Surface Studies of Polymer Blends. 4. An ESCA, IR, and DSC Study of the Effect of Homopolymer Molecular Weight on Crystallinity and Miscibility of Poly(ε-caprolactone)/Poly(vinyl chloride) Homopolymer Blends

Michael B. Clark, Jr.,† **Cindy A. Burkhardt, and Joseph A. Gardella, Jr.***

Department of Chemistry, State University of New York at Buffalo,
Buffalo, New York 14214

Received February 26, 1990; Revised Manuscript Received July 10, 1990

ABSTRACT: The studies presented explore the effects of homopolymer crystallinity and molecular weight on the surface composition of a homopolymer blend system. Angle-dependent electron spectroscopy for chemical analysis (ESCA or XPS (X-ray photoelectron spectroscopy)), Fourier transform infrared spectroscopy coupled with attenuated total reflectance (ATR-FTIR), and differential scanning calorimetry (DSC) results are presented for miscible and immiscible solvent-cast homopolymer blends of poly(ε-caprolactone) (PCL) and poly(vinyl chloride) (PVC). From these studies, it was found that the surface composition of a PCL/PVC homopolymer blend is governed by a combination of the homopolymer molecular weight and degree of crystallinity.

Introduction

The blending or simple mixing of polymers is an easy and inexpensive method of modifying various properties of a polymer such as flexibility, heat distortion, and processibility.[1,2] It is believed that property modification is directly related to compatibility or miscibility of polymers forming a blend.[3] Totally miscible homopolymers are microscopically homogeneous (i.e., mixed on a molecular scale) and partially miscible blends display microscopic heterogeneity.[2] Partially miscible homopolymer blends can contain a significant degree of homopolymer segment mixing on a molecular scale, thus effectively producing mechanically compatible phases. Conversely, immiscible homopolymer blends are macroscopically heterogeneous, displaying multiphase behavior.

An in-depth discussion of the definitions of homopolymer miscibility has been previously presented.[4] In general, a miscible blend can be defined by optical clarity,[5] display of a single glass transition temperature,[2,6] or an infrared spectrum that is not equivalent to the scaled addition of the individual homopolymer spectra.[7–9]

Fundamental factors that determine if homopolymer blends will be miscible or mixed on a molecular level include thermodynamic driving forces (e.g., energy of mixing or surface energetics), kinetic factors, crystallinity, and molecular weight. Obviously, structural characteristics such as degree of crystallinity and molecular weight will have a direct influence on the thermodynamics of such a process.[10] One of the driving forces for separation in multicomponent polymer systems is the difference in surface free energies of the respective components. The component with the lowest surface free energy will enrich the polymer/air interface, resulting in an overall minimization of the total free energy of the polymer system. The extent of surface-driven separation depends on bulk miscibility. However, slight surface separation can occur even in miscible blends.[11]

Polymers are not usually ordered in three dimensions, and the term "crystallinity" is used to describe the degree of order within the polymer matrix. Most crystalline polymers contain both crystalline and amorphous domains.[12] Also, the degree of crystallinity is influenced by many factors. For example, tacticity, branching, cross-linking, crystallization temperature, and molecular weight have been discussed in detail.[12] Of these parameters, crystallization temperature and homopolymer molecular weight have the greatest effect on the degree of crystallinity.[12]

The molecular weight of a polymer affects its surface free energy, mobility, and morphology. The surface tension (related to surface energy) of a homopolymer has been shown to be dependent on its molecular weight.[13] This dependence has been expressed as an empirical expression of the form

$$\gamma = \gamma_\infty - k_e/\bar{M}_n^{\,2/3}$$

where γ is the surface tension, γ_∞ is the surface tension at infinite molecular weight, k_e is an empirical constant, and $\bar{M}_n$ is the number-average molecular weight. In addition, the kinetics of crystal growth, from crystallization rate studies,[14,15] decrease as the molecular weight of the polymer increases.

Koberstein et al.[16] observed this $\bar{M}_n^{-2/3}$ dependence when studying miscible blends of polystyrene and poly(vinyl methyl ether). Surface characterizations were made by surface tension measurements of blends in the melt utilizing an automated pendant drop apparatus and by ESCA of thin films.

In general, the majority of homopolymer blends are immiscible, exhibiting segregation or multiphase behavior. One exception is the homopolymer blend system of poly(ε-caprolactone) (PCL) and poly(vinyl chloride) (PVC). Homopolymer PCL and PVC blends have been studied extensively[17–22] and were found to be miscible in the amorphous or molten state throughout the composition range 10–90 wt % PCL. In addition, these studies have shown that PCL becomes semicrystalline in blends containing 50 wt % or more PCL. Although crystalline PCL was detected, these blends were still considered to be miscible. The molecular weight polydispersities of the PCL and PVC homopolymers have been shown by small-angle X-ray scattering studies to affect the domain size in the bulk of PCL/PVC blends.[21]

As in the previous study,[22] the present work utilized ESCA, ATR-FTIR, and DSC results to compare the surface composition to that of the bulk and determine the degree of miscibility for a series of PCL/PVC blends. In contrast

---

* Author to whom correspondence should be addressed.

† Current address: Rohm and Haas Co., Norristown Road, Spring House, PA 19477.

0024-9297/91/2224-0799$02.50/0

Table I
Homopolymers Used in PCL/PVC Homopolymer Blends

polymer desig[a]	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	supplier
poly(ε-caprolactone)	33 000[b]	3.08	Scientific Polymer Products, Inc.
poly(vinyl chloride) (77PVC)	77 300[b]	1.95	Scientific Polymer Products, Inc.
poly(vinyl chloride), (190PVC)	190 000	2	Aldrich Chemical Co.
poly(vinyl chloride) (275PVC)	275 000	1.80	Scientific Polymer Products, Inc.

