

Miscible Blends of Polystyrene and Poly(ϵ -caprolactone) with Phenylacetylene–Carbon Monoxide Alternating Copolymer

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ABSTRACT: The alternating copolymer of phenylacetylene (PA) and carbon monoxide (CO) (poly(PA-*alt*-CO)) synthesized by palladium complex has been blended with polystyrene (PS) and poly(ϵ -caprolactone) (PCL). The miscibility of the blends was investigated by differential scanning calorimetry (DSC). A single T_g was observed over the entire composition range for both blending systems, indicating that PS and PCL were miscible with poly(PA-*alt*-CO). The effect of blending with poly(PA-*alt*-CO) on the crystallization behavior of PCL was also studied. Both the degree of crystallinity and the crystallization rate of PCL were found to be depressed with the presence of copolymer. Blending with poly(PA-*alt*-CO) also exerted a strong effect on the melting behavior of PCL. The recrystallization of PCL in the melting region was hindered by poly(PA-*alt*-CO).

KEY WORDS Phenylacetylene–Carbon Monoxide Copolymer / Polystyrene / Poly(ϵ -caprolactone) / Blends / Miscibility / Crystallization /

There has been a growing interest recently in the copolymerization of carbon monoxide (CO) due to several advantages offered by the resultant copolymers.^{1–6} In a prior study, Liaw *et al.* have successfully synthesized an alternating copolymer of CO and phenylacetylene (PA) by palladium complex.⁷ Poly(PA-*alt*-CO) is an amorphous material with a glass transition temperature (T_g) around 100°C. This material may have the potential of being a conducting polymer because of the conjugated double bonds in the chemical structure.

The properties of polymer materials may also be tailored by physical blending. Blending is a low cost method to obtain the materials of desired properties and to extend the application window of a polymer. Since poly(PA-*alt*-CO) is a new material, it will be of interest to explore the miscible binary pairs of this copolymer with some commercial polymers. In this paper, the binary blends of poly(PA-*alt*-CO) with polystyrene (PS) and poly(ϵ -caprolactone) (PCL) are studied. The miscibility of these binary combinations will be discussed on the basis of thermal analysis. In addition, the effect of blending with poly(PA-*alt*-CO) on the crystallization and melting behavior of PCL will be described.

EXPERIMENTAL

Poly(PA-*alt*-CO) was synthesized by palladium complex. The synthetic scheme and method of the copolymer have been reported in the previous publication.⁷ PS sample used in this study was obtained from Taida Chemical Co., Ltd., Taiwan, and its molecular weights were $M_n=197300$ and $M_w=414200$. PCL with the molecular weights $M_n=34000$ and $M_w=69900$ was purchased from Aldrich.

Blendings of poly(PA-*alt*-CO) with PS and PCL were carried out by solution precipitation. The co-

polymer and the commercial polymer were dissolved in toluene at room temperature yielding a 1 wt% solution. The blends were subsequently recovered by precipitating them in twenty-fold excess volume of methanol. The blends were washed with a large amount of methanol and then dried *in vacuo* at 40°C for two days.

Thermal analysis of the blends were performed with a TA Instrument 2000 differential scanning calorimeter. The samples were first annealed at 115°C for 3 min to erase previous thermal history followed by quenching to room temperature. The samples were subsequently scanned at 20°C min⁻¹ to 135°C.

RESULTS AND DISCUSSION

In the present study, poly(PA-*alt*-CO) was blended with PS and PCL. The miscibility of these binary combinations was evaluated by differential scanning calorimetry (DSC). Figure 1 displays the thermograms of

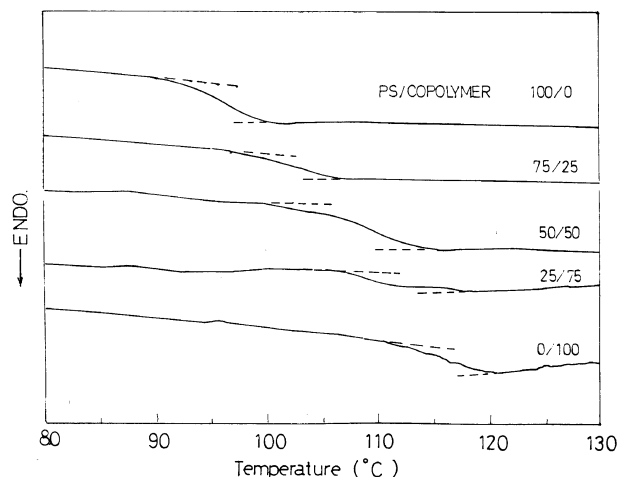


Figure 1. DSC thermograms of the blends of PS and poly(PA-*alt*-CO).

