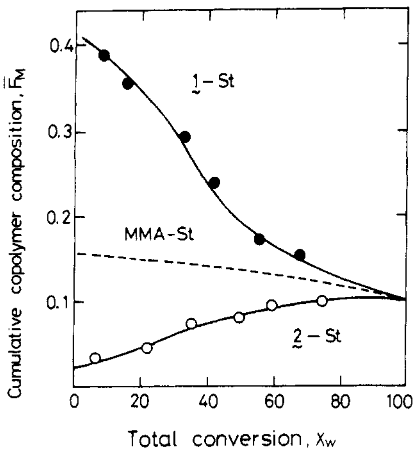
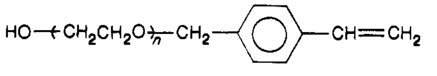


Figure 3. Relationship between cumulative copolymer composition ($\bar{F}_M$) and total conversion (X_w, wt %): black circle, 1–St; white circle, 2–St; dotted line, calculated value for the MMA–St system.

equation.[6] This deviation will not be attributable to a heterogeneity in the copolymerization system because the copolymerization reaction proceeded homogeneously up to high conversion without any precipitation. A drastic enhancement of the content of 1 incorporated in the copolymer in comparison with MMA is surprising considering the results of SOE as we reported,[3] in which the



SOE, n = 46, 120

copolymerizability of SOE was much lower than that of St as a model monomer, probably reflecting the steric effect of the bulky poly(oxyethylene) chain. However, the homopolymerization of 1 proceeded much more rapidly than that of SOE up to high conversion.

On the other hand, the copolymerization profile of 2–St showed a reversed trend (as also shown in Figure 3). Copolymerizability of 2 is poorer than that of MMA in contrast to the case of 1. The difference in molecular structure between 1 and 2 exists in the hydrophobic tail which consists of a fluorocarbon-chain or a hydrocarbon-chain. Therefore, the unique behavior of 1 in its copolymerization as described above, that is, the extremely enhanced copolymerizability of 1, may be ascribable to the increase of effective macromonomer concentration as the result of formation of some aggregates and/or domains of 1 in organic solvent due to a peculiar lipophobicity of fluorocarbons.

We expect that these amphiphilic graft copolymers containing fluorocarbon chains are useful for functional applications, which are now in progress, on the basis of their aggregation states and characteristic microstructures in nonaqueous solvents.

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Registry No. 1, 113451-47-1; (1)(St) (copolymer), 113474-58-1.

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Masazo Niwa* and Nobuyuki Higashi
Department of Applied Chemistry
Faculty of Engineering, Doshisha University
Karasuma-Imadegawa, Kamikyo-ku, Kyoto 602, Japan

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Estimation of the Interfacial Fraction in Partially Miscible Polymer Blends from Differential Scanning Calorimetry Measurements

During DSC studies of the partially miscible polymer blend poly[(phenylene oxide)-*co*-(sulfonylated phenylene oxide)]/polystyrene, Kang[1] found that as the sulfonylated phenylene oxide content in the copolymer is decreased toward the threshold concentration of 0.32, the ΔC_p's of the two glass transition temperatures of the blend constituents move toward each other along the temperature axis and decrease in magnitude. Fried[2] observed similar behavior in the blend poly(2,6-dimethyl-1,4-phenylene oxide)/poly(styrene-*co*-4-chlorostyrene) as the 4-chlorostyrene content of the copolymer was decreased. Fried attributed the behavior in his system to the presence of a large amount of material in the interfacial region and postulated that the amount of this material could be related to the ratio F:

$$F = \frac{w_1 \Delta C_{pu} + w_2 \Delta C_{pl}}{w_1 \Delta C_p{}^\circ{}_1 + w_2 \Delta C_p{}^\circ{}_2} \qquad (1)$$

where the ΔC_{pi}'s are the step increases in heat capacity at the T_g's of the constituents before mixing, ΔC_{pu} and ΔC_{pl} are the measured increases in heat capacity at the two T_g's observed for the blend, and the w_i's are the total weight fractions of the constituents. (The ΔC_{pi}'s are assumed temperature independent). An infinitely sharp interface is therefore represented by an F-value of 1.0. While the Fried ratio may provide a qualitative measure of the extent of the actual diffuse interface in the polymer blends, it is only an approximation since the contribution of the interface is overestimated by use of the total weight fractions in the numerator of eq 1. The use of the actual weight fractions contributing to the ΔC_{pu} and ΔC_{pl} can provide an analytical expression for the amount of material in the interface, as will be shown below.

