/PBA 4 blends, some partial miscibility is present as suggested by the displacement of the glass transitions relative to those of the pure polymers. The lower of the two glass transitions was difficult to assess at high MPC concentrations due to the presence of PBA 4 crystallization and melting in the same temperature range. Nevertheless, we conclude that MPC and PEA 3 are essentially immiscible blends.

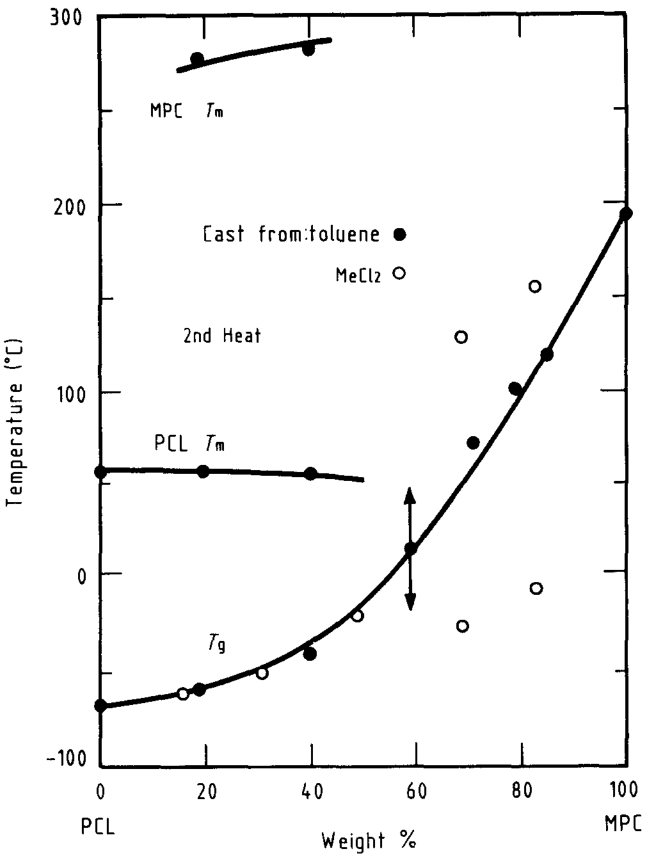


Figure 1 Glass transition and melting point behaviour for MPC blends with PCL, cast from toluene and $MeCl_2$

Blends of MPC with PHD 8, PDS 9, or PDEDE 10 were tested in detail for melting point depression as described below, but only one composition (usually a blend containing about 70% of MPC to minimize the effects due to polyester crystallinity) was examined by d.s.c. for glass transition behaviour. We concluded that all these polyesters form miscible blends with MPC because of the amount the blend glass transition was depressed relative to that for MPC. These conclusions were confirmed *a posteriori* by the negative interaction parameters found from melting point depression analysis.

MPC was also blended with a branched polyester, PDPS, and a polyester containing a cyclic unit in its structure, PCDS. Blends of MPC with PCDS show two phase behaviour independent of the solvent used. As shown in *Figure 4*, where the glass transitions are plotted *versus* composition, one phase is pure PCDS while the other one contains both polymers but is apparently rich in MPC. The branched polyester was found to be essentially immiscible with MPC as suggested by the temperatures at which the two glass transitions were observed.

Some comments should be made about the crystallization behaviour of MPC. This polymer was

