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Miscibility in Blends of Poly(vinyl chloride) and Polylactones

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ABSTRACT: The miscibility of blends of poly(vinyl chloride) (PVC) with polylactones of the β-propiolactone series (poly(α-methyl-α-*n*-propyl-β-propiolactone) (MPPL), poly(α,α-dimethyl-β-propiolactone) or polypivalolactone (PPL), and poly(α-methyl-α-ethyl-β-propiolactone) (MEPL)) has been studied by measurements of specific heat, mechanical relaxation, and density. These measurements indicate that there is extensive mixing between the segments of the two components of each blend since a single glass transition temperature and a decrease in melting point have been observed. From the depression in the melting point data, the interaction parameter χ_{12} has been shown to be equal to −0.29 and −0.05 for PVC/MPPL and PVC/PPL blends, respectively.

Even if it is well known that poly(ε-caprolactone) (PCL) is miscible with a large number of polymers,[1] it is not clearly understood why this is so. However, it has often been suggested that specific interactions can be the driving force toward the formation of blends. For example, Olabisi[2] has concluded that the PCL/poly(vinyl chloride) (PVC) blends are a result of the proton donating character of the α-hydrogens of PVC combined with the proton accepting character of the carbonyl groups of PCL. On the basis of this conclusion, one can rationalize why PCL is generally miscible with polymers containing hydrogens with a proton donating character, or hydroxyl groups, as for example poly(hydroxy ether), poly(epichlorohydrin), and poly(3,3-bis(chloromethyl)oxacyclobutane) (penton). Similar specific interactions have been suggested in blends of poly(butylene terephthalate)/poly(hydroxy ether of Bisphenol A) (3), Nylon 6/ethyleneacrylic acid copolymer,[4] poly(vinyl chloride)/ethylene–vinyl acetate–SO_2 terpolymers,[5] poly(hydroxy ether of Bisphenol A)/poly(cyclohexylenedimethylene tere/isophthalate),[3] poly(caprolactone)/poly(hydroxy ether of Bisphenol A),[3] poly(vinyl chloride)/poly(butylene terephthalate),[6] poly(styrene)/poly(phenylene oxide),[7] poly(vinylidene fluoride)/poly(methyl acrylate),[8] poly(vinylidene fluoride)/poly(ethyl acrylate),[8] poly(vinylidene fluoride)/poly(vinyl acetate),[9] poly(vinylidene fluoride)/poly(methyl methacrylate),[10] poly(vinylidene fluoride)/poly(ethyl methacrylate),[10] and poly(methyl methacrylate)/styrene–acrylonitrile copolymers.[11]

Following Olabisi's proposal, blends of PVC with common polyesters are expected to be thermodynamically miscible. In order to check this hypothesis, we have chosen polyesters derived from β-propiolactone substituted in α,α. This series of polymers presents a wide range of physical properties including degrees of crystallinity ranging from 10 to 80% and melting points ranging from 25 to 240 °C.[12,13]

It is then the purpose of the present paper to study the degree of miscibility of PVC/polylactone blends by measurements of glass transition temperature (T_g), melting point (T_m), density, and mechanical relaxation. These blends will be shown to be thermodynamically miscible at all compositions in agreement with Olabisi's proposal. These results support the hypothesis of a specific interaction between the carbonyl group of the polyester and the α-hydrogens of PVC.

Experimental Section

Three different polylactones have been used in the present study. A polypivalolactone (PPL) sample has been obtained from the Shell Laboratories in Amsterdam. Its main characteristics are reported in Table I. This polymer has a high degree of crystallinity under normal conditions.[14] Two other polylactones have also been used: poly(α-methyl-α-*n*-propyl-β-propiolactone) (MPPL) and poly(α-methyl-α-ethyl-β-propiolactone) (MEPL). Their main characteristics are also given in Table I. These latter polymers have low degrees of crystallinity.[15,16] Two different PVC's, having different molecular weights (Table I), have been used. Both samples were supplied by the Shawinigan Chemical Co., Shawinigan, P.Q. Unless otherwise specified, all results reported herein have been obtained from the PVC1 sample. However, the differences observed upon using PVC1 or PVC2 are negligible.