A qualitative picture of the actual interface and the resulting DSC thermogram are shown in Figure 1. The bulk regions A and B and the interface I are divided into layers of constant composition Φ_2. The T_g of each layer is a function of its composition. The ΔC_p for each layer is dependent upon the total mass in the layer. In regions of constant composition (far from the interface) such as A and B, the T_g will be fairly constant from layer to layer and therefore the ΔC_p of the layers in these regions will be additive, resulting in the two major ΔC_p's in Figure 1b.

The Couchman equation,[3]

$$\ln T_g = \frac{w_1 \Delta C_p{}^\circ{}_1 \ln T^\circ{}_{1g} + w_2 \Delta C_p{}^\circ{}_2 \ln T^\circ{}_{2g}}{w_1 \Delta C_p{}^\circ{}_1 + w_2 \Delta C_p{}^\circ{}_2} \qquad (2)$$

(where $T^\circ{}_{1g}$ and $T^\circ{}_{2g}$ are the T_g's of the pure blend con-

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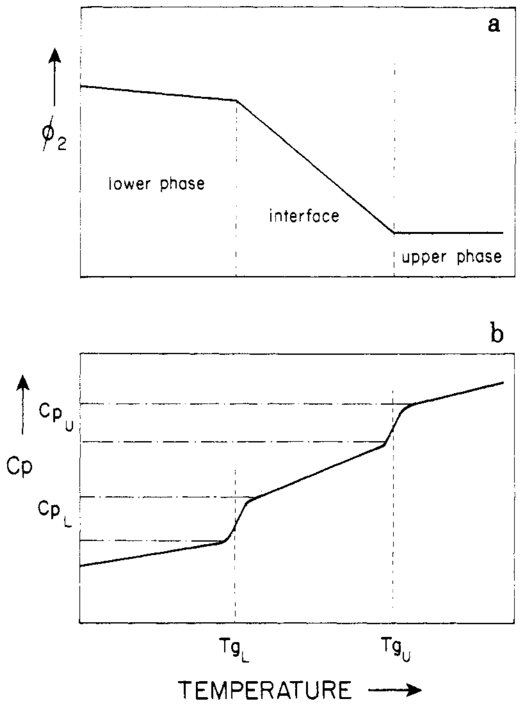


Figure 1. (a) Concentration profile of the interfacial region of a phase-separated blend of two amorphous polymers. (b) DSC thermogram of a phase-separated blend of amorphous polymers.

stituents), is assumed to apply to both the upper and lower phases and is used to express the weight fractions of the blend constituents in the two phases as functions of the shifts in the T_g's.

$$\ln T_{gl} = \frac{w_{1l}\Delta C_p{}^\circ{}_1 \ln T^\circ{}_{1g} + w_{2l}\Delta C_p{}^\circ{}_2 \ln T^\circ{}_{2g}}{w_{1l}\Delta C_p{}^\circ{}_1 + w_{2l}\Delta C_p{}^\circ{}_2} \tag{2a}$$

$$\ln T_{gu} = \frac{w_{1u}\Delta C_p{}^\circ{}_1 \ln T^\circ{}_{1g} + w_{2u}\Delta C_p{}^\circ{}_2 \ln T^\circ{}_{2g}}{w_{1u}\Delta C_p{}^\circ{}_1 + w_{2u}\Delta C_p{}^\circ{}_2} \tag{2b}$$

where, for example, $w_{1u} = m_{1u}/(m_{1u} + m_{2u})$. Assuming limited mutual solubility to be the sole reason for the T_g shifts, we write

$$\Delta C_{pu} = \Delta C_p{}^\circ{}_1(m_{1u}/m_T) + \Delta C_p{}^\circ{}_2(m_{2u}/m_T) \tag{3}$$

