



TABLE I  
Carboxylation of PPO and Characteristics of the Derivatives<sup>a</sup>

Sample	Molar ratio BuLi/PPO	Degree of carboxylation (mol % repeat units)	A <sup>1</sup>	T <sub>g</sub> <sup>b</sup> (°K)	[η] <sup>25°C</sup> (THF)	Solvents
PPO				478		Chloroform <sup>c</sup> Pyridine Benzene
C <sup>2</sup> -PPO	0.33	4.8	0.09	490		Chloroform Pyridine Benzene
C <sup>3</sup> -PPO	0.41	11.8	0.25	490	0.37	THF Dioxane
C <sup>4</sup> -PPO	0.45	15.0	0.41	498	0.52	Pyridine Chloroform
C <sup>5</sup> -PPO	0.83	35.0	1.17	516	0.55	THF Dioxane Chloroform

<sup>a</sup> Ratio of integrated absorbance at 1720 cm<sup>-1</sup> to that at 1605 cm<sup>-1</sup>; see text.

<sup>b</sup> By SC.

powders were compression molded above their T<sub>g</sub>'s to form films followed by slow cooling to room temperature. Differential scanning calorimetry measurements were carried out with the Perkin-Elmer DSC 1-B at 20°/min on the films thus prepared. Data were collected on the C<sup>3</sup>-PPO/PS and the C<sup>6</sup>-PPO/PS blends only. Since thermal history is known to be important in partially miscible blends, the samples were treated as follows: (1) run at a heating rate of 20°/min from 330 K to 540 K and then allowed to cool slowly in the pan; (2) run at a heating rate of 20°/min from room temperature to 540 K and then cooled at 2.5°/min; (3) run at a heating rate of 20°/min from room temperature to 540 K. Transition temperatures observed remained constant when subjected to this treatment.

For the C<sup>3</sup>-PPO/PS blends, single composition dependent T<sub>g</sub>'s were observed as shown in Figure 1 and Table II, indicating miscibility. The blend T<sub>g</sub>'s were very much broadened, however, at the high C<sup>3</sup>-PPO contents (Fig. 1). It may also be seen that the composition dependence of the T<sub>g</sub> does not follow the Fox equation (Table II), but is almost sigmoidal in character. Very similar results to these were obtained by Fried and Hanna in a study of unmodified PPO blends with styrene-maleic anhydride copolymers containing 8 wt % of maleic anhydride.<sup>6</sup> Fried and Hanna explained this phenomenon as a consequence of the presence of two microphases in their blends, one rich in PPO and one rich in the polystyrene copolymer. It would appear that this explanation is also valid in our case, but it is not possible to establish it with certainty without further work.

TABLE II  
Comparison of DSC T<sub>g</sub>'s of C<sup>3</sup>-PPO/PS Blends with those Calculated from the Fox Equation<sup>a</sup>

Blend composition (wt %) C <sup>3</sup> -PPO	100	80	60	40	20	0
T <sub>g</sub> DCS (°K)	490	446	404	391	370	377
T <sub>g</sub> cal <sup>a</sup> (°K)	—	462	438	413	395	—

$$^a 1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

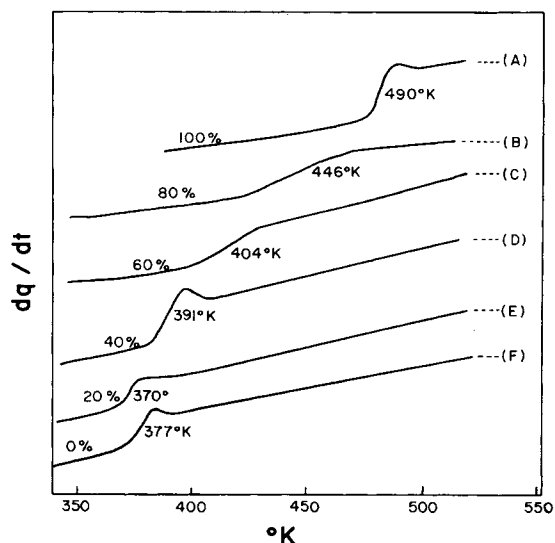


Fig. 1. As recorded DSC thermograms of C<sup>3</sup>-PPO/PS blends. Each curve has been arbitrarily shifted along the ordinate to facilitate comparison. Numbers appearing above each curve represent the weight fraction C<sup>3</sup>-PPO in the blend. The indicated  $T_g$ 's are taken as the midpoints of the steps in heat capacity.

Blends of C<sup>5</sup>-PPO with PS showed two  $T_g$ 's over the entire composition range by DSC (Fig. 2). In this case the high temperature  $T_g$  is lowered somewhat compared to its value for pure C<sup>5</sup>-PPO. The effect is particularly marked in the case of the blend containing 20% of C<sup>5</sup>-PPO. In this case it appears that more extensive phase separation exists than for the C<sup>3</sup>-PPO blends. This situation is analogous to the PPO blends with styrene-maleic anhydride copolymers containing 14 wt % maleic anhydride studied by Fried and Hanna.<sup>6</sup>

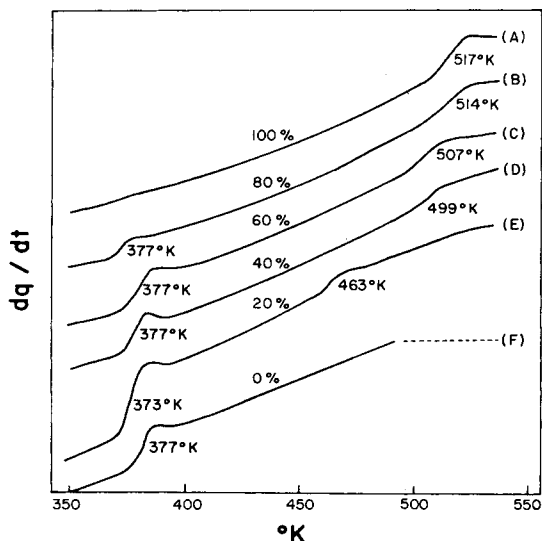


Fig. 2. As recorded DSC thermograms of C<sup>5</sup>-PPO/PS blends. Each curve has been arbitrarily shifted along the ordinate to facilitate comparison. Numbers appearing above each curve represent the weight fraction C<sup>5</sup>-PPO in the blend. The indicated  $T_g$ 's are taken as the midpoints of the steps in the heat capacity.

The preliminary results obtained here suggest a good deal of additional work on this new blend system. For example, sequence distribution of the carboxylic acid groups along the PPO chain need to be determined. Molecular weight effects may also be important and much more extensive property-structure investigations are necessary in order to establish the existence of microphases and their morphologies. Phase diagrams should also be determined using scattering methods.

### References

1. J. R. Fried, F. E. Karasz, and W. J. MacKnight, *Macromol.*, **11**, 150 (1978).
2. N. E. Weeks, F. E. Karasz, and W. J. MacKnight, *J. Appl. Phys.*, **48**, 4068 (1977).
3. F. E. Karasz and W. J. MacKnight, *Pure Appl. Chem.*, **52**, 409 (1980).
4. R. P. Kambour, J. T. Bendler and R. C. Bopp, *Macromol.*, **16**, 753 (1983).
5. A. J. Chalk and A. S. Hay, *J. Polym. Sci., A1*, **7**, 691 (1968).
6. J. R. Fried and G. A. Hanna, *Polym. Eng. Sci.*, **22**(11), 705 (1982).

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