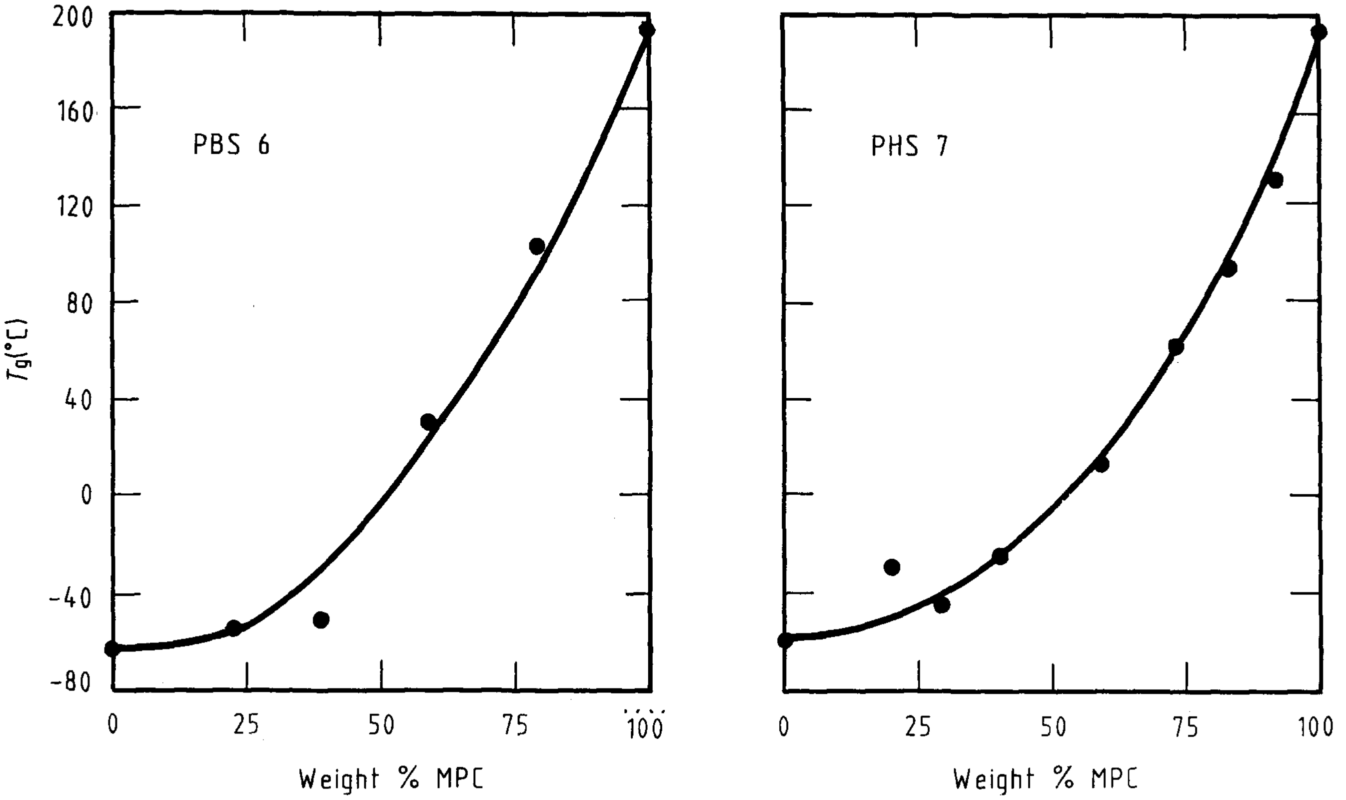


Figure 2 Glass transitions for MPC/PBS 6 and for MPC/PHS 7 blends cast from $MeCl_2$