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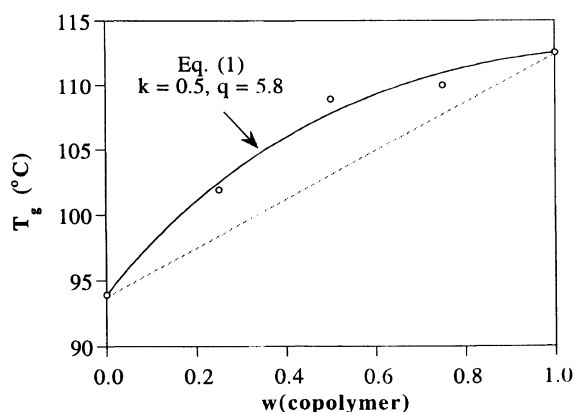


Figure 2. Composition dependence of T_g for PS/copolymer blends. The curve represents the fit by eq 1 with the values of $k = 0.5$ and $q = 5.8$.

PS/copolymer blends. The observed T_g of PS was around 95°C and that of the copolymer was about 110°C . Because of the proximity of T_g s of these two polymers, the single- T_g criterion may have difficulty to be applied to justify their miscibility. Nevertheless, it can be seen in Figure 1 that the T_g of the blend increases with increasing copolymer content, which shows that poly(PA-*alt*-CO) was miscible with PS. Although the T_g s of PS and the copolymer are different by only 15°C , the relative narrow glass transition widths of both PS (11°C) and copolymer (9°C) appear to allow the composition variation of T_g to be resolved by DSC.

The T_g s of PS/copolymer blends are plotted against the copolymer composition in Figure 2. The T_g -composition variation exhibits a slight positive deviation from linear additivity. The experimental curve can be described by an equation proposed by Kwei⁸:

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

where w_i is the weight fraction of component i , k and q are constants obtained from curve fit. q has been suggested to closely relate to the magnitude of intermolecular interaction in the blends. $q = 0$ signifies a random mixing between the blending components and in this case eq 1 reduces to the Gordon-Taylor's equation⁹; $q > 0$ implies a greater backbone stabilization energy in the blends than the weighted average energy of the homopolymers and this occurs when favorable intermolecular interaction exists between the blending components; the opposite is true when q is negative.⁸ The fit of the experimental data using eq 1 yielded the values of $k = 0.50$ and $q = 5.8$. The positive value of q would imply a favorable interaction between PS and the copolymer. However, this value is relatively small compared with the q obtained for the blend systems involving strong interaction such as electron donor-acceptor interaction.⁸ This suggests that the favorable interaction between PS and poly(PA-*alt*-CO) was probably fairly weak.

The other system investigated in this study is the blends of PCL and poly(PA-*alt*-CO). The glass transition regions of PCL/copolymer blends are shown in Figure 3. The miscibility between PCL and poly(PA-*alt*-CO) is manifested by the observations of a single T_g over the entire composition range and the monotonic

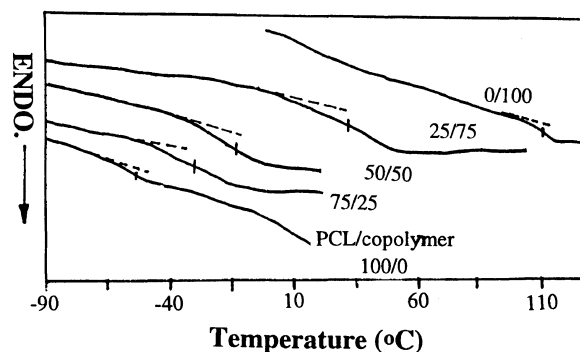


Figure 3. Glass transition regions of the blends of PCL and poly(PA-*alt*-CO). The melting endotherms are not shown in this figure.

increase of T_g with increasing copolymer composition. The observed blend T_g is plotted against the "initial blend composition" in Figure 4 along with the observed melting point. It is noted that pure PCL, 75/25, and 50/50 blends were actually crystalline prior to the DSC scans. This is manifested by the fact that melting endotherms were observed but no cold crystallization exotherm was identified in the DSC scans. The crystallization of PCL from the miscible blends would shift the composition of the miscible amorphous phase, and the composition of the amorphous phase responsible for the observed T_g can no longer be identified as the composition of the as-prepared blends (*i.e.*, the initial blend composition). Therefore, the composition scale in Figure 4 has to be adjusted by considering the composition shift due to PCL crystallization. For the simplest model, if the blends contained only two phases after PCL crystallization, *viz.*, the PCL crystalline phase and the miscible amorphous phase, the composition of the miscible amorphous phase can be calculated once the PCL degree of crystallinity is known. The degree of crystallinity (w_c) of PCL can be determined by $\Delta h_f / \Delta h_f^0$ with Δh_f being the measured enthalpy of melting and $\Delta h_f^0 = 167 \text{ J g}^{-1}$ the bulk enthalpy of melting of PCL. The composition of the remaining amorphous phase is then given by

$$w'_{\text{copolymer}} = \frac{w_{\text{copolymer}}}{w_{\text{copolymer}} + w_{\text{PCL}} - w_c} = \frac{w_{\text{copolymer}}}{1 - w_c} \quad (2)$$

where $w_{\text{copolymer}}$ and w_{PCL} are the initial weight fraction of copolymer and PCL, respectively. Figure 4 also displays the plot of T_g vs. the composition after adjusting for the PCL crystallization. The composition variation of T_g shown in Figure 4 can be described by the Gordon-Taylor's equation with the value of $k = 3.44$. This implies that the mixing between PCL and poly(PA-*alt*-CO) was close to random.