[a] These designations will be used throughout the discussion of the PCL/PVC homopolymer blends. [b] Secondary molecular weight standard.

to the earlier work, the number-average molecular weight of PVC was varied to determine molecular weight effects under the constraints of crystallinity. ESCA experiments yield quantitative information over a sampling depth of 80 Å, while ATR-FTIR samples much deeper into the surface (1–10.9 μm). These techniques which measure the surface composition, bonding, and structure and provide a limited compositional profile, are combined with DSC experiments which measure the bulk characteristics (i.e., miscibility and degree of crystallinity) of the PCL/PVC blends.

Experimental Section

Sample Preparation. The molecular weights and sources of polymers used in this study are listed in Table I. The three PVC samples were purified by dissolving the polymer in tetrahydrofuran (THF, Fisher), filtering, and reprecipitating by addition of absolute ethanol. This procedure produced a PVC with an oxygen content below the detectability of ESCA. Preparation of the blends was the same as previously described.[22] Briefly, thick (200–300 μm) films of the blends were prepared by solvent casting mixtures of the homopolymers from 2% (w/v) THF solutions. THF was chosen so direct comparisons with other work on this system could be made possible. ESCA and DSC results were collected in triplicate from three separate cast films. A Ge and KRS-5 ATR-FTIR spectrum was recorded for each PCL/190PVC (PVC with $\bar{M}_w$ = 190 000) and PCL/77PVC (PVC with $\bar{M}_w$ = 77 300) blend of the individual castings to ensure reproducibility.

Instrumentation. The instrumental parameters used were those described in the previous study.[22] The angle-dependent ESCA experiments were performed on a Perkin-Elmer Electronics Model 5100 ESCA using a hemispherical analyzer. All data manipulation (peak area integration, linear background subtraction, and curve fitting) was accomplished with a Perkin-Elmer 7700 computer running PHI ESCA version 2.0 software.

No degradation of the homopolymers, e.g., dehydrochlorination of PVC, was detected in twice the total analysis time used for the angle-dependent ESCA measurements. All binding energies were referenced to the carbon 1s CH_x component set to 285.0 eV.

As in the previous paper,[22] two methods of quantitation were used to calculate the surface composition of a polymer blend from the ESCA results. The first method simply relates peak areas of the elements of interest to a surface percentage through the use of homopolymer calibration references. The second method of calculating the surface composition involves curve fitting the high-resolution carbon 1s spectra and determining the relative contribution from the individual polymers to the carbon 1s peak shape.

The infrared experiments were performed on a Nicolet 7199A spectrometer with a liquid nitrogen cooled mercury–cadmium–tellurium detector. Reproducible sample contact with the internal reflection element was ensured by using a torque wrench set at 32 oz/in. The ATR-FTIR spectra were collected at 4-cm^{-1} resolution, while the transmission spectra were collected at 2-cm^{-1} resolution.

The DSC measurements were made with a DuPont 990/1090 DSC. All samples were quench cooled to 163 K and then heated to 393 K at a rate of 40 K/min with a continuous nitrogen flow rate of 20 cm^3/min. The samples were held at an isotherm for 5 min, quench cooled with liquid nitrogen, and reheated to 393 K at a rate of 40 K/min. The T_g was taken as the onset of the change of slope in heat capacity plots. This was determined by extrapolating both slopes to the point of intersection. The DSC results reported were taken from the first scans. The second scans contained a recrystallization exotherm at 293 K, attributed to PCL. Therefore, the first scans were felt to be representative of the films analyzed by the other techniques. These data were reproduced from three different castings, and the values shown are the averages of three pieces of material from each of three casts.

Table II
DSC Results for the PCL and PVC Homopolymers

homopolymer	T_g, K	T_m, K	% cryst
PCL	208.0	340.2	76.3
77PVC	331.8	ND[a]	0.0
190PVC	329.0	ND	0.0
275PVC	323.0	ND	0.0

[a] ND = not detected.

Results and Discussion

All of the PCL/PVC blend films were visually inspected for optical clarity. The blends from 77 000 $\bar{M}_w$ PVC having 10/90 and 25/75 (PCL/PVC) compositions were clear. All blend films containing <40 wt % PCL and either 190 000 $\bar{M}_w$ PVC or 275 000 $\bar{M}_w$ PVC appeared to be optically clear. Above 40 wt % PCL, the films became increasingly opaque. The above films which appeared to be clear would be considered miscible by the "optical clarity" definition.

DSC Results. The DSC results of the homopolymers used in these studies are listed in Table II. As can be seen in this table, the T_g of PCL was determined to be 208 K, and a crystalline melting temperature (T_m), attributed to crystalline PCL, was also detected at 340.2 K. This T_m was expected since PCL is a semicrystalline homopolymer. With the approach of Aubin and Prud'homme,[18] the percent crystallinity in the PCL homopolymer was calculated from the DSC results and determined to be 76.3%. The percent crystalline PCL found in this study is slightly greater than that found by Aubin and Prud'homme. This increased amount of crystalline PCL may be due to the higher molecular weight (33 000 versus 20 000[18]) of the PCL used in this study and/or the thermal history of the sample. As discussed in the Introduction, the degree of crystallinity is a function of molecular weight and temperature.[12] The PVC samples of different molecular weights displayed only a single T_g which decreased with increasing molecular weight.

A typical thermogram is shown in Figure 1. Both a T_g and a crystalline melting transition (T_m) can be detected for this 60 wt % PCL blend. A summary of the DSC results for the PCL/PVC blends is presented in Figure 2. A single T_g, between the characteristic T_g's of the homopolymers, was observed for all PCL/PVC blends, suggesting miscibility. Similar to results reported by others,[23,24] a negative deviation from linearity is observed when T_g is plotted against composition. This may be expected for blends in the composition range where crystallinity becomes a factor. A T_m was observed for the PCL/77PVC blends containing ≥25 wt % PCL and also the PCL/190PVC and PCL/275PVC blends with ≥50 wt % PCL, suggesting that a crystalline PCL phase is present in these blends. Because of the detection of crystalline PCL, these blends were considered immiscible (i.e., not completely mixed on a molecular scale). The percent

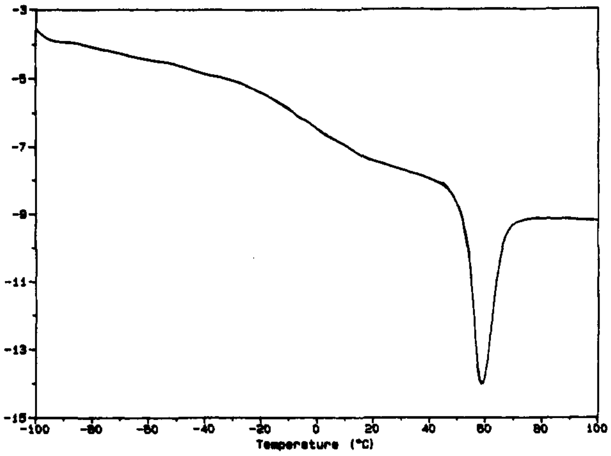

Figure 1. First-heat DSC thermogram of 60% PCL blend.