Polymer films were cast from 1% solutions in tetrahydrofuran (MPPL, MEPL, and their mixtures) or in *o*-dichlorobenzene (PPL and its mixtures). The PPL–dichlorobenzene solutions were prepared at 180 °C. Solvent evaporation was conducted at room temperature (tetrahydrofuran) or at about 80 °C under reduced pressure ($\sim$30 mm) for 1 week (*o*-dichlorobenzene). The resulting films were dried under vacuum until they reached constant weight. The film thickness was about 200 μm. All of the films were transparent although the PPL and PPL/PVC films were slightly hazy due to the high degree of crystallinity of PPL which gives rise to light scattering.[17] The transparency of blends is a necessary condition to miscibility, but it is not a sufficient one.[18]

Differential scanning calorimetry (DSC) measurements were conducted on a Perkin-Elmer DSC-2 apparatus which was calibrated with *n*-octane (216 K) and indium (429 K). Reported T_m were recorded at the end of the melting curve, and a heating rate of 40 °C/min was used in all cases.

Dynamic mechanical measurements were conducted using a Rheovibron DDV-II apparatus (Toyo Baldwin Co.). The observed tan δ were corrected according to Massa's equation.[19,20]

Density measurements were made at 23 °C by the floating method, using KI solutions.

Results and Discussion

1. PVC/MPPL Blends. DSC scans in the T_g transition zone lead to the curves shown in Figure 1 for PVC, MPPL, and their mixtures. All blends present a single T_g which increases regularly with composition. MPPL has a T_g of 275 K which is in agreement with values determined previously from dynamic mechanical and relaxation experiments.[21] PVC has its T_g at 337.5 K, in agreement with literature values.[22]

The regular increase in T_g of the blends is shown in Figure 2 and Table II. These results are satisfactorily represented (in Figure 2) by the Fox equation[23]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

where T_g, T_{g1}, and T_{g2} are the glass temperatures of the blend, of PVC, and of MPPL, respectively, and w_1 and w_2 are the weight fractions of PVC and MPPL. The experimental data can alternatively be represented by the Gordon–Taylor equation[24] or the Bueche–Kelley equation.[25] The results are not precise enough or regular enough to allow one to distinguish between these different possibilities. The latter equation was derived by assuming additivity of free volume and it suggests extensive mixing

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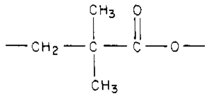
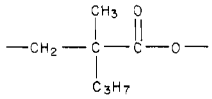
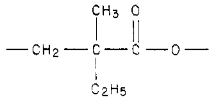
Table I
Characterization Data of Polymers

symbol	structure	mol wt,[a] g mol^{-1}	density, g cm^{-3}	enthalpy of fusion, kJ mol^{-1}	ref
PPL	 $-CH_2-C(CH_3)_2-C(=O)-O-$	280 000 ($\overline{M}_v$)	1.185	14.5	13, 14
MPPL	 $-CH_2-C(CH_3)(C_3H_7)-C(=O)-O-$	131 000 ($\overline{M}_w$) 88 000 ($\overline{M}_n$)	1.07	14.6	13, 15
MEPL	 $-CH_2-C(CH_3)(C_2H_5)-C(=O)-O-$	80 000 ($\overline{M}_w$)	1.12		13, 16
PVC1	$-CH_2-CHCl-$	80 000 ($\overline{M}_w$)	1.385		
PVC2	$-CH_2-CHCl-$	160 000 ($\overline{M}_w$)	1.41		

[a] $\overline{M}_n$ = number average molecular weight, $\overline{M}_v$ = viscosity average molecular weight, and $\overline{M}_w$ = weight average molecular weight (GPC determination).

Table II
Glass Transition Temperature, Melting Temperature, and Enthalpy of Fusion of PVC, MPPL, and Their Mixtures

% PVC	T_g, K	T_m, K	ΔH_2, J g^{-1}
0	275	370	27
10	281.5	367	27
20	286.5	364.5	16
40	298	358.5	11
50	305.5	356	
70	311		
80	318		
90	325		
95	328		
100	337.5		