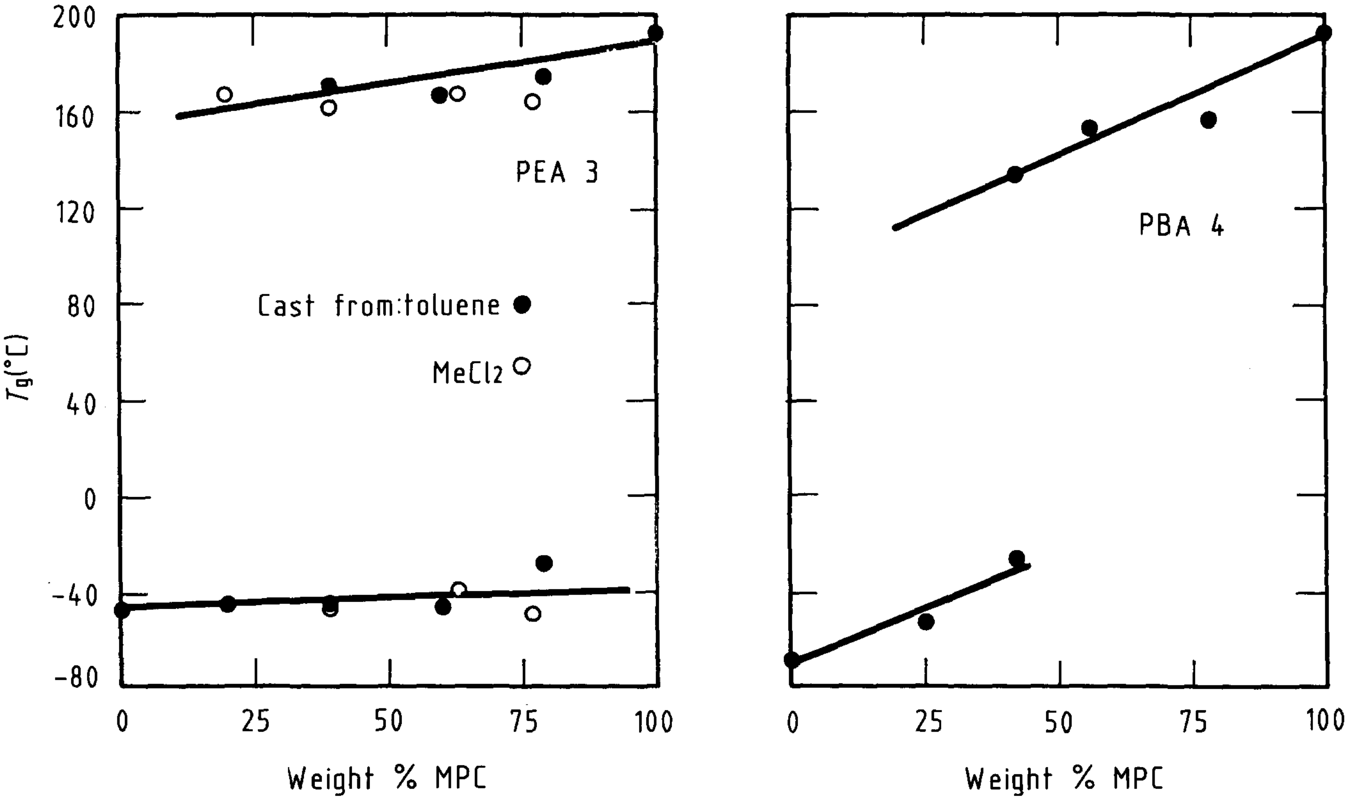


Figure 3 Glass transitions for MPC/PEA 3 blends cast from $MeCl_2$ and toluene and for MPC/PBA 4 blends cast from $MeCl_2$

previously found to undergo solvent induced crystallization when toluene or THF were used as the solvent to cast pure MPC or blends containing MPC[8]. However, no crystallization occurred if $MeCl_2$ was used instead. In some cases here, thermally induced crystallization took place in addition to the solvent induced crystallization, as suggested from our visual observations on heating.

Blends of MPC with all aliphatic polyesters show some crystallinity when cast from either toluene or $MeCl_2$, although the crystallinity observed in the latter case is much less than in the former as seen in *Figure 5*. No

