Thermal Blob: The Why and What of it.

What: (Following Strobl p. 52):

The thermic blob (thermal blob) is governed by the blob size $\xi_t$ (or $\xi_p$) so it is desirable to obtain an expression for $\xi_t$ in terms of known features of the system, the persistence length, $l_p$, the interaction parameter, $\chi$, and the like. This can be done in a fairly simple scaling analysis as shown by Strobl on page 52. We define the number of persistence units in the chain as $N$, number of persistence units in a thermic blob as $n_t$, and the number of thermic blobs in the chain as $N_t = N/n_t$. The thermic blob size is given by, $\xi_t = n_t^{1/2} l_p$. The Flory radius for the chain is given by,

$$ R_F = N^{3/5} \xi_t = (N/n_t)^{3/5} \xi_t = (N/(\xi_t/l_p)^3)^{3/5} \xi_t = N^{3/5} \xi_t^{-1/5} l_p^{6/5} $$

The expanded chain can also be described by the Flory-Krigbaum derivation in terms of the excluded volume, $V = V_c (1-2\chi) = l_p^3 (1-2\chi)$,

$$ R_F = N^{3/5} a_F = N^{3/5} l_p^{-3/5} V^{1/5} $$

where $a_F = l_p^{2/3} V^{1/3}$ from our expression $(R_F)^5 = (V \sqrt{N/l_p})^3 (l_p^5 N^{3/2}) = V l_p^2 N^{6/2}$, or

$$ R_F = V^{1/5} N^{3/5} l_p^{2/5} $$

By setting the two expressions for $R_F$ equal, an expression for $\xi_t$ can be obtained,

$$ V^{1/5} N^{3/5} l_p^{2/5} = N^{3/5} \xi_t^{-1/5} l_p^{6/5} $$

$$ V^{1/5} l_p^{-4/5} = \xi_t^{-1/5} $$

$$ \xi_t = l_p^2/V = l_p^2/(V_c (1-2\chi)) = l_p^4/(l_p^3 (1-2\chi)) = l_p/(1-2\chi) = l_p/(1-2z\Delta\varepsilon/kT) $$

where the latter expression gives the temperature dependence of the thermic blob size.

Why:

The last expression shows that the thermic blob decreases in size as the excluded volume increases. The function can be considered to enhance the persistence length, $l_p$, by the ratio of the hard-core volume to the enthalpic and hard core volume. We can look at certain conditions for this expression in terms of the interaction parameter $\chi$. 
When \( \chi \) is 0, \( \xi_t = l_p \) and the solvent is a very good solvent. Since the thermal blob can grow no smaller than the persistence length this is the terminal value for all negative \( \chi \)'s.

When \( \chi \) is negative, \( \xi_t = l_p \) since the thermal blob can grow no smaller than the persistence length this is the terminal value for all negative \( \chi \)'s.

When \( \chi \) is positive but less than 0.5, \( \xi_t > l_p \) and the blob grows with temperature until the theta temperature is reached or until \( \xi_t = R_F \). The equation above predicts that a thermal blob is only seen when enthalpic interactions oppose mixing of the polymer, i.e. positive \( \chi \). The blob occurs to mitigate enthalpically driven demixing and entropically driven miscibility. Apparently the balance between these effects is size-scale dependent as discussed below.

When \( \chi \) is 1/2, the denominator goes to 0 and \( \xi_t \) goes to infinity or to \( R_F \) which is the largest possible size for a finite molecular weight. At this point the coil is Gaussian and the theta-state has been reached.

**Size-scale dependence to the entropy/enthalpy balance for 0<\( \chi \)<0.5:**

The change in entropy on mixing per lattice site for a polymer coil of length, \( N \), at a volume fraction \( \phi_p \) in a solvent (\( N_s = 1 \)) is given in the Gaussian, Flory lattice model as \( kT (1/N) \phi_p \ln \phi_p + (1-\phi_p) \ln(1-\phi_p) \). The change in enthalpy on mixing per lattice site is \( kT \chi \phi_p(1-\phi_p) \). In the context of renormalization using blobs it is clear that there is a size-scale dependence (through \( N \)) to the free energy that has been ignored. That is, if we consider blobs of different size they must correspond to chains of different \( N \). The source of this size scale dependence is the entropy of mixing term which is dependent on the size of the blob from the \( N \) term. That is, for chains of small blob size \( N \) is big, \( N = N_{\text{persistence}} \xi_t l_p / \xi_t \). Then, it is not surprising that miscibility differences at different length scales could drive the formation of a thermic blob when enthalpic conditions are poor for mixing, i.e. for a good solvent but not for a very good solvent. As the blob size becomes larger (i.e. when \( n_t \) becomes larger and \( N = N_{\text{persistence}}/n_t \) becomes effectively smaller) entropy drives good-solvent miscibility. As the blob becomes smaller (i.e. when \( n_t \) becomes smaller and \( N \) becomes larger) the miscibility limit (theta scaling), theta temperature, can be reached at a local level while maintaining miscibility (good solvent scaling) at large sizes. The chain has essentially phase separated at a local scale while maintaining miscibility at large scales. This discussion must remain of a qualitative nature since there is no expression for the free energy of a coil in either a very good solvent condition or a good solvent condition. That is, the use of the FH free energy expression is not appropriate where the chain scaling deviates from Brownian.