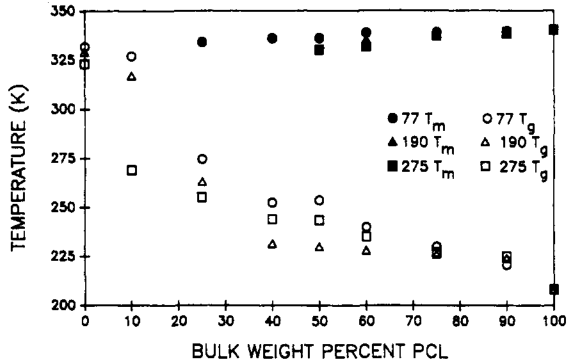

Figure 2. Plot of T_g and T_m versus bulk weight percent PCL for PCL/PVC blends.

Table III
Percent Crystallinity in PCL/PVC Blends[a]

wt % PCL	77PVC	190PVC	275PVC
0	0.0	0.0	0.0
10	0.0	0.0	0.0
25	1.3	0.0	0.0
40	7.0	0.0	0.0
50	22.5	23.9	13.7
60	38.0	28.1	40.0
75	57.1	41.9	58.1
90	69.1	43.2	65.9
100		76.3	

[a] Calculated from DSC results.

crystalline PCL in the PCL/PVC blends is shown in Table III. The percent crystalline PCL found in the PCL/77PVC blends was very similar to the percentages reported for 20 000 $\bar{M}_w$ PCL/80 000 $\bar{M}_w$ PVC blends.[18]

The percent crystallinity in the 50/50 PCL/275PVC blend was ca. 10% lower than the same composition made from PCL/77PVC and PCL/190PVC. This result would indicate the molecular weight of the homopolymers affects the degree of crystallinity in these blends. The percent crystallinity found in the 60–90 wt % PCL/275PVC blends was very similar to the percentages found for the PCL/77PVC blends. This observation contradicts the conclusions made from the percent crystallinities found for the 50/50 blends. The reason for the difference in the percent crystallinities between the 60/40 to 90/10 PCL/275PVC and PCL/190PVC is not clear. Unfortunately, an exact explanation for the differences in percent crystallinity is not available without further extensive crystallization kinetics and thermal investigations. Although these investigations would be very interesting, they are not within the scope of these studies. However, it should be noted that great care was taken to ensure a constant casting temperature and constant rate of evaporation during the preparation of all blends.

ATR-FTIR Results. To complement ESCA data, infrared spectroscopy with attenuated total reflectance (ATR-FTIR) can be used. Compositional profiles can be obtained at a greater sampling depth by using ATR-FTIR spectroscopy than ESCA. Harrick[25] and Mirabella[26] have shown that the sampling depth of an ATR-FTIR experiment is a function of the refractive indices of the sample and the internal reflective element or crystal, the wavelength of interest, and the incident angle of the infrared beam. The sampling depths calculated for 45° Ge and 45° KRS-5 crystals for the frequencies (cm^{-1}) of interest show the effective sampling depth of a 45° KRS-5 crystal is 3 times that of a 45° Ge crystal.[22] Therefore, by comparing the ATR-FTIR spectra of the PCL/PVC blends acquired with these different crystals, one may gain information on domain size, composition, crystallinity, and polymer–polymer (inter- and intrachain) interactions. This information is derived from band intensities, shifts, and broadening.

The ATR-FTIR spectra of the PCL and 190 000 $\bar{M}_w$ PVC homopolymers have been discussed in detail.[22] The semicrystalline PCL homopolymer yielded characteristic peaks at 1722 cm^{-1} and 1192 cm^{-1} assigned to the C=O and C–O stretching, respectively. The ATR-FTIR spectra of the 77PVC and 190PVC homopolymers showed characteristic and intense absorbance bands at 1258 cm^{-1} and 610 cm^{-1} due to C–C and C–Cl stretching, respectively.

As previously described, the results of the PCL/190PVC blends showed that samples with <50 wt % PCL were completely amorphous and homogeneous.[22] The carbonyl band of amorphous PCL was found to be broader than the carbonyl band of crystalline PCL and was shifted to 1734 cm^{-1}. The C–O stretching band was also shifted to 1160 cm^{-1} from 1190 cm^{-1} for these blends.

The infrared results of the PCL/190PVC blends with >50 wt % PCL present were very similar to those of the semicrystalline PCL homopolymer. This may be due to the sensitivity of infrared being greater for crystalline PCL than amorphous PCL.[22] In addition, the Ge and KRS-5 ATR-FTIR analyses indicated that the semicrystalline, unblended PCL domains may be found in higher concentrations near the surface (i.e., top 1.7 μm) of the film.