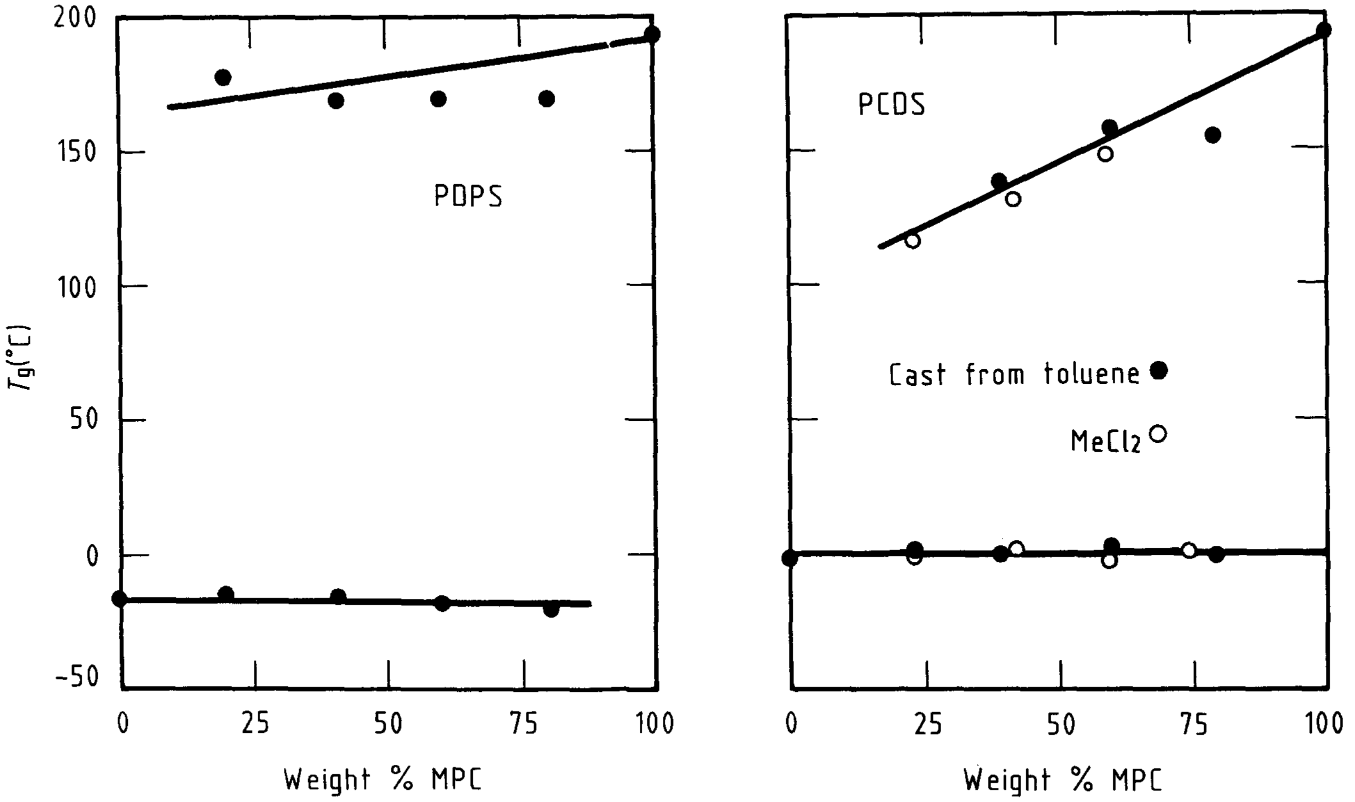


Figure 4 Glass transition behaviour for MPC/PDPS blends cast from toluene and for MPC/PCDS blends cast from toluene and $MeCl_2$

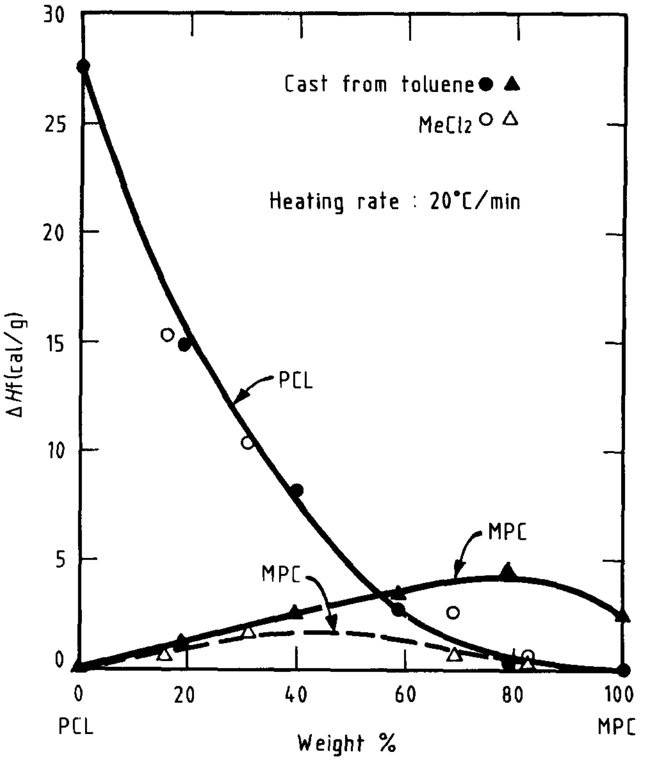


Figure 5 Enthalpy of fusion for MPC and PCL in blends cast from toluene (●, PCL and ▲, MPC) and in blends cast from $MeCl_2$ (○, PCL and △, MPC)

