A Useful Relationship for the Differential Scanning Calorimetry Determination of Phase Purity in Partially Phase Mixed Copolymers

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Received February 26, 1990

This paper reports the derivation of a useful relationship (eq 4) for the quantitative differential scanning calorimetry (DSC) determination of soft- and hard-segment purity without restricting the value of the hard-segment change in heat capacity (ΔC_p^H).

DSC has been shown to be a useful tool in the determination of microphase separation, and there are a number of papers that detail the methods of obtaining the weight fraction of soft segment in the soft phase (M_{SS}) from Wood's or Fox's equations.[1,2] However, determination of M_{SS} alone provides no information about the hard phase.

Camberlin and Pascault introduced a method of determining the soft-segment segregation (SR_S):[3-6]

$$SR_S = (\Delta C_p^{obs}/W_S)/\Delta C_p^S \qquad (1)$$

where $\Delta C_p^{obs}/W_S$ represents the observed change in heat capacity per gram of soft segment in the copolymer and where ΔC_p^S represents the change in heat capacity of the ideally microphase-separated soft segment (see Glossary of Terms). By combining these two methods a complete description of the microphase separation behavior can be obtained, thereby providing information about the soft and hard phases.[7]

Camberlin and Pascault admit that because the contribution to ΔC_p^{obs} by the excluded hard segments is ignored, eq 1 is applicable only in situations in which ΔC_p^H is almost zero. Situations where this is not true can easily arise, and given the availability of DSC analysis, it is desirable to use DSC to obtain a quantitative evaluation of the microphase separation in these situations as well.

The formation of microphases occurs in block and segmented copolymers in which differing segments are incompatible, such as poly(urethane ethers) and poly(ester ethers). In the case of a segmented copolymer containing hard and soft segments, crystallization can provide an additional driving force for phase separation if semicrystalline hard phases can form. Unfortunately, microphase separation often is thought to involve the formation of nearly pure semicrystalline hard phases which are found in an amorphous matrix consisting of soft segments and excluded hard segments.[8-11] Where this is true, a good description of the microphase separation can be obtained solely by determination of M_{SS}.[1,2] A high degree of hard-segment purity is indicated by crystalline melting points that are equal to the melting point of the hard-segment homopolymer.[1,2,13] Other materials contain hard phases that are not pure since they exhibit melting points that are much lower than the melting point of the hard-segment homopolymer.[3-7] In these materials phase mixing of soft segments into the semicrystalline hard phase is an equally important consideration.

SR_S is defined as the weight fraction of soft segment in the soft phase with respect to the total weight of soft segment in the copolymer—this parameter is termed a rate in the original treatment due to the time dependence of microphase separation.[3-7] SR_S is related to M_{SS} by the equation

$$SR_S = M_{SS}W_{SP}/W_S \qquad (2)$$

where W_{SP} represents the weight fraction of the soft phase and where W_S represents the weight fraction of the soft segment in the copolymer.

One can account for contributions to ΔC_p^{obs} from both the soft and hard segments by using the generally accepted principle that the observed change in heat capacity of a single-phase two-component system is the linear weighted addition of the two individual component changes in heat capacities. Applying this relation to a fully amorphous soft phase yields the equation[1]

$$\Delta C_p^{obs}/W_{SP} = M_{SS}\Delta C_p^S + (1 - M_{SS})\Delta C_p^H \qquad (3)$$

where $\Delta C_p^{obs}/W_{SP}$ represents the observed change in heat capacity per gram of the soft phase. Unfortunately, W_{SP} cannot be directly determined by DSC, but given eq 2 and 3, SR_S can be determined by the relationship

$$SR_S = \frac{M_{SS}\Delta C_p^{obs}/W_S}{M_{SS}\Delta C_p^S + (1 - M_{SS})\Delta C_p^H} \qquad (4)$$

With eq 4 analysis can be extended beyond M_{SS} by the calculation of SR_S without restricting the value of ΔC_p^H, provided that suitable data are obtained from model compounds for the ideally microphase-separated hard and soft phases (ΔC_p^H and ΔC_p^S, respectively).

The conditions for which eq 1 is valid become obvious when it is realized that eq 4 reduces to eq 1 if the following approximation is allowed:

$$M_{SS}\Delta C_p^S + (1 - M_{SS})\Delta C_p^H \approx M_{SS}\Delta C_p^S \qquad (5)$$

Thus, eq 5 dictates the condition that permits the use of eq 1 for the determination of SR_S. This condition is met by any of the following circumstances: (1) ΔC_p^H is small such that $\Delta C_p^S \gg \Delta C_p^H$ or (2) the sample is substantially microphase separated such that $M_{SS} \gg (1 - M_{SS})$.

When none of these situations apply and ΔC_p^H is known, SR_S can still be determined by eq 4. Further, because eq 4 takes into account the contributions of both components to ΔC_p^{obs}, its application is not limited to the hard segment–soft segment combination. It also applies to other combinations, including soft segment–soft segment combinations, such as poly(siloxane ethers), of which there is an increasing interest.[14]

Once both M_{SS} and SR_S are known, it is a simple matter to determine the composition of the hard phase. Assuming that only two phases are formed, the weight fraction of the hard segment in the hard phase (M_{HH}) can be estimated:[3,7]

$$M_{HH} = 1 - [M_{SS}W_S(1 - SR_S)/(M_{SS} - SR_SW_S)] \qquad (6)$$

Furthermore, similar to SR_S, the hard-segment segregation (SR_H) is calculated by the equation[7]

$$SR_H = (M_{SS}M_{HH} - SR_SW_SM_{HH})/M_{SS}W_H \qquad (7)$$

where W_H represents the weight fraction of the hard segment in the copolymer.

The strength of this process lies in its ability to produce a complete description of the microphase separation behavior, providing information about the soft and hard phases. By use of these equations, a complete description of phase purity can be obtained by DSC analysis for a wider variety of microphase-separated materials.

0024-9297/91/2224-0618$02.50/0 © 1991 American Chemical Society

Glossary of Terms

$\Delta C_p^{\mathrm{obs}}$	observed change in specific heat capacity of the soft phase in the copolymer per unit mass of copolymer
ΔC_p^{H}	change in specific heat capacity of the ideally microphase-separated hard phase per unit mass of pure-component material
ΔC_p^{S}	change in specific heat capacity of the ideally microphase-separated soft phase per unit mass of pure-component material
$\mathrm{SR_S}$	soft-segment segregation; weight fraction of soft segments in the soft phase with respect to the total weight of soft segment in the copolymer
$\mathrm{SR_H}$	hard-segment segregation; weight fraction of hard segments in the hard phase with respect to the total weight of hard segment in the copolymer
W_{S}	weight fraction of the soft segment in the copolymer
W_{H}	weight fraction of the hard segment in the copolymer
W_{SP}	weight fraction of the soft phase
M_{SS}	weight fraction of soft segments in the soft phase
M_{HH}	weight fraction of hard segments in the hard phase

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