Colloid Polym Sci (2004) 283: 284–290
DOI 10.1007/s00396-004-1137-9

ORIGINAL CONTRIBUTION

Sarah G. Schulz
Hubert Kuhn
Günter Schmid
Christian Mund
Joachim Venzmer

Phase behavior of amphiphilic polymers: A dissipative particles dynamics study

Received: 25 November 2003
Accepted: 01 April 2004

S. G. Schulz (✉) · H. Kuhn
AlCove-Molecular Dynamics-GmbH,
Am Wiesenbusch 2, 45966 Gladbeck,
Germany
E-mail: sarah.schulz@uni-essen.de

S. G. Schulz · G. Schmid
Department of Inorganic Chemistry,
University Duisburg-Essen, Universitätsstr.
5–7, 45117 Essen, Germany

C. Mund · J. Venzmer
Degussa Oligomers & Silicones,
Goldschmidt AG, Goldschmidtstr. 100,
45127 Essen, Germany

Abstract Dissipative particle dynamics is a mesoscopic simulation method which allows one to predict the self-assembly of amphiphilic polymers and surfactants. It was possible to reproduce the formation of microemulsions of the oil/water (o/w), water/oil (w/o), and L_3-type of C10E4 in water and *n*-decane with excellent accuracy. We are able to predict the experimentally not investigated emulsion formation of a poly(ethylene butylene)–poly(ethylene oxide) in water and methylcyclohexane.

Keywords Dissipative particle dynamics · Microemulsion · Amphiphiles

Introduction

Complex nanostructured self-assemblies such as colloidal suspensions, micelles, immiscible mixtures, microemulsions, etc., represent a challenge for conventional methods of simulation due to the presence of different time scales in their dynamics.

We have recently successfully applied a novel computer simulation technique, dissipative particle dynamics (DPD) [1], to model the behavior of diblock copolymers at the water/oil (w/o) interface. With the use of a simple model we have performed simulations of polymer/water/oil systems at different concentrations.

DPD is a mesoscale simulation technique that has been introduced to simulate three-dimensional structures of organic polymer aggregates [2, 3, 4]. In DPD the polymer is modeled by using particles which are interacting by conservative, dissipative, and random forces. Particles are not regarded as molecules but rather as droplets or nanoclusters of molecules.

We applied this technique to simulate the three-dimensional structures of microemulsions (e.g., the bicontinuous phase of C10E4 in water and *n*-decane) and found remarkable agreement with the experimental phase diagram [5]. We also characterized the phase behavior of a poly(ethylene butylene)–poly(ethylene oxide) diblock copolymer in water and methylcyclohexane, in domains of less than 100 nm. The different structures of the polymer/water/oil system were effectively characterized with DPD.

Methods

In DPD the fluid is modeled with point particles that interact through conservative, dissipative, and random forces. These point particles are of the same size and are not regarded as the fluid molecules, but rather as droplets or clusters of molecules. The total force on each bead is given by Eq. (1):

$$F_i = \sum_{i \neq j} \left(F_{ij}^C + F_{ij}^D + F_{ij}^R \right) \tag{1}$$

The conservative component is taken to be linear up to a cut-off radius in particle separation r_c, and zero outside of this [Eq. (2)]:

$$F_{ij}^C = \begin{cases} a_{ij} \cdot \hat{r}_{ij} \cdot \left(1 - \frac{r_{ij}}{r_c}\right) & (r_{ij} < r_c) \\ 0 & (r_{ij} > r_c) \end{cases} \tag{2}$$

where $\hat{r}_{ij} = r_{ij} / \left| r_{ij} \right|$, and a_{ij} is the repulsion parameter.

The dissipative force is proportional to the relative velocities of two beads and acts as to reduce their relative momentum. The random force provides an energy input into the system and builds together with the dissipative force a thermostat.

The repulsion