Germanium and KRS-5 ATR-FTIR spectra were collected for each PCL/77PVC blend composition. The 45° Ge spectra obtained are presented in Figure 3. The ATR-FTIR spectra reveal that the transition from amorphous to semicrystalline PCL occurs between the compositions of 25/75 and 40/60 (PCL/PVC). The blends with <40 wt % PCL displayed absorbance bands at ca. 1734 and 1160 cm^{-1}, which are characteristic of blended, amorphous PCL. The Ge ATR-FTIR spectrum of the 40/60 PCL/77PVC blend featured absorbance bands, characteristic of semicrystalline PCL, at 1722 and 1190 cm^{-1} for the C=O and C–O stretching vibrations, respectively. In addition, the Ge ATR-FTIR spectrum of this blend displayed a band at 1160 cm^{-1}, indicating the detection of some amorphous PCL within the topmost 1.7 μm of the film. The blends with a PCL concentration of >40 wt % yielded ATR-FTIR spectra that were equivalent to that of semicrystalline PCL.

The 45° Ge and KRS-5 ATR-FTIR spectra of the PCL/77PVC blends with <40 wt % PCL were equivalent, indicating these blends were homogeneous over the sampling depth (1–10 μm) of the ATR-FTIR experiment. The Ge and KRS-5 ATR-FTIR spectra of the PCL/77PVC blends with >40 wt % PCL were also equivalent and

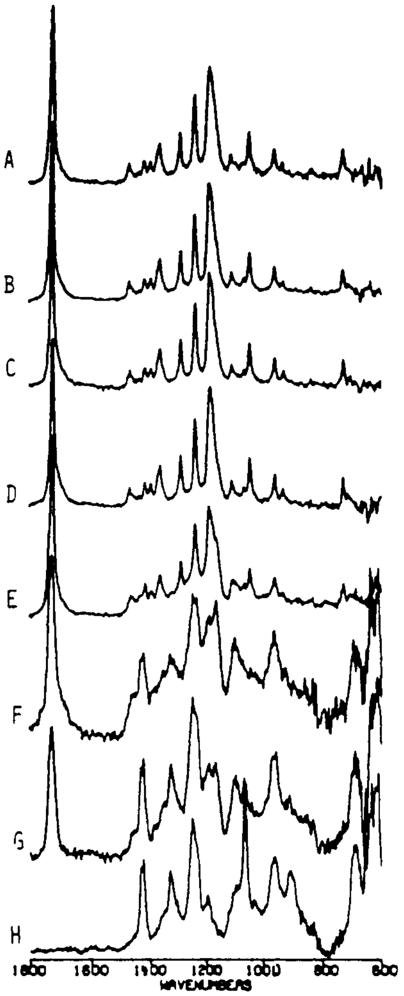

Figure 3. 45° Ge ATR-FTIR spectra of PCL/77PVC blends: (A) 90/10; (B) 75/25; (C) 60/40; (D) 50/50; (E) 40/60; (F) 25/75; (G) 10/90; (H) 77PVC homopolymer.

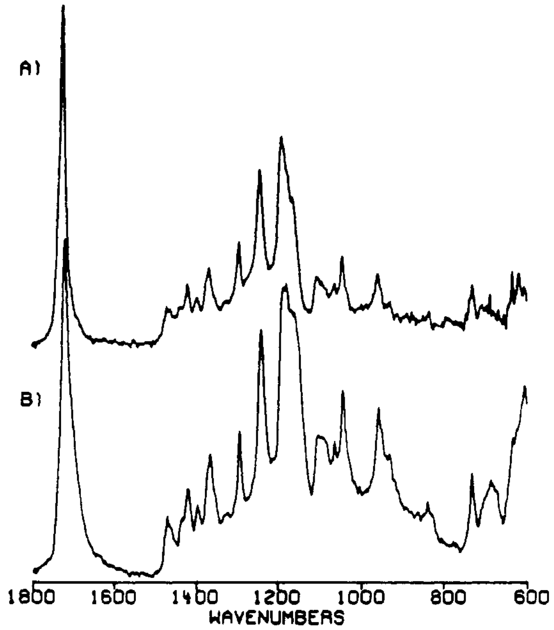

Figure 4. ATR-FTIR spectra of the 40/60 PCL/PVC blend: (A) 45° Ge ATR-FTIR; (B) 45° KRS-5 ATR-FTIR.

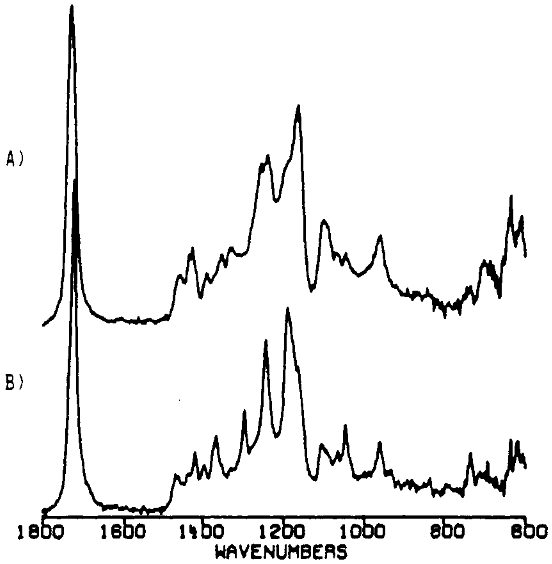

Figure 5. 45° Ge ATR-FTIR spectra of the 40/60 PCL/PVC blends: (A) PCL/190PVC; (B) PCL/77PVC.

contained absorbance bands characteristic of semicrystalline PCL. The spectra of the 40/60 PCL/77PVC blend are presented in Figure 4. Comparison of these spectra clearly shows that the relative concentration of amorphous PCL increases with greater sampling depths obtained from the 45° KRS-5 crystal. This increase in amorphous PCL concentration is supported by the relative increase of the amorphous C–O absorbance band at 1160 cm^{-1} to the crystalline C–O stretch at 1190 cm^{-1}. In addition to the observed difference in amorphous PCL concentration, the KRS-5 ATR-FTIR spectrum also contained an absorbance band at 610 cm^{-1} due to PVC which was absent in the Ge ATR-FTIR spectrum. If we assume that the semicrystalline PCL is unblended and the blended PCL is amorphous, these observations would suggest the semicrystalline, unblended PCL is located within the top 1.7 μm of the film and the blended PCL/77PVC phase is found in a higher concentration within the bulk of the film.