significant differences were observed in PCL crystallinity for blends cast from toluene or $MeCl_2$ as *Figure 5* shows. Similar behaviour was observed for blends of bisphenol-A polycarbonate with aliphatic polyesters even when melt blended[14]. The presence of crystallinity was attributed to the plasticizing effect of PCL. We believe that the observed MPC crystallinity in blends cast from $MeCl_2$ is probably due to the plasticizing effect of PCL also since no MPC crystallinity in it all was observed for blends cast from $MeCl_2$ containing MPC and other polymers with high T_gs[8]. For blends cast from toluene, the crystallization may have two different origins of plasticization, i.e. the polyester and the solvent. An indirect proof of the plasticizing effect of PCL in MPC is seen in the fact that there is still some MPC crystallinity present, even after the PCL rich blends were quenched from the molten state to about −63°C. The depression in the glass transition of MPC after blending with PCL allowed the otherwise rigid chains the mobility to crystallize.

It should no noted, however, that the amount of crystallinity left after the quenching process is extremely small (the heat of fusion is less than 1 cal/g). This kind of behaviour was observed not only for blends containing PCL but also for all the other miscible blends containing MPC and aliphatic polyesters.

All the miscible blends were tested for lower critical solution temperatures, *LCST*, behaviour. In general, the blends were quite cloudy at room temperature. On heating the films above the polyester melting point, the cloudiness decreased but it only completely vanished above the MPC melting point. In all cases, the blends remained clear above this temperature until decomposition took place. In some cases an increase in cloudiness between the polyester and MPC melting points was observed. This additional cloudiness is probably due to thermally induced crystallization of MPC, as previously suggested[8]. In contrast, MPC blends containing PBA 4 or PEA 3 remained cloudy on heating up to decomposition. In conclusion, these visual observations of the blends on heating are in good agreement with the d.s.c. conclusions.

PPO blends

As mentioned earlier, there are structural similarities between MPC and PPO so it would be quite interesting to know if PPO is miscible with any aliphatic polyesters. Thus, some exploratory experiments were done to investigate this question. *Figure 6* shows the glass transition behaviour observed for PPO/PCL blends. A glass transition was detected for all blend compositions at a temperature slightly less than the glass transition of pure PPO. We could not detect a glass transition corresponding to a PCL rich phase. These blends were cloudy or white and remained so after heating well above the PPO melting point. Based on the above, this blend was judged to be essentially immiscible. Preliminary results for PPO/PBS 6 and PPO/PBA 4 blends of a single composition in each case seem to indicate similar results. Thus, it appears unlikely that PPO is miscible with any aliphatic polyesters.

EVALUATION OF INTERACTION PARAMETERS

The melting point depression phenomenon, observed in many miscible polymer blends containing at least one crystallizable component, has proved to be a quick and useful way to make quantitative estimates of the strength of the interactions in polymer blends expressed in terms of the interaction energy density, *B*, defined by the following:

$$\Delta H_{\mathrm{mix}} = B\phi_1\phi_2$$

Using the expression appropriate for a crystalline–amorphous polymer pair derived by Nishi and Wang[15], based on Scott's equation[16] for thermodynamic mixing of two polymers, the interaction energy density, *B*, can be directly determined from the slope of the line obtained by plotting melting point *versus* the square of the volume fraction of the amorphous component. This treatment assumes that the interaction energy density *B* is independent of composition. The direct application of this analysis to the current system is complicated by the fact that both polymers crystallize. To minimize the effects due to the presence of MPC crystallinity, the samples were heated above the melting point of MPC by approximately 30°C during the heating–cooling cycle as described in the Experimental section. This procedure reduced the amount of MPC crystallinity to a rather low level.