The effect of blending on the crystallizability of PCL was also evaluated. The degree of crystallinity calculated from the melting endotherms is plotted against the blend composition in Figure 5. The crystallinity shown in Figure 5 has been normalized by the weight fraction of PCL in the blend. It is seen that the degree of crystallinity decreases monotonically with increasing copolymer content as the weight fraction of the copolymer ex-

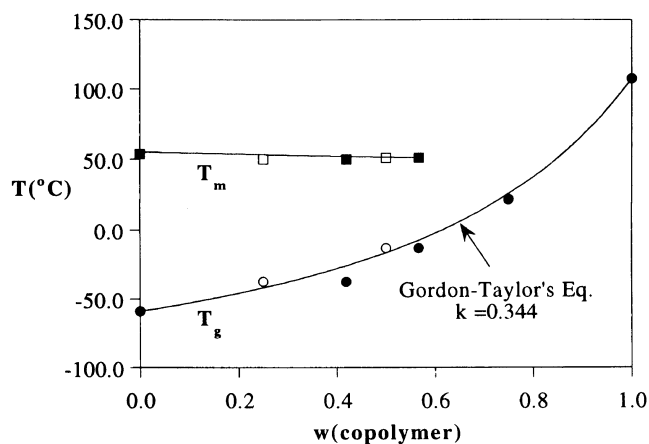


Figure 4. T_g and melting point vs. the initial (open symbol) and the adjusted (filled symbol) blend composition of PCL/copolymer blends. The curve for T_g represents the fit by the Gordon-Taylor's equation with $k=0.344$.

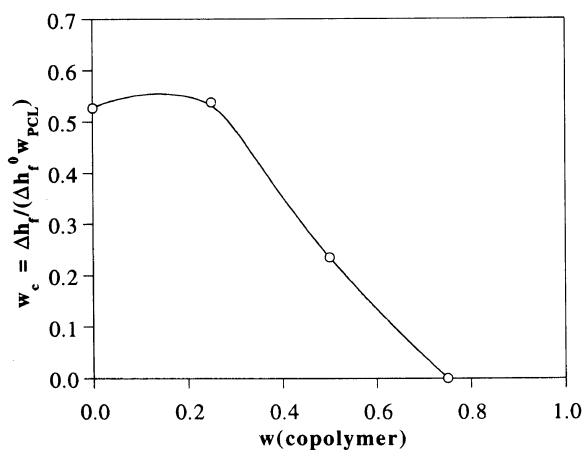


Figure 5. The degree of crystallinity of PCL in PCL/copolymer blends. The crystallinity has been normalized by the weight fraction of PCL.

ceeded 0.25. The 25/75 blend was uncrystallizable after quenching from the melt to room temperature. The reduction of PCL crystallizability can be ascribed to the narrowing in crystallization window upon blending. In Figure 4 it can be seen that the crystallization window (the region between T_g and T_m) becomes narrower as the composition of the copolymer increases. The T_g of the blend even exceeds the melting point as the content of the copolymer reaches above *ca.* 80 wt%, it is expected that PCL will become totally uncrystallizable above this composition.

The effect of blending with poly(PA-*alt*-CO) on the crystallization kinetics of PCL was also examined here. It is known that blending may exert a strong effect on both the thermodynamic and kinetic factors governing the kinetics of crystallization. The miscibility lowers the equilibrium melting point and hence depresses the thermodynamic driving force of crystallization. Furthermore, if the amorphous component has a higher T_g (as the case of PCL/copolymer blends), blending will reduce the mobility of the crystalline component and consequently decrease the crystallization rate. The effect of blending on the crystallization kinetics of PCL was evaluated by the DSC cooling experiment. Figure 6