If the DSC and ATR-FTIR results of the PCL/77PVC and PCL/190PVC blends are combined, the limitations of the use of infrared spectroscopy to evaluate polymer blend miscibility can be clearly recognized. The 25/75 PCL/77PVC blend contains 1.3% crystalline PCL in the bulk (by DSC, Table III). The infrared analysis of this blend failed to detect this concentration of crystalline PCL. DSC analysis of the 40/60 PCL/77PVC blend showed it contained 7.0% crystalline PCL in the bulk (Table III). Comparison of the Ge ATR-FTIR spectra of this blend to the 40/60 PCL/190PVC blend (Figure 5) shows the presence of only 7% crystalline PCL produced an infrared spectrum which was equivalent to that of the semicrystalline PCL homopolymer (except for the increase in amorphous C–O stretch at 1160 cm^{-1}). This observation also supports the thesis of the increased sensitivity of the infrared to crystalline PCL relative to amorphous PCL. The use of infrared measurements to evaluate polymer miscibility appears to be limited in the ability to detect and quantitate the various phases that may exist in a polymer blend.

ESCA Results. The ESCA characterization of the homopolymers has been previously discussed in detail.[22] The homopolymers and the PCL/PVC blends from at least three separate casts were analyzed by using take-off angles of 15, 45, and 90°. The sampling depths, estimated from Seah and Dench's empirical approach,[27] for these angles of the carbon 1s photoelectron are 21, 57, and 80 Å, respectively.

The surface composition from C/O peak area ratios versus the bulk composition for the PCL/77PVC, PCL/

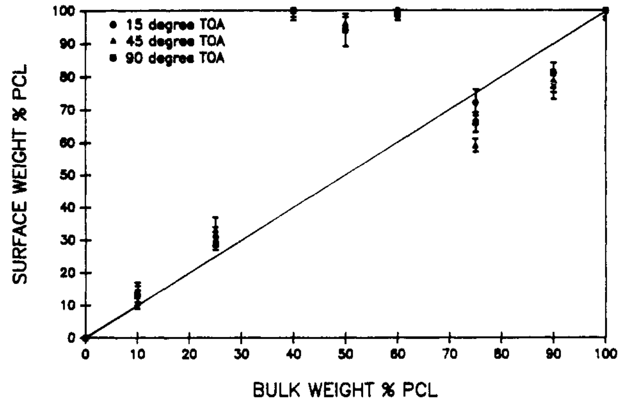

Figure 6. Plot of angle-dependent ESCA results of surface composition versus bulk composition of PCL/77PVC blends. Surface compositions were calculated from ESCA C/O peak area ratios.

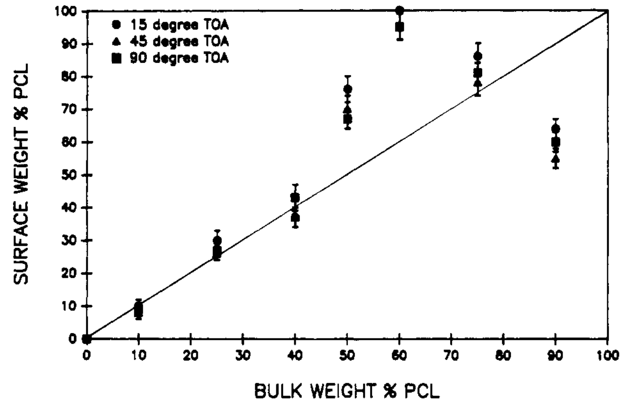

Figure 7. Plot of angle-dependent ESCA results of surface composition versus bulk composition of PCL/190PVC blends. Surface compositions were calculated from ESCA C/O peak area ratios.

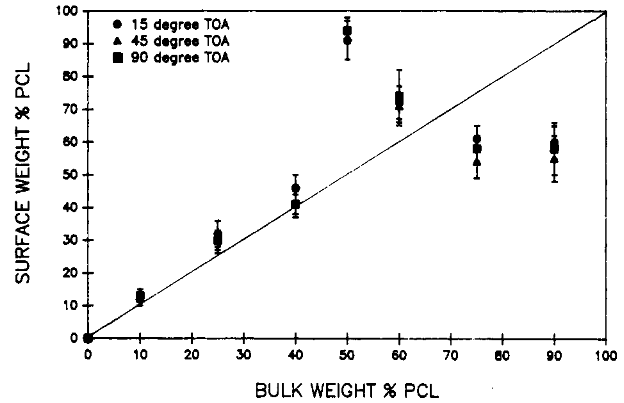

Figure 8. Plot of angle-dependent ESCA results of surface composition versus bulk composition of PCL/275PVC blends. Surface compositions were calculated from ESCA C/O peak area ratios.

Table IV
ESCA Results for PCL/77PVC Homopolymer Blends: Surface Compositions Calculated from Ratios and Curve Fitting

wt % PCL	TOA[a]	C/O	C/Cl	curve fitting
0	15	0 ± 1	0 ± 1	0 ± 1
	45	0 ± 1	0 ± 1	0 ± 1
	90	0 ± 1	0 ± 1	0 ± 1
10	15	13 ± 4	10 ± 2	10 ± 2
	45	13 ± 3	11 ± 2	10 ± 1
	90	14 ± 3	11 ± 1	12 ± 2
25	15	31 ± 3	26 ± 2	29 ± 3
	45	33 ± 4	28 ± 2	24 ± 2
	90	29 ± 2	28 ± 3	28 ± 3
40	15	100 ± 3	100 ± 5	100 ± 3
	45	100 ± 1	100 ± 5	100 ± 2
	90	100 ± 2	100 ± 4	100 ± 2
50	15	94 ± 5	94 ± 5	100 ± 4
	45	96 ± 2	95 ± 1	100 ± 1
	90	94 ± 1	95 ± 2	100 ± 2
60	15	100 ± 2	100 ± 5	100 ± 3
	45	100 ± 2	100 ± 2	100 ± 2
	90	99 ± 2	100 ± 2	100 ± 3
75	15	72 ± 4	67 ± 3	66 ± 7
	45	59 ± 2	58 ± 1	56 ± 6
	90	66 ± 3	63 ± 2	59 ± 3
90	15	78 ± 3	79 ± 3	73 ± 7
	45	77 ± 4	77 ± 2	72 ± 5
	90	81 ± 3	81 ± 2	75 ± 4
100	15	100 ± 3	100 ± 4	100 ± 2
	45	100 ± 2	100 ± 3	100 ± 2
	90	100 ± 2	100 ± 3	100 ± 2

[a] TOA = take-off angle.