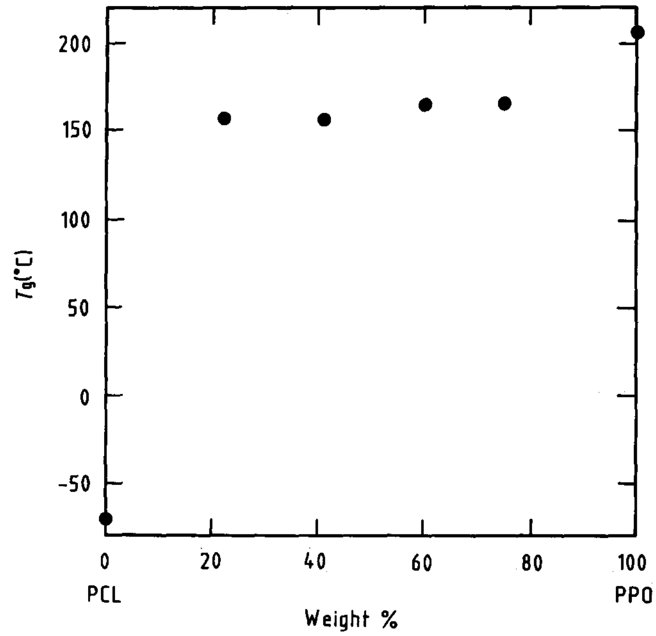


Figure 6 Glass transitions for PPO blends with PCL

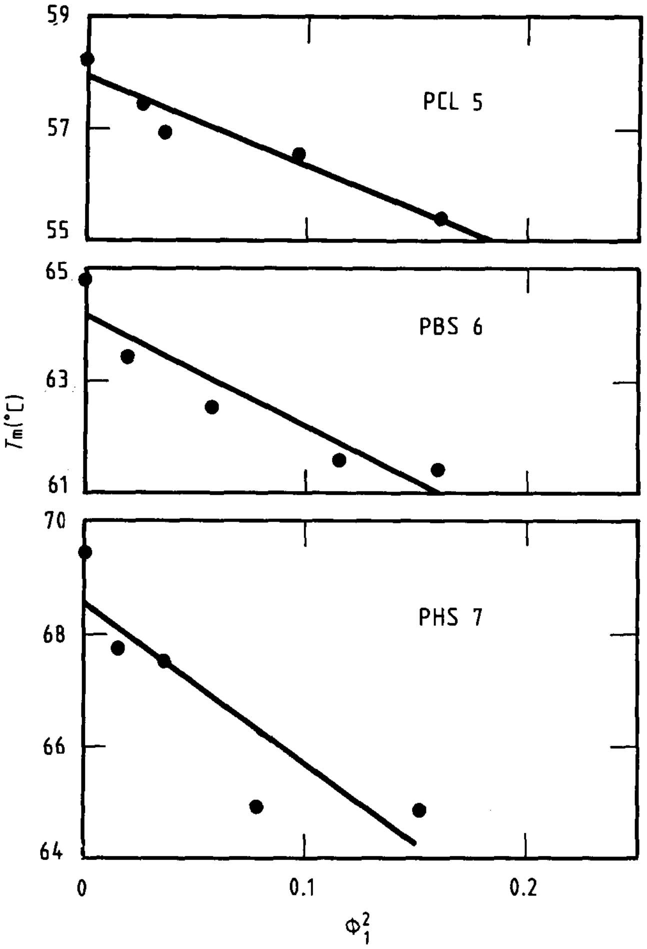


Figure 7 Analysis of PCL 5, PBS 6 and PHS 7 melting point depression in blends with MPC

In the first heat MPC showed a higher degree of crystallinity in blends cast from toluene than in blends cast from $MeCl_2$ (*Figure 5*). After conditioning the blends at 317°C and then slow cooling at 10°C/min, the second heat revealed no differences in MPC crystallinity for blends cast in the two solvents.