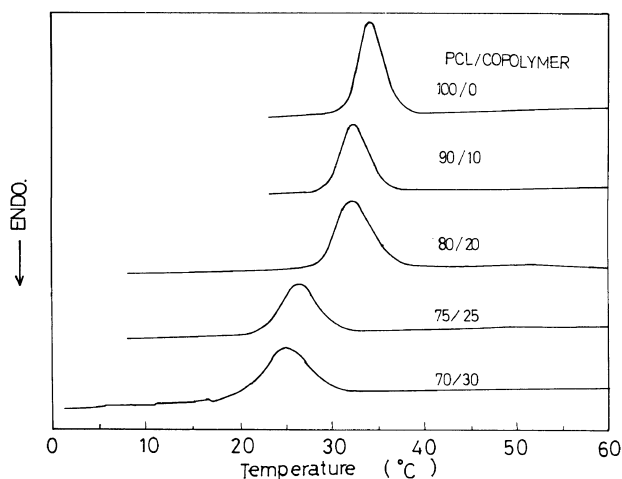


Figure 6. DSC cooling curves of PCL/copolymer blends. The cooling curves were recorded by cooling the samples from 115°C at $-10^\circ\text{C min}^{-1}$.

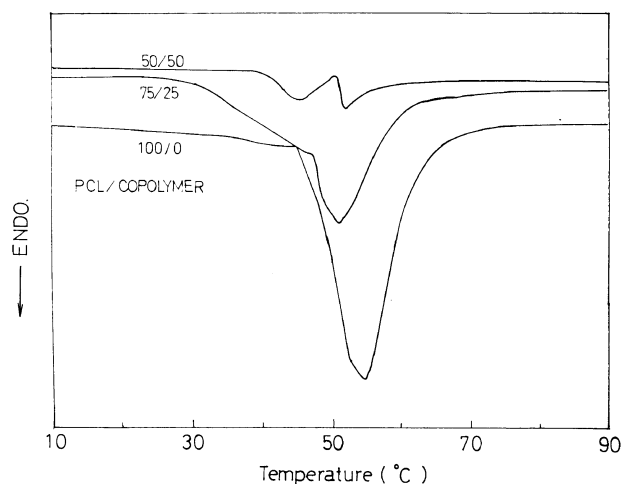


Figure 7. Melting endotherms of PCL and PCL/copolymer blends.

displays the DSC cooling curves of PCL/copolymer blends. The curves were recorded by cooling the blends from 115°C at $-10^\circ\text{C min}^{-1}$. The peak temperature of the crystallization exotherm (T_p) decreases with increasing copolymer concentration indicating that the crystallization rate of PCL was decreased by blending with poly(PA-*alt*-CO). This depression of PCL crystallization rate is also an indicative for the miscibility between these two polymers. Since the T_g of poly(PA-*alt*-CO) is 170°C higher than that of PCL, blending with the copolymer caused a significant reduction in the mobility of PCL molecules, which in turn led to a depression in the crystallization rate of PCL.

The melting behavior of PCL was also found to be affected by blending. Figure 7 shows the melting endotherms of PCL/copolymer blends scanned after quenching from 115°C. Only one melting endotherm located at 54°C is observed for pure PCL. On the other hand, two melting endotherms can be identified for the blends. A broad shoulder beside the melting endotherm at 51°C is observed for 75/25 blend and two melting peaks are clearly identified for 50/50 blend. The size of the higher melting endotherm relative to that of the lower melting endotherm was larger for 75/25 blend than that for 50/50 blend. The observed composition variation of the PCL

melting curves can be ascribed to the increased hindrance of recrystallization upon blending. Since the chain-folded polymer crystals are metastable in nature, a recrystallization may take place after the melting of the initial crystals and the occurrence of such a process could give rise to two melting endotherms in the DSC scans with the higher melting endotherm being associated with the melting of the crystals formed in the recrystallization.^{10,11} For pure PCL, the crystals formed prior to the DSC scan probably had higher perfection (as manifested by the higher onset of melting), thus the driving force toward the subsequent recrystallization was smaller.¹² As a result, PCL did not show significant recrystallization after the initial melting and hence only one melting endotherm was observed.

As PCL was blended with the copolymer, the PCL crystals formed from the miscible melt had lower perfection (as manifested by the lower onset of melting) and hence they exhibited stronger tendency toward recrystallization. Nevertheless, the presence of copolymer could hinder the recrystallization of PCL. When the PCL crystals were melted, the melted PCL would enter into the mixed melt and hence a remixing took place. Such a remixing would impede the subsequent recrystallization of PCL. Since recrystallization was more difficult in the 50/50 blend than in the 75/25 blend, the relative size of the higher melting endotherm was smaller for 50/50 blend than that for 75/25 blend.

CONCLUSION

Two miscible binary blends of poly(PA-*alt*-CO) have

been discovered in this study. Poly(PA-*alt*-CO) was found to be miscible with PS and PCL. Blending with poly-(PA-*alt*-CO) caused significant reductions in both the crystallizability and crystallization rate of PCL. Such reductions were due to the decrease of the PCL molecular mobility upon blending. Blending with the copolymer also hindered the recrystallization of PCL during DSC scans. Such an observation can be interpreted by considering the remixing effect after the initial melting.

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