$$\Delta C_{pl} = \Delta C_p{}^\circ{}_1(m_{1l}/m_T) + \Delta C_p{}^\circ{}_2(m_{2l}/m_T) \tag{4}$$

where the m_{iu}'s and m_{il}'s are the masses of constituent i in the upper and lower phases and m_T is the total mass of the system. Note that in this approximation the ΔC_p's are assumed to vary linearly with mass fractions and $\Delta C_p{}^\circ$'s. If necessary, quadratic terms could be added to eq 3 and 4 without changing the essential structure of the model.

In the interfacial zone I, the composition in the layers changes relatively rapidly from the lower phase to the upper phase such that T_g varies smoothly from T_{gl} to T_{gu}. The ΔC_p's of the layers in this region are too small to be distinguished individually; the result is a smooth curve with positive slope between ΔC_{pl} and ΔC_{pu}.

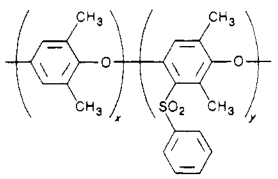
The weight fraction of the blend constituents in the interface is given by

$$w_I = 1 - \frac{m_{1u} + m_{2u}}{m_T} - \frac{m_{1l} + m_{2l}}{m_T} \tag{5}$$

Table I
Weight Fraction of Interfacial Material in 50/50 Blends of Sulfonylated PPO[a] and Polystyrene[b]

mole fractn sulfonylated PPO	w_I from eq 6	$1 - F$
0.388	0.28 ± 0.07	0.63 ± 0.04
0.466	0.21 ± 0.08	0.60 ± 0.04
0.54	0.14 ± 0.08	0.56 ± 0.04

[a] Sulfonylated PPO:



[b] Narrow molecular weight distribution polystyrene ($\bar{M}_w/\bar{M}_n$ = 1.1) with $\bar{M}_n$ = 115 000.

Now, since eq 2–5 are linear in all the masses, we may combine them to express w_I in terms of ΔC_p's and T_g's only:

$$w_I = 1 - \frac{\Delta C_{pu}(\Delta C_p{}^\circ{}_2 \ln (T^\circ{}_{2g}/T_{gu}) - \Delta C_p{}^\circ{}_1 \ln (T^\circ{}_{1g}/T_{gu})}{\Delta C_p{}^\circ{}_1 \Delta C_p{}^\circ{}_2 \ln (T^\circ{}_{2g}/T_{1g})} - \frac{\Delta C_{pl}(\Delta C_p{}^\circ{}_2 \ln (T^\circ{}_{2g}/T_{gl}) - \Delta C_p{}^\circ{}_1 \ln (T^\circ{}_{1g}/T_{gl})}{\Delta C_p{}^\circ{}_1 \Delta C_p{}^\circ{}_2 \ln (T^\circ{}_{2g}/T_{1g})} \tag{6}$$

The Couchman equation is used as a first approximation; other relations such as that by Kanig[4] could also be used but usually require additional information not readily obtainable by DSC measurements alone.

The results of the application of eq 6 to Kang's data are summarized in Table I and compared with the value of 1 − F, where F is the Fried ratio. If there is no material present in the interface, then 1 − F will be zero whereas if essentially all of the material is in the interface 1 − F will be 1.0. The Fried ratio is seen to predict larger amounts of material in the interface than does eq 6. We currently have no means of checking these results by independent measurements. Because accurate measurement of the ΔC_p's is difficult, the error in w_I can be high. Nevertheless, such a treatment may have importance in the analysis of amorphous blends, filled blends, and other systems where the interface plays an important role and the only data available are DSC thermograms.

Registry No. Polystyrene, 9003-53-6.

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E. J. Beckman, F. E. Karasz, R. S. Porter, and W. J. MacKnight*

Polymer Science & Engineering Department
University of Massachusetts
Amherst, Massachusetts 01003

J. Van Hunsel and R. Koningsveld

Department of Chemistry, University of Antwerp, U.I.A.
B-2610 Wilrijk, Antwerp, Belgium

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