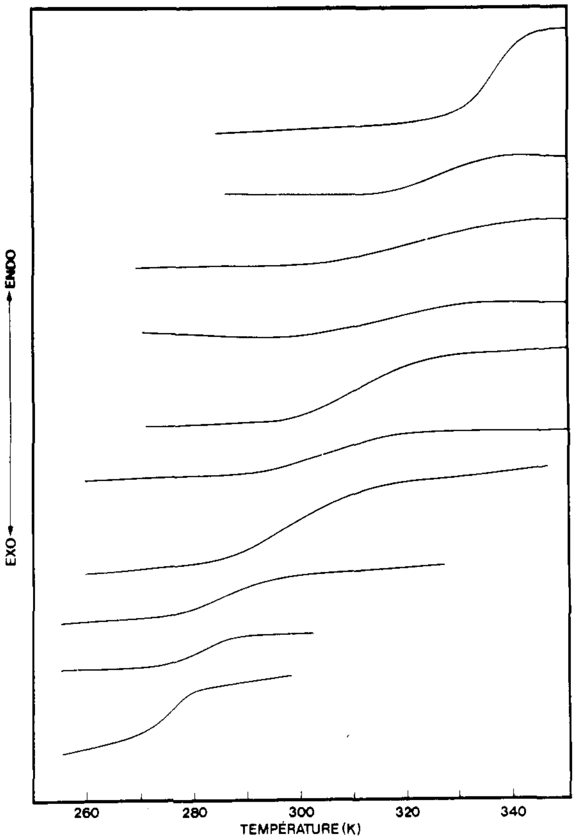


Figure 1. DSC curves in the T_g transition zone for PVC/MPPL blends. The lower curve is that of MPPL and the higher one that of PVC. The intermediate curves, from bottom to top, correspond to 0.1, 0.2, 0.3, 0.5, 0.6, 0.8, 0.9 and 0.95 weight fraction of PVC, respectively.

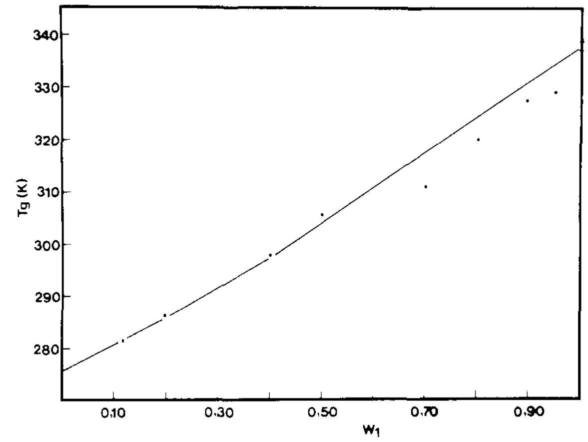


Figure 2. Glass transition temperatures of PVC/MPPL blends as a function of weight fraction of PVC. The solid line is drawn according to eq 1.

of the different segments of the blend.

It is also observed in Figure 1 that the width of the transition zone changes with composition. For MPPL and PVC, the width of the transition zone covers about 10 K. But for most blends, the width of the transition is of the order of 20 K. It is believed that such broadening for so-called miscible blends is indicative of partial miscibility.[18,26,27] It has been interpreted as due to microheterogeneities where local composition fluctuations are in excess of normal density and temperature fluctuations.[18,28] Similar broadenings are observed in the transition zone of heterogenous copolymers.[29] For PVC/MPPL blends, the presence of a single T_g for each blend certainly indicates an extensive degree of miscibility, but at the same time the broadening of the transition zone indicates that miscibility does not occur completely at the molecular level.

The degree of miscibility of blends where one component is semicrystalline can also be followed by measurement of T_m. As shown in Figure 3 and Table II, the melting temperature of MPPL decreases significantly in the blends. This result can also be interpreted as being due to extensive mixing of the segments of the blends. Quantitatively, it has been shown that depression in the melting point data can be interpreted according to the equation[30]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_2}{\Delta H_2 V_1} \chi_{12}\phi_1^2 \qquad (2)$$

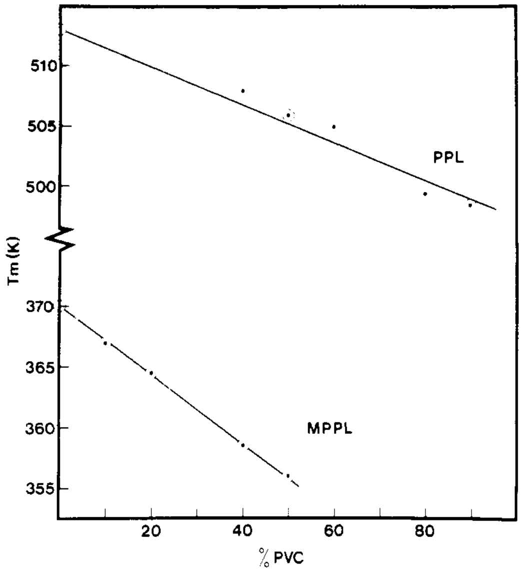


Figure 3. Melting temperatures of PVC/MPPL and PVC/PPL blends as a function of weight fraction of PVC. The data reported are averages obtained from several measurements.