Plots of melting point *versus* $\phi_1'^2$ are shown in *Figures 7* and *8* for the miscible MPC–polyester systems. Morra and Stein[17] pointed out that lamellar thicknesses of crystallites are usually finite and this fact can complicate the interpretation of the melting point data. This problem may be minimized by using Hoffman–Weeks plots[18] to estimate the melting point at infinite lamellar thickness; however, this approach imposes other complications for the present systems since such annealing will also promote MPC crystallization. Consequently, we elected to analyse the current data without correction in this manner which should give at least a useful estimate of the interaction parameter. A least squares analysis was used to construct the lines shown in *Figures 7* and *9* and *B* was computed from the slope according to the Nishi–Wang equation.

The experimental values for *B* deduced in the manner described above are plotted in *Figure 9 versus* the

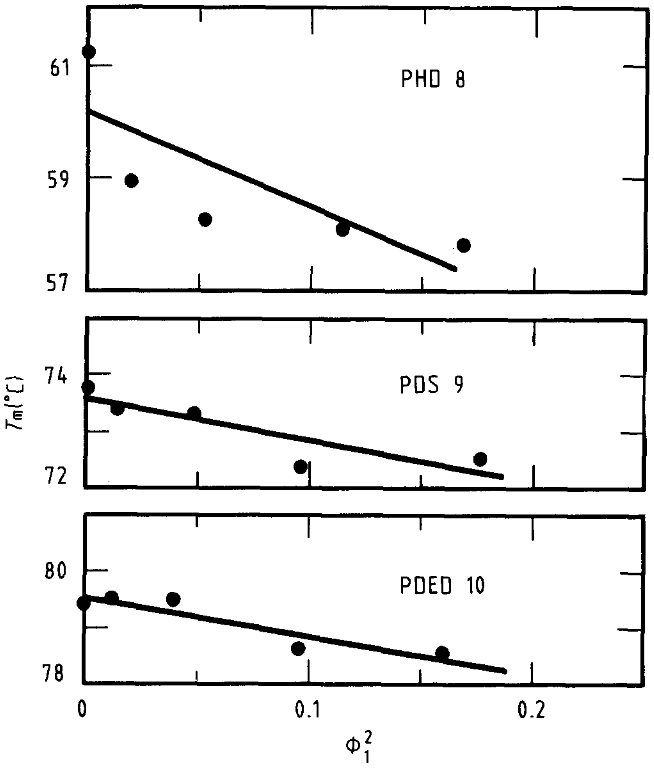


Figure 8 Analysis of PHD 8, PDS 9 and PDEDE 10 melting point depression in blends with MPC

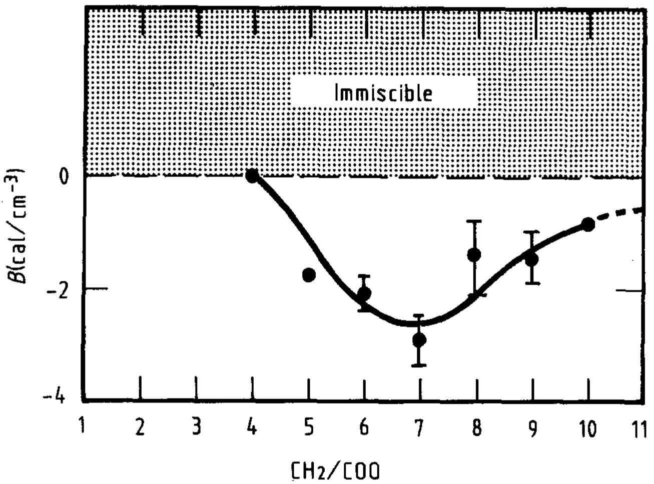


Figure 9 Interaction parameters for MPC–polyester blends obtained by melting depression analysis

CH_2/COO ratio for the polyester components. In some cases, bars are shown rather than points to indicate the limits of B calculated by including or by not the melting point for the pure polyester. The solid line constructed through the points in *Figure 9* was drawn considering $B=0$ for MPC/PBA 4, since MPC was found to be partially miscible with PBA 4 based on glass transition behaviour and essentially no melting point depression was found for this system. A dashed line is shown in *Figure 9* for a CH_2/COO ratio larger than 10, since those polyesters were not tested for melting point depression.