Table V
ESCA Results for PCL/190PVC Homopolymer Blends: Surface Compositions Calculated from Ratios and Curve Fitting

wt % PCL	TOA[a]	C/O	C/Cl	curve fitting
0	15	0 ± 1	0 ± 1	0 ± 1
	45	0 ± 1	0 ± 1	0 ± 1
	90	0 ± 1	0 ± 1	0 ± 1
10	15	10 ± 2	11 ± 2	12 ± 1
	45	8 ± 2	9 ± 1	12 ± 1
	90	9 ± 2	10 ± 2	12 ± 2
25	15	30 ± 3	28 ± 2	27 ± 3
	45	26 ± 2	27 ± 3	25 ± 2
	90	27 ± 2	28 ± 3	26 ± 2
40	15	37 ± 3	39 ± 3	47 ± 5
	45	37 ± 3	35 ± 4	44 ± 5
	90	43 ± 4	40 ± 4	43 ± 4
50	15	76 ± 4	75 ± 5	72 ± 2
	45	70 ± 4	70 ± 4	66 ± 2
	90	67 ± 3	72 ± 3	63 ± 2
60	15	100 ± 5	96 ± 4	96 ± 3
	45	95 ± 4	97 ± 3	95 ± 4
	90	95 ± 4	93 ± 5	94 ± 2
75	15	86 ± 4	87 ± 5	81 ± 3
	45	78 ± 4	79 ± 2	82 ± 2
	90	81 ± 3	82 ± 4	80 ± 4
90	15	64 ± 3	62 ± 3	68 ± 3
	45	55 ± 3	54 ± 4	67 ± 3
	90	60 ± 3	60 ± 3	66 ± 2

[a] TOA = take-off angle.

190PVC, and PCL/275PVC blends can be seen in Figures 6–8, respectively. Tables IV–VI give results of surface compositions calculated from the C/O and C/Cl peak area ratios along with the second method of using C 1s curve fitting. Comparison of the results of the three angles within each composition examined shows that the surface compositions are homogeneous over the sampling depth of the ESCA experiment (21–80 Å).

For the blends with <50 wt % PCL and the 10/90 PCL/77PVC blend, it can be concluded that the surface composition is equivalent to the bulk composition. No surface enrichment of PCL at the polymer/air interface was detected for these blends even with the most surface-sensitive sampling depth, i.e., 21 Å. This result indicates the thermodynamics of mixing in these blends can overcome the surface energy differences of the homopolymers (PCL is 1.1 dyn/cm lower as discussed in detail later in the text), producing a polymer/air interface that is homogeneously mixed. These results agree with the optical clarity, DSC, and ATR-FTIR results and suggest these blends are miscible in the bulk, with the miscibility extending to the polymer/air interface.

Table VI
ESCA Results for PCL/275PVC Homopolymer Blends: Surface Compositions Calculated from Ratios and Curve Fitting

wt % PCL	TOA[a]	C/O	C/Cl	curve fitting
0	15	0 ± 1	0 ± 3	0 ± 1
	45	0 ± 1	0 ± 2	0 ± 1
	90	0 ± 1	0 ± 2	0 ± 1
10	15	12 ± 2	12 ± 2	9 ± 2
	45	13 ± 2	13 ± 2	11 ± 1
	90	13 ± 2	12 ± 3	11 ± 1
25	15	32 ± 4	28 ± 4	34 ± 2
	45	31 ± 5	29 ± 3	30 ± 2
	90	30 ± 3	27 ± 3	28 ± 3
40	15	46 ± 4	42 ± 4	47 ± 2
	45	41 ± 4	41 ± 3	45 ± 2
	90	41 ± 3	43 ± 2	43 ± 2
50	15	91 ± 6	91 ± 5	91 ± 8
	45	94 ± 4	94 ± 4	89 ± 9
	90	94 ± 4	94 ± 4	90 ± 9
60	15	72 ± 5	75 ± 3	65 ± 3
	45	71 ± 6	71 ± 4	65 ± 3
	90	74 ± 8	68 ± 2	66 ± 1
75	15	61 ± 4	61 ± 3	54 ± 2
	45	54 ± 5	54 ± 4	53 ± 3
	90	58 ± 4	60 ± 3	53 ± 3
90	15	60 ± 5	60 ± 5	62 ± 5
	45	55 ± 7	56 ± 6	62 ± 4
	90	58 ± 8	59 ± 6	63 ± 4

[a] TOA = take-off angle.

The remaining PCL/PVC blends contained a surface excess of one of the hompolymers forming the blend. All PCL/PVC blends in the concentration range 50–60 wt % PCL displayed a surface excess of PCL. In addition, the 25/75 and 40/60 PCL/77PVC blends contained a surface excess of PCL at the polymer/air interface.

Evaluation of the solid surface tensions of semicrystalline PCL and PVC homopolymers by the contact angle technique yielded values of 42.9[28] and 44.0 dyn/cm,[28,29] respectively. Although the solid surface tension is not an exact measure of the surface free energy, comparison of the two values can provide an empirical measure of the surface energetics. Even if polymer blends are completely miscible in the bulk and there is not sufficient interaction between the homopolymers, a difference in surface energies of 0.1 dyn/cm can lead to an enrichment of the lower surface energy component at the polymer/air interface.[11] Because of the difference in the solid surface tensions for these homopolymers, it is not surprising that the PCL dominates the surface of these blends in the concentration ranges mentioned above, where incomplete mixing is detected.