where T_m is the melting point of the blend, T_m^0 is the melting point of pure MPPL, R is the gas constant, ΔH_2 is the enthalpy of fusion of MPPL, V_2 and V_1 are the molar volumes of the repeating units of MPPL and PVC, respectively, ϕ_1 is the volume fraction of PVC, and χ_{12} is the PVC/MPPL thermodynamic interaction parameter. As shown in Figure 4, a plot of $1/T_m$ as a function of ϕ_1^2 leads to a straight line, from which χ_{12} can be calculated. If V_2 and V_1 are taken equal to 119.6 cm^3 mol^{-1} and 44.3 cm^3 mol^{-1}, respectively, and ΔH_2 is equal to 14.6 kJ mol^{-1},[31] $\chi_{12} = -0.29$ for the PVC/MPPL blend. A negative value of χ_{12} indicates the formation of a thermodynamically miscible blend above the melting point of MPPL. The magnitude of the χ_{12} value is of the same order as those found previously for poly(vinylidene fluoride)/poly(methyl methacrylate),[30] poly(caprolactone)/poly(vinyl chloride),[2] and poly(styrene)/poly(vinyl methyl ether).[32]

Values of the enthalpy of fusion, ΔH_2, reported in units of kilojoules per gram of MPPL, are also given in Table II. Blends containing more than 50% PVC do not allow MPPL to crystallize. Blends containing from 0 to 40% PVC have values of ΔH_2 which decrease regularly as the composition in PVC increases. Similar examples can be found in the literature for several other blends.[31,33,34] The presence of PVC, which acts as a polymer diluent, increases the viscosity of the medium and slows down the crystallization rate of MPPL. For blends containing 50% or more PVC, it stops it completely, at least under the conditions of sample preparation followed herein.

Densities of PVC/MPPL blends have also been measured and compared to those calculated from the relation

$$\frac{1}{d} = \frac{w_1}{d_1} + \frac{w_2}{d_2} \qquad (3)$$

where d is the density of the blend and d_1 and d_2 are the densities of PVC and MPPL, respectively. Theoretical blend densities have been calculated by using the density of MPPL corresponding to its real degree of crystallinity in the blend. A value of 1.04 g cm^{-3} is used for an amorphous blend while a value of 1.07 g cm^{-3} is preferred for a 25% crystallinity blend. It is then observed that the experimental values of density are in general slightly larger than those calculated from eq 3, although the difference is not very large. This difference is believed to be significant and suggests specific interactions between the two components of the blends which result in an increase in density. Similar observations have been made for other miscible blends[18,32,35-40] although one case is known where an increase in density has been observed for an immiscible blend.[41]

Table III
Experimental and Theoretical Density Values of PVC/MPPL Blends, Measured at 23 °C

% PVC	deg of cryst, %	exptl density, g cm^{-3}	theor density (eq 3), g cm^{-3}
0	25	1.07 (1.04)[a]	
10	25	1.10	1.10
20	15	1.12	1.12
40	10.5	1.18	1.16
50	0	1.20	1.19
70	0	1.28	1.26
80	0	1.32	1.30
90	0	1.34	1.34
95	0	1.37	1.36
100	0	1.39	

[a] Value measured for an amorphous sample.[30]

Table IV
Melting Temperature and Enthalpy of Fusion of PVC, PPL, and Their Mixtures

% PVC	T_m, K	ΔH_2, J g^{-1}
0	513	94
40	508	
50	506	99
60	505	
80	502	101
90	501	104

Finally, dynamic mechanical measurements have been made in order to confirm previous conclusions. It is generally felt that the segmental microbrownian motions responsible for the dynamic mechanical loss peaks involve smaller range motions than the molecular processes responsible for the discontinuity observed in heat capacity by DSC.[18,42] Consequently, measurements of T_g by dynamic mechanical analysis are a more sensitive test than the DSC in order to detect microheterogeneities in blends.

Values of storage modulus, E', loss modulus, E'', and loss angle, tan δ, have then been measured at 110 Hz as a function of temperature. All of these measurements indicate the presence of a single glass transition temperature for each blend, the value of which increases with an increase in PVC composition. These results again indicate extensive mixing between MPPL and PVC.

