DILUTE SOLUTION BEHAVIOUR OF COPOLYMERS

LECHOSIAW A. UTRACKI
GULF OIL CANADA LTD., SHAWINIGAN RESEARCH
STE. ANNE DE BELLEVUE, QUEBEC
CANADA

Recently a two parameter dilute solution theory of homopolymers was successfully applied \(^1\) to statistical copolymer-solvent and block polymer-solvent systems. The following basic assumptions were made:

I. Under a hypothetical Q-condition all individual long range interaction parameters \(\beta_{ij}\) vanish identically and the size of the copolymer coil is solely defined by short range interaction parameters \(a_{ij}\) (i, j = 1, 2, ... n, in a n-component system):

\[
a_c^2 = \sum_{ij} \left( a_{ii}^2 X_{ii} + a_{ij}^2 X_{ij} \right)
\]

\[
a_i^2 = M_{oi} \langle r_0^2 \rangle / M_i
\]

where subscripts c and i refer to the copolymer and its component i respectively, \(X_{ij}\)'s are the appropriate probabilities of i-j contact along the backbone chain, \(M_{oi}\) and \(M_i\) are segmental molecular weight calculated per one backbone carbon atom and total molecular weight of component i respectively, \(\langle r_0^2 \rangle\) is the unperturbed mean square end-to-end distance.

II. Under normal experimental conditions at least one \(\beta_{ij} \neq 0\). Provided the solvent is not much poorer than Q-solvent for any of the macromolecular components of the system we can write:

\[
\beta_c = \sum_{ij} \beta_{ij} Z_{ij}
\]

where \(\beta_{ij}\) is the binary cluster integral and \(Z_{ij}\) probability of i-j contact within a coil volume.
These two assumptions with a proper evaluation of $X_{ij}$ and $Z_{ij}$ are sufficient for a total description of a multicomponent copolymer - solvent system.

**BLOCK POLYMERS**

Here the probability of heterocontacts along the backbone chain as expressed by $X_{ij}$ is relatively small:

$$X_{ij} \ll X_{ii} \quad \text{and} \quad X_{ii} = x_i$$

where $x_i$ is the mole fraction of species $i$. The probability of long range interaction contacts, $Z_{ij}$, can be arbitrarily expressed as:

$$Z_{ij} = x_i x_j$$

This assumption is strictly valid for a random distribution of disconnected $i$ and $j$ segments within a coil volume.

Equations (1) - (4) have been used to analyze the intrinsic viscosity ($\eta$) and/or second virial coefficient ($A_2$) solution data of the following four block polymers: I Styrene (S) - Butadiene (B), SB and SBS blocks in toluene, dioxane and cyclohexane. II S - Methylmethacrylate (M), SM and MSM blocks in benzene and toluene. III Recently Kotaka et al. analyzed their data of MSM in six solvents. IV MSM in toluene and butanone. Using the given values of $[\eta]$, $M_w$ and $M_n$, as well as the short and long range interaction parameters calculated before, $\beta_{12}$ was computed by means of the Stockmayer-Fixman relation. In Fig. 1 two sets of $\beta_{12}$ calculated for IV are plotted vs. $M_w/M_n$ - one calculated using the weight average molecular weight, the second using the number average molecular weight of the copolymer samples. It can be seen that extrapolation to $M_w/M_n = 0$ leads to a common intercept: $\beta_{12} = 2.0 \text{Å}^3$ for toluene and $\beta_{12} = 1.5 \text{Å}^3$ for butanone. These values are in good agreement with the previous computations.

In all four cases the method was found to be adequate. For the system I the values of $M_c$ calculated from $[\eta]$ and/or $A_2$ agreed within 10% with the values measured. For systems II and III the stability of $\beta_{12}$ calculated from $[\eta]$'s was within $\pm 0.4 \text{Å}^3$.

**STATISTICAL AND ALTERNATE COPOLYMERS**

In statistical copolymers the $X_{ii}$ and $X_{ij}$ must be calculated from the monomers reactivity ratios available either from the literature or from kinetic measurements. The parameters $Z_{ij}$ can either be expressed by eq. (4) as for block polymers, or computed as dyadic segmental interactions with a solvent. The following three systems were analyzed: I S-M statistical