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Carboxylation of Poly(2,6-dimethyl-1,4-Phenylene Oxide) and Thermal Properties of Blends with Atactic Polystyrene

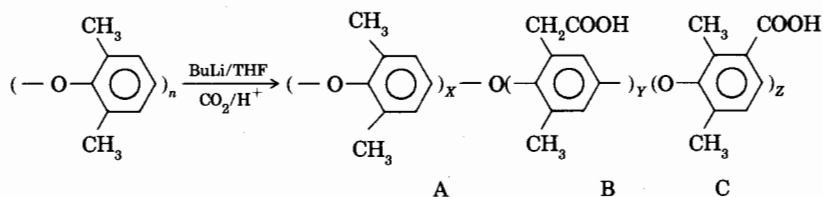
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and atactic polystyrene (PS) form one of the best-known examples of thermodynamically miscible polymer blends. Thus a single, composition-dependent glass transition temperature T_g exists for all blend compositions,¹ and the segmental interaction parameter χ between PPO and PS has been shown to be negative.² Chemical modifications of either PPO or PS tend to decrease miscibility and, when carried far enough, will lead to incompatibility. This has been established through studies of various halogenated PS blends with PPO and brominated PPO blends with PS.^{3,4}

Carboxylation of PPO has been reported using lithiation followed by treatment with CO_2 .⁵ These polymers are interesting in their own right in that they can be modified to form various carboxylate derivatives such as esters, salts, amides, anhydrides, etc. It is also to be expected that such carboxylated PPO derivatives would exhibit partial miscibility with PS or perhaps complete immiscibility depending upon their compositions.

Here we report on the carboxylation of PPO through the aforementioned route, and we provide some preliminary information about the miscibility behavior of blends of PPO with differing concentrations of carboxylic acid (C-PPO) and PS.

The PPO was carboxylated according to the method of Chalk and Hay.⁵ About 5 g PPO (\bar{M}_w 2.3×10^4 , sample provided by General Electric) were dissolved under nitrogen in 200 mL of freshly distilled THF. The solution was cooled to room temperature and the desired amount of BuLi (1.6M in hexane, Aldrich) was added dropwise. The reaction mixture was then poured over dry ice, acidified with dilute hydrochloric acid, and precipitated with hexane. The polymer was then purified further by washing in dioxane and hexane. The degree of carboxylation was assessed by titration in pyridine with alcoholic 0.1M KOH using phenanthrene-ethanol as indicator. Infrared spectra of KBr pellets of the polymers were obtained using a Perkin-Elmer IR-283 Spectrometer. The integrated absorbances of the carbonyl group stretching vibration at 1720 cm^{-1} and the aromatic ring vibration at 1605 cm^{-1} were measured, and the ratio of the two correlated well with the degree of carboxylation determined by titration. These data are collected in Table I.

The carboxylation reaction may be represented as follows:



In agreement with previous work, unit B represents the preferred carboxylation location. This is evident from $^1\text{H-NMR}$ spectra, which showed a peak at 3.46–3.61 ppm in the various derivatives. This is assigned to a methylene proton on an aromatic ring. Peaks at 40.8 ppm and 168.5 ppm also appear in the $^{13}\text{C-NMR}$ spectra of the derivatives and these are assigned to $\text{---CH}_2\text{---}$ and ---CO--- in unit B above.

Finally, the IR absorption at 1380 cm^{-1} due to the CH_3 group on the aromatic ring showed a large decrease in magnitude in the C-PPO's compared to unmodified PPO. $^1\text{H-NMR}$ spectra were obtained on a Varian T-60 Instrument and $^{13}\text{C-NMR}$ spectra were obtained on a Varian CFT-20 Instrument.

Blends were prepared by freeze drying solutions of C-PPO and PS (\bar{M}_w 250,000). Blend compositions of 80%, 60%, 40%, and 20% C-PPO by weight were prepared. The freeze dried

TABLE I
Carboxylation of PPO and Characteristics of the Derivatives^a

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

^a Ratio of integrated absorbance at 1720 cm⁻¹ to that at 1605 cm⁻¹; see text.

^b By SC.

powders were compression molded above their T_g'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 C³-PPO/PS and the C⁵-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 C³-PPO/PS blends, single composition dependent T_g's were observed as shown in Figure 1 and Table II, indicating miscibility. The blend T_g's were very much broadened, however, at the high C³-PPO contents (Fig. 1). It may also be seen that the composition dependence of the T_g 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.⁶ 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_g's of C³-PPO/PS Blends with those Calculated
from the Fox Equation^a

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

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

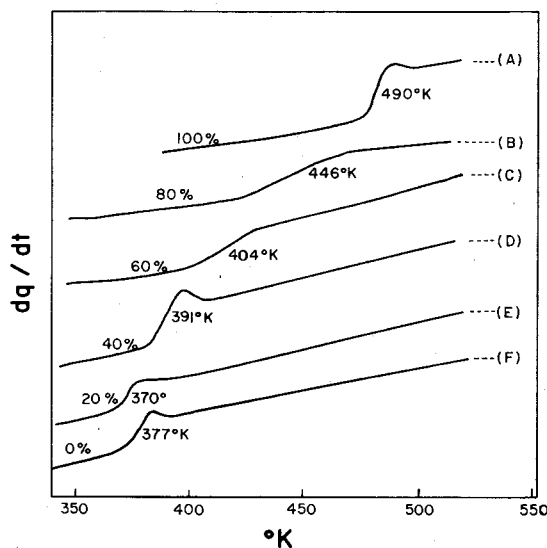


Fig. 1. As recorded DSC thermograms of C³-PPO/PS blends. Each curve has been arbitrarily shifted along the ordinate to facilitate comparison. Numbers appearing above each curve represent the weight fraction C³-PPO in the blend. The indicated T_g 's are taken as the midpoints of the steps in heat capacity.

Blends of C⁵-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 C⁵-PPO. The effect is particularly marked in the case of the blend containing 20% of C⁵-PPO. In this case it appears that more extensive phase separation exists than for the C³-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.⁶

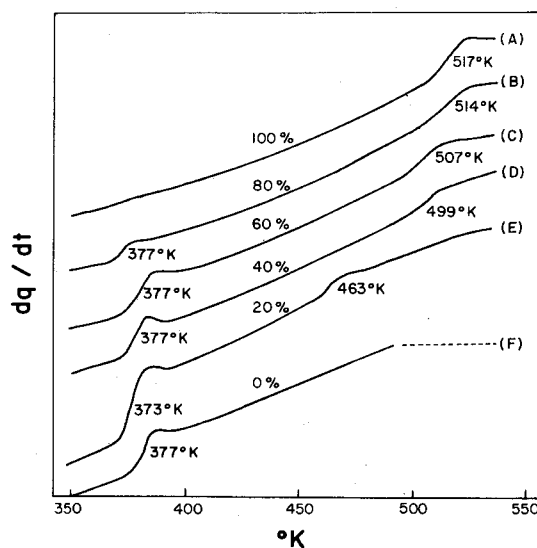


Fig. 2. As recorded DSC thermograms of C⁵-PPO/PS blends. Each curve has been arbitrarily shifted along the ordinate to facilitate comparison. Numbers appearing above each curve represent the weight fraction C⁵-PPO in the blend. The indicated T_g 's are taken as the midpoints of the steps in the heat 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.

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