2. PVC/PPL Blends. If the miscibility of PVC/MPPL blends is due to specific interactions between PVC and MPPL homopolymers, other polylactones of the same series are expected to be equally miscible with PVC. Attempts have then been made to replace MPPL by PPL. However, PPL has a T_g of 373 K, as measured on the Rheovibron at 110 Hz,[14] as compared to a T_g of 361 K for PVC under the same conditions. Both T_g being very close, it seems rather difficult to use T_g measurements to prove the miscibility of the corresponding blends, and another technique must be used for that purpose.

As reported in Table IV, measurements of melting point and enthalpy of fusion have been done. A significant decrease in melting point is observed as the PVC fraction increases. The decrease is however not as important as that already reported for PVC/MPPL blends (Figure 3). These data lead to a straight line when plotted according to eq 2. Assuming that $V_2 = 83.3$ cm^3 mol^{-1} and $\Delta H_2 = 14.5$ kJ mol^{-1},[43] an interaction parameter $\chi_{12} = -0.05$ is found. The negative sign of χ_{12} certainly indicates the

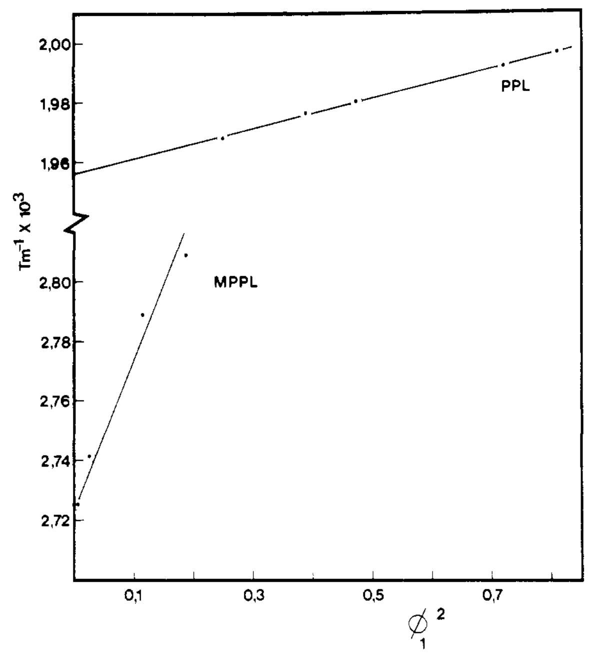


Figure 4. Plot of (the melting temperature)$^{-1}$ of PVC/MPPL and PVC/PPL blends as a function of (volume fraction of PVC)^2.

formation of a thermodynamically miscible blend above the melting point of PPL, but this value is six times smaller than that previously found for the system PVC/MPPL. Values of χ_{12} of the same order of magnitude have been reported for the mixture poly(methyl methacrylate)/poly(vinylidene fluoride)[44] which has been shown to be totally miscible on the basis of the observation of a single T_g.

At the same time, one observes from Table IV that the enthalpy of fusion of PPL in the PVC/PPL blends remains about constant and independent of the composition of the blend, emphasizing the strong tendency of PPL to crystallize. For example, in the blend containing 90% PVC, since an enthalpy of fusion of 104 J g^{-1} corresponds to a degree of crystallinity of 70%, the amorphous phase of the sample contains only 4% PPL and 96% PVC. Similarly in a blend containing 50% PVC, the amorphous phase is made of 77% PVC and only 23% PPL. These results point out the very strong tendency of PPL to crystallize. A polymer with a smaller tendency toward crystallization is expected to become amorphous when its composition in a blend is reduced to 50% or less. This behavior is effectively observed for PVC/MPPL blends and for several others.[30,33,34] On the other hand, other semicrystalline polymers have shown their ability to crystallize over the complete range of composition with a constant degree of crystallinity. This behavior has been found for poly(phenylene oxide) in poly(styrene)/poly(phenylene oxide) blends,[45] for poly(vinylidene fluoride) in poly(methyl methacrylate)/poly(vinylidene fluoride) blends,[30] and for poly(caprolactone) and poly(vinylidene fluoride) in the mixtures of these two semicrystalline polymers.[46]

Finally, experimental and theoretical (eq 3) values of density are reported in Table V. The theoretical densities were calculated by assuming the same degree of crystallinity of PPL for all blends. Experimental data are often slightly larger than the theoretical ones, but the tendency is not very pronounced, and these data are rather inconclusive.

