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Dedicated to Professor H. J. Cantow on the occasion of his 70th birthday.

Abstract. — A straightforward thermodynamic model is suggested to describe the (conductometrically measured) variation of the percolation temperature \( \Delta T_c \) of a w/o microemulsion (\( \text{H}_2\text{O}/\text{AOT/isoctane} \)) as a function of the initial concentration ratio \( R = P_\text{p}/D_\text{o} \) of ABA triblock copolymers (b-POE-b-PI-b-POE) and nanodroplets. Two copolymer concentration ranges are predicted, i.e. \( \Delta T_c \sim R^{1/3} \) for \( R \ll 10 \) and \( \Delta T_c \sim R \) for \( R \gg 10 \) which are compatible with our experiments.

Introduction.

Triblock ABA copolymers may form mesophases, i.e. physical networks, in which different A-blocks are bridged by B-blocks [1]. Such systems can be transformed into mesogels by selectively solvating (swelling) the A or the B-blocks or both. This latter process can be easily carried out by dissolving triblock copolymers in a microemulsion, where both blocks may be matched by the corresponding good or \( \theta \)-solvents.

Such a case is realized by a b-POE-b-PI-b-POE block copolymer which is dissolved in a ternary w/o microemulsion composed of water/AOT/2,2,4 trimethylpentane (isoctane). The anionic surfactant AOT, i.e. sodium bis(2-ethylhexyl)sulfosuccinate, serves to (thermodynamically) stabilize the microemulsion and to make it electrically conductive.

Addition of the ABA block copolymers to the w/o microemulsion modifies the interaction potential of the aqueous nanodroplets and changes, accordingly, the percolation temperature of the system relative to that of the pure microemulsion. A detailed thermodynamic interpretation has already been published elsewhere [2] giving a quantitative explanation of the solubility of the copolymers for various chain lengths of A and B blocks, however at dilute copolymer concentrations. It considered changes of the chemical potentials of the nanodroplets (considered as a pseudo-component) in the clustered and dispersed states and of the chemical potential of the copolymer.
At higher block copolymer concentrations it appears preferable to choose an equilibrium model based on a stoichiometric equation which describes the dissociation of the nanodroplet cluster in the presence of block copolymers. This approach is straightforward and seems to be justified by experiments which confirm for the present system reversible network formation [3]. We thus assume that the amount of the postulated aggregates between block copolymer and nanodroplets is proportional to the experimentally observed shift of the percolation temperature (see Fig. 1). Hence we start from a nanodroplet cluster $D_r$, consisting of $r$ droplets which will be decomposed into $n$ subunits ($D_{r/n}$ $P_{m/n}$) by $mP$ copolymers, where $r/n$ nanodroplets are bridged by $m/n$ copolymers.

![Figure 1](image)

Fig. 1. — Specific electric conductivity ($\sigma$) against temperature in the percolation regime; parameter: $R = [\text{copolymers}]/[\text{nanodroplets}]$; system: water/AOT/isoctane(i-C8) w/o-microemulsion + ABA (POE-b-PI-b-POE), $M_n(\text{POE})$: 22 000, $M_n(\text{PI})$: 39 000; weight-ratio: $m(\text{H}_2\text{O})/m(\text{AOT}) = 2.5$; weight fraction of nanodroplets $\{m(\text{H}_2\text{O}) + m(\text{AOT})\} / \{m(\text{H}_2\text{O}) + m(\text{AOT}) + m(\text{i-C8})\} = 0.35$.

**Model.**

The above reaction can be expressed by an equilibrium, i.e.

$$D_r + mP \rightarrow (K) n(D_{r/n} P_{m/n}).$$

(1)

Applying the mass action law (neglecting spatial correlations), the concentration of subunits is found to be

$$[D_{r/n} P_{m/n}] = (K)^{1/n} [D_r]^{1/n} [P]^{m/n}$$

(2)
If $D_0$, $P_0$ are the initial and $[D]$, $[P]$ the actual concentrations of nanodroplets and copolymers, respectively, the mass balances require

$$D_0 = [D] + r[D_j] + r/n[D_{rin} P_{min}]$$
$$P_0 = [P] + m/n[D_{rin} P_{min}] .$$

(3)

Within the percolation regime we neglect the concentration of nanodroplets $[D]$ compared to the other terms, leading to

$$[D_j] = D_0/r - 1/n[D_{rin} P_{min}] .$$

Hence we find from equations (2) and (3)

$$[D_{rin} P_{min}] = (K)^{1/n} (D_0/r - 1/n[D_{rin} P_{min}])^{1/n} (P_0 - (m/n)[D_{rin} P_{min}])^{m/n}$$

(4)

Expanding the brackets of equation (4) for small cluster concentrations into power series, and retaining only the linear terms, results in

$$[D_{rin} P_{min}] = K^{1/n} P_0^{m/n} (D_0/r)^{1/n} \times$$

$$\times \left( 1 - \left( \frac{m}{n} \right)^2 \frac{[D_{rin} P_{min}]}{P_0} - \left( \frac{r}{n^2} \right) \frac{[D_{rin} P_{min}]}{D_0} + O \left( \frac{[D_{rin} P_{min}]^2}{D_0 P_0} \right) \right) .$$

(5)

Introducing the initial copolymer/nanodroplet concentration ratio $(R = P_0/D_0)$ into equation (5), one finally arrives at

$$\Delta T_c \approx [D_{rin} P_{min}] \approx \frac{\left( \frac{K}{r} \right)^{1/n} D_0^{(m+1)/n} R^{m/n}}{1 + \left( \frac{K}{r} \right)^{1/n} \left( \frac{1}{n} \right)^2 (D_0)^{(m+1-n)/n} R^{m/n} \left( \frac{m^2}{R} + r \right)} .$$

(6)

According to the comments in the «Introduction» we have set $\Delta T_c$ proportional to the concentration of clusters. Since bridging effects by blockcopolymers hamper clustering of pure nanodroplets (see [4]) increased temperatures are required to percolate such interlinked droplets (see Fig. 1).

Discussion.

Figure 2 shows two different branches of the experimental plot: for small $R \ll 1$ (low block copolymer concentration limit) $\left( \frac{K}{r} \right)^{1/n} \left( \frac{1}{n} \right)^2 (D_0)^{(m+1-n)/n} R^{m/n} \left( \frac{m^2}{R} + r \right) \ll 1$, i.e.,

$$\Delta T_c \sim (K/r)^{1/n} D_0^{(m+1)/n} R^{m/n} .$$

From a double logarithmic plot one obtains $m/n = 0.2$ and $(K/r)^{1/n}$ since $D_0$ is known. The $\Delta T_c \sim (R)^{1/5}$ relationship for $0 \leq R \leq 10$ could describe the building up of pre-network block copolymer-nanodroplet aggregates which — beyond a certain copolymer concentration — pass into a three-dimensional network. Then, however, as seen from the constant slope above $R = 10$ the network does not change its structure with increasing copolymer concentration but only its strength changing from the «mesogel» to the gel state. From the structure of the expansion (Eq. (6)) and in view of the complete solution (Eq. (4)) which shows for large $R$-values to become linear in $R$, it is tacitly assumed that equation (6) describes the graph also for intermediate $R$-values (within the experimental $R$-range); then the above approximation
predicts a transition from a sloped branch into a linear portion, i.e., an increase of the cluster concentration (i.e. of $\Delta T_c$) if the second term in the denominator is taken to be $> 1$ and $m^2 > rR$ which conforms to the physical situation prevailing at intermediate $R$ (see Fig. 2).

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