For example, ESCA results for the 25/75 PCL/77PVC blend indicated a surface excess of ca. 6% PCL, while DSC analysis detected 1.3% crystalline PCL in the bulk. The surface compositions of the 40–60 wt % PCL/77PVC blends were found to be 94–100% PCL by ESCA. These ESCA results support the ATR-FTIR results, which indicated the near polymer/air interface region may contain a higher concentration of semicrystalline, unblended PCL.

The solid surface tension of the 77,300 $\bar{M}_w$ PVC homopolymer, obtained from contact angle measurements, was 44.0 dyn/cm. Therefore, this enormous increase in the amount of PCL present at the polymer/air interface was not a result of differences in surface energetics alone. The DSC results of these blends indicated a slight increase in the percent crystalline PCL in the PCL/77PVC blends compared to the same composition of PCL/190PVC blends. Therefore, the surface enrichment of PCL in the PCL/77PVC blends may be a result of an increase in the degree of crystallinity in these blends and/or the lower molecular weight (shorter chain length) PVC being unable to inhibit the segregation of the semicrystalline PCL to the polymer/air interface. Supporting evidence of this thesis can be gained by comparing the DSC and ESCA results of the 50/50 PCL/77PVC and PCL/190PVC blends. The percent crystallinity found by DSC analysis was similar at ca. 23%. Comparison of the ESCA results of the 50/50 blends showed an increase of ca. 20% PCL at the polymer/air interface for the blend fabricated from the 77 300 $\bar{M}_w$ PVC.

The 50/50 PCL/275PVC blend was found to have a 20% higher PCL concentration at the polymer/air interface than the 50/50 PCL/190PVC blend. From DSC measurements, the 50/50 PCL/275PVC blend contained ca. 10% less crystalline PCL than the 50/50 PCL/190PVC blends. Therefore, the change in surface composition may be the result of the differences in molecular weight for the respective PVC samples. The 60/40 PCL/275PVC blend was found to be ca. 35% lower in PCL concentration at the polymer/air interface than the 60/40 PCL/190PVC blend. This may be evidence that the 275 000 $\bar{M}_w$ PVC inhibits the segregation of the crystalline PCL to the polymer/air interface more than the 190 000 $\bar{M}_w$ PVC.

The ESCA results for the 75/25 and 90/10 PCL/77PVC blends showed an enrichment of blended PVC at the surface. The 90/10 PCL/77PVC had a surface composition of ca. 78/22 PCL/PVC, which was ca. 18% greater in PCL concentration than the 90/10 PCL/190PVC blend. Conversely, the surface composition of the 75/25 PCL/77PVC blend had 25% less PCL concentration over the top 80 Å as compared to the 75/25 PCL/190PVC blend. The polymer/air interface of the 75/25 and 90/10 PCL/275PVC blends was ca. 60 wt % PCL. One possible explanation for this increase is that the higher molecular weight (i.e., longer chain length) PVC inhibits the segregation of the PCL to the interface.

Conclusions

In this study, quantitative angle-dependent ESCA coupled with infrared spectroscopy and DSC measurements was used to investigate the miscibility of PCL with three PVC samples of differing molecular weight. The results of these studies indicated that the PCL/190PVC and PCL/275PVC blends were completely miscible (in the bulk and surface region) between 10 and 40 wt % PCL. Of the PCL/77PVC blends, only the 10/90 composition was completely miscible. These conclusions are based on these blends producing (1) an optically clear film, (2) thermograms showing a single T_g and no T_m, (3) infrared spectra showing peak shifts and the presence of only amorphous PCL, (4) ATR-FTIR and transmission infrared spectra showing the PCL/190PVC blends to be homogeneous, and (5) ESCA results showing that the blend surface composition is equivalent to the bulk composition. These results, taken together, suggest molecular-scale miscibility with domain sizes no greater than tens of angstroms. In addition, it may be concluded that the thermodynamics of mixing overcome surface energetic driving forces for surface excess in these particular PCL/PVC blends.

The PCL/190PVC and PCL/275PVC blends fabricated with >40 wt % PCL and all but the 10/90 PCL/77PVC blends were found to be immiscible. These blends were opaque. The observance of a T_m in the DSC measurements for these blends indicated the presence of crystalline PCL. Although a single glass transition temperature is observed for these blends, one must conclude that there are at least two different phases of PCL present, i.e., one in which

PCL is blended with PVC and the other consisting exclusively of PCL. Therefore, they are not completely miscible (i.e., mixed on a molecular scale). This observation was not consistent with the infrared results. Both transmission and ATR-FTIR spectra for the PCL/190PVC blends and the ATR-FTIR spectra of the PCL/77PVC blends in this composition range showed PCL present only in the semicrystalline form. However, the sensitivity of infrared to the amorphous PCL component is very poor. Ge and KRS-5 ATR-FTIR spectra of the 50/50 PCL/190PVC, 60/40 PCL/190PVC, and the 40/60 PCL/77PVC blends indicated that the semicrystalline PCL was surface segregated and amorphous or blended PCL was present in the deeper regions.

The surface composition for the PCL/PVC blends that contained semicrystalline PCL showed a surface excess or enrichment of one of the homopolymers. PCL dominates the surface for blends with 40–60 wt % PCL/77PVC, 50–75 wt % PCL/190PVC, and 50–60 wt % PCL/275PVC. These results were consistent with simple surface energetic considerations of semicrystalline PCL and PVC homopolymers. ESCA results for the remaining PCL/PVC blends indicated that the surface composition contained an enrichment of blended amorphous PCL/PVC when compared to the bulk DSC results.