No measurements have been made on blends containing less than 40% PVC since these samples were extremely brittle and difficult to handle.

Table V
Experimental and Theoretical Density Values of PVC/PPL Blends, Measured at 23 °C[b]

% PVC	exptl density,[a] g cm^{-3}	theor density (eq 3),[a] g cm^{-3}
0	1.18	
49	1.27	1.28
50	1.30	1.28
55	(1.30)	(1.29)
81	1.36	1.34
90	(1.38)	(1.38)
90	1.38	1.36
92	(1.38)	(1.38)
95	(1.38)	(1.39)
95	(1.39)	(1.39)
100	1.39 (1.40)	

[a] Values in parentheses were obtained for samples made from PVC2 (Table I). [b] All calculations were performed assuming a constant degree of crystallinity for PPL.

Table VI
Glass Transition Temperature, Melting Temperature, and Enthalpy of Fusion of PVC, MEPL, and Their Mixtures

% PVC	T_g, K exptl	T_g, K eq 1	T_m, K	ΔH_2, J g^{-1}
0	260		397	30.2
25	276	276	384	7.7
65	302.5	305		
100	338			

3. **PVC/MEPL Blends.** In order to further substantiate the generality of the miscibility phenomenon between polylactones and PVC, additional measurements have been made on two PVC/MEPL blends. The results of this investigation are shown in Table VI. A single T_g is found in both cases, and they satisfactorily agree with the T_g calculated on the basis of eq 1. An important decrease in the melting point is also observed along with a decrease in the enthalpy of fusion and an absence of melting point for the blend containing 65% PVC. This blend seems to behave very similarly to the PVC/MPPL blend.

Conclusions

The experimental evidence presented in this paper leads to the conclusion that there is extensive mixing between PVC and polylactones when they are prepared from solution. Most data, including specific heat (T_g and T_m), density, and mechanical relaxation, indicate complete miscibility. Of course, a single series of polyester has been considered, but the conclusion reached in this paper seems to be more general since PVC has been shown to be totally miscible with PCL[1,2] and poly(butylene terephthalate).[6] The miscibility of PVC with polyesters seems then to be a quite general phenomenon.

We have found interaction parameters equal to −0.29 for PVC/MPPL blends and to −0.05 for PVC/PPL blends. The large difference between these two values is a little surprising considering the similarity in structure between MPPL and PPL. It may be due in part to the higher molecular weight of PPL since it is known that an increase in molecular weight reduces the miscibility between blend components,[45,47] and consequently it decreases χ_{12}. It can also be related to the conditions of preparation of the samples which were slightly different. Solvent evaporation for PVC/MPPL blends was conducted at 25 K above the T_g of MPPL and below that of PVC while it was conducted for PVC/PPL blends at a temperature slightly above the T_g of both PVC and PPL [reference is being made here to the T_g recorded by DSC and not to those recorded by dynamic mechanical measurements]. Indeed, Roerdink and Challa have shown that the interaction parameter of polymer–polymer blends depends heavily upon the conditions of preparation of the samples.[44] Consequently, a quantitative comparison of interaction parameters must be reserved to samples prepared in well controlled and meaningful conditions of crystallization, which is not the case here.

When dealing with polymer–polymer blends, reference is often made to solubility parameters in order to gain some qualitative information on the tendency toward miscibility of two polymers. Using Hoy's tables,[47] we have computed solubility parameters equal to 9.2, 8.8, and 8.2 for PVC, PPL, and MPPL, respectively. Calculations according to Small's tables were even worse since they lead to polylactone solubility parameters totally different from that of PVC. The immiscibility of PVC/polylactone blends predicted by these calculations is of course denied by the experimental results presented in this paper. This contradiction points out the futility of the solubility parameter argument in predicting the miscibility of polar polymer blends. Numerous similar examples are known in the literature.[47,48]

Finally, our results are consistent with the suggestion of a specific interaction between the proton donating character of the α-hydrogens of PVC and the proton accepting character of the carbonyl groups of polyesters. Of course, additional data need to be obtained in order to prove directly this assertion, especially when considering that in a series of blends where such interactions have been suggested and tested on a large number of systems exceptions are found which are not easily explained.[46,49]

Note Added in Proof: After the submission of this paper for publication, an article by Coleman and Zarian[50] has shown from Fourier-transform infrared spectroscopy measurements that the specific interaction between PCL and PVC implies the carbonyl group of PCL. No indication is given in this paper about the nature of the interaction in PVC.

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