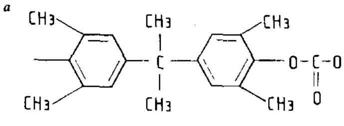
SUMMARY

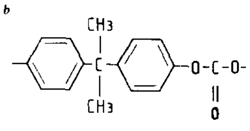
The observations described above demonstrate that tetramethyl bisphenol-A polycarbonate or MPC is miscible with linear aliphatic polyesters having five to at least ten aliphatic carbons per ester group in the repeat structure. Poly(butylene adipate) and poly(1,4-cyclohexane dimethylene succinate) show some partial miscibility with MPC whereas poly(ethylene adipate) and poly(2,2-dimethyl-1,3-propylene succinate) blends with MPC were completely phase separated. These results are summarized in *Table 2*.

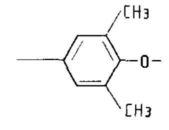
Owing to the structural similarities of MPC with bisphenol-A polycarbonate, PC, and with poly(phenylene oxide), PPO, available information about the phase behaviour of blends of these polymers with the various polyesters are also included in *Table 2* for comparison. Several important points become apparent. The four methyl groups which distinguish the repeat units of MPC and PC cause a considerable shift in the range of polyester structures for which miscible blends are formed with these two polymers. PC is miscible with polyesters having low CH_2/COO ratios; whereas, MPC is only miscible with polyesters at the higher end of the CH_2/COO scale. In fact, poly(ε-caprolactone) is the only one of these polyesters with which both PC and MPC are miscible. Interestingly, PC blends with PCL exhibit *LCST* behaviour[14]; whereas, MPC blends with PCL do not phase separate on heating prior to decomposition suggesting stronger favourable interactions for the latter than the former[19]. Several factors may be working simultaneously to cause this shift in CH_2/COO range for miscibility with MPC compared with PC including: the increased aliphatic hydrocarbon content of MPC relative to PC which would affect dispersive interactions and might favour polyesters with higher hydrocarbon contents, the methyl groups may partially shield

Table 2 Summary of phase behaviour for blends containing MPC, PC and PPO with aliphatic polyesters

	MPC[a]	PC[b]	PPO[c]
PES 2	n.t.[d]	miscible[f]	n.t.[d]
PEA 3	immiscible[e]	miscible[f]	n.t.[d]
PBA 4	partially miscible	miscible[f]	tentatively[e] partially miscible
PCL 5	miscible[e]	miscible[f]	partially[e] miscible
PBS 6	miscible[e]	n.t.[d]	tentatively[e] partially miscible
PHS 7	miscible[e]	partially mmiscible	n.t.[d]
PHD 8	miscible[e]	n.t.[d]	n.t.[d]
PDS 9	miscible[e]	n.t.[d]	n.t.[d]
PDEDE 10	miscible[e]	n.t.[d]	n.t.[d]
PDPS	immiscible[e]	partially miscible[f]	n.t.[d]
PCDS	partially miscible[e]	miscible	n.t.[d]

a


b


c


[d] n.t. = not tested
[e] This study
[f] Refs. 1, 14 and 23

interactions involving the carbonate group, and, of course, ring substitution is known to cause important inductive .effects. Since PPO is apparently not fully miscible with any aliphatic polyester suggests that aromatic ring interactions (even when strengthened by substitution of methyl groups) with the ester groups are not sufficient to cause miscibility. The presence of the carbonate group is, thus, apparently an important factor in the observed miscibility of polyesters with PC and MPC.

Melting point depression was used to estimate interaction parameters for miscible blends of polyesters with MPC. The trends with structure of the polyester, i.e. the CH_2/COO ratio, shown in *Figure 9*, are quite similar to those observed for blends of polyesters with other polymers[2-5,7]. Unfortuantely, interaction parameters have not been determined for blends with PC so no comparisons with the present results can be made; however, we can say that MPC seems to be miscible with a wider but different range of polyesters than PC is.

As a final point, we mention the difficulties encountered in this study with phase separation during solution casting. This points out the importance of choosing the solvent for blend preparation. Without care and attention to this issue, one can erroneously conclude that two polymers are immiscible when in fact they are fully miscible. We have encountered this possibility in other systems.

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