An overall view of the data showed that miscibility of a PCL/PVC blend was affected by the molecular weight of the homopolymers. The homopolymer molecular weight had an effect on the degree of crystallinity within the PCL/PVC blend. In general, it is a combination of the degree of crystallinity and the molecular weight (chain length) of the PVC that governs the surface composition of such blends. If the molecular weight of PVC is decreased, then the percent crystallinity and the surface concentration of PCL increase. Completely amorphous PCL/PVC blends by DSC measurements were homogeneous over the top 80 Å, as shown by angle-dependent ESCA. From the ESCA results, if microdomains exist, then the domain sizes are larger than 100 Å in diameter. Ge and KRS-5 ATR-FTIR spectra of completely amorphous PCL/PVC blends were found to be equivalent, suggesting these blends were homogeneous over the sampling depths of the ATR-FTIR experiment (1–11 μm). There was a relative increase in the intensity of the amorphous PCL band (1160 cm^{-1}) to the crystalline PCL band (1190 cm^{-1}) for the 50/50 and 60/40 PCL/190 PVC and 40/60 PCL/77PVC blends in the KRS-5 ATR-FTIR spectra compared to the Ge ATR-FTIR spectra, suggesting the semicrystalline PCL is located over the top 1.7 μm of the polymer/air interface.

Finally, with the PCL and PVC homopolymers used in these studies, it has been shown that the molecular weight of the PVC affects the degree of crystallinity in a PCL/PVC blend. As the chain length is decreased (a decreased molecular weight), the PVC is not as effective at inhibiting PCL–PCL interactions, which lead to crystallinity. In addition, as the chain length is decreased, the PVC is less effective in stopping the segregation of the crystalline, unblended PCL domains to the polymer/air interface.

If a lower molecular weight PCL was used for these studies, one would suspect that a decrease in the degree of crystallinity would be found because the PVC may be more effective in decreasing the amount of PCL chain–chain interactions. However, a lower molecular weight PCL may be more mobile and have a lower solid surface free energy, which may result in a segregation and enrichment of the PCL at the polymer/air interface.

This study explored the effects of homopolymer molecular weight on the surface composition of a blend system in which crystallinity was an issue. We are currently studying a binary blend system in which neither component crystallizes and are systematically varying the molecular weight of both homopolymers.[30]

Acknowledgment. We thank Dr. Robert Osteryoung and Dr. George Nancollas of the Department of Chemistry, SUNY at Buffalo, for the use of the FTIR spectrometer and differential scanning calorimeter, respectively. We are grateful to the Michigan Molecular Institute for the time utilizing their thermal analysis equipment. The surface tension measurements were performed by Mr. Gary Palmer of the Surface Science Center and Department of Biophysics, Roswell Park Memorial Institute (Buffalo, NY). This work was supported by the National Science Foundation, Division of Materials Research (Polymers Program), Grant No. 8720650. M.B.C. acknowledges the financial support of the Lawrence M. Gelb Foundation. The ESCA instrumentation used in this study was funded by a grant from Perkin-Elmer Corp. and the Research Foundation of the State of New York.

References and Notes

(1) Rudin, A. In *The Elements of Polymer Science and Engineering*; Academic: New York, 1982.
(2) Hofmann, G. H. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; Martinus Nijhoff: Boston, 1985; p 117.
(3) Paul, D. R. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: New York, 1978; Vol. 1, pp 1–14.
(4) Schmidt, J. J.; Gardella, J. A., Jr.; Salvati, L., Jr. *Macromolecules* **1989**, *22*, 4489.
(5) *Composite Polymeric Materials*; Sheldon, R. P., Ed.; Elsevier: London, 1982; p 157.
(6) Polymer–Polymer Miscibility; Olabisi, O., Robeson, L. M., Shaw, M. T., Eds.; Academic: New York, 1979; pp 119–121.
(7) Coleman, M. M.; Painter, P. C. *J. Macromol. Sci., Rev. Macromol. Chem.* **1977**, *C16* (2), 197.
(8) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228.
(9) Coleman, M. M.; Moskala, E. J. *Polymer* **1983**, *24*, 251.
(10) Elias, H. G. In *Macromolecules*; Plenum: New York, 1977; Vol. 1.
(11) Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. *Phys. Rev. Lett.* **1989**, *62*, 280.
(12) Magill, J. H. In *Treatise on Materials Science and Technology*; Schultz, J. M., Ed.; Academic: New York, 1977; Vol. 10A, pp 3–368.
(13) LeGrand, D. G.; Gaines, G. L., Jr. *J. Colloid Interface Sci.* **1969**, *31*, 162.
(14) Holland, V. F.; Lindenmeyer, P. H. *J. Polym. Sci.* **1962**, *57*, 589.
(15) Nardini, M. J.; Price, F. P. in *Crystal Growth*; Peiser, H. S., Ed.; Pergamon: Oxford, 1967; p 395.
(16) Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2166.
(17) Prud'homme, R. E. *Polym. Eng. Sci.* **1982**, *22*, 90.
(18) Aubin, M.; Prud'homme, R. E. *Macromolecules* **1988**, *21*, 2945.
(19) Coleman, M. M.; Zarian, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 837.
(20) Cousin, P.; Prud'homme, R. E. in *Multicomponent Polymer Materials*; Paul, D. R., Sperling, L. H., Eds.; American Chemical Society: Washington, DC, 1986; p 87.
(21) Russell, T. P.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 999.
(22) Clark, M. B.; Burkhardt, C. A.; Gardella, J. A., Jr. *Macromolecules* **1989**, *22*, 4495.
(23) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 795.
(24) Ziska, J. J.; Barlow, J. W.; Paul, D. R. *Polymer* **1981**, *22*, 918.
(25) Harrick, N. J. In *Internal Reflection Spectroscopy*; John Wiley: New York, 1979; p 30.
(26) Mirabella, F. M.; Harrick, N. J. In *Internal Reflection Spectroscopy: Review and Supplement*; Marcel Dekker: New York, 1985; p 6.
(27) Seah, M. P.; Dench, W. A. *Surf. Inter. Anal.* **1979**, *1*, 2.
(28) Palmer, G., Department of Biophysics, Roswell Park Memorial Institute, personal communication, 1988.
(29) Dahal, E. N. *Langmuir* **1987**, *3*, 1009.
(30) Burkhardt, C. A.; Gardella, J. A., Jr., work in progress.

Registry No. PCL (homopolymer, 24980-41-4; PCL (SRU), 25248-42-4; PVC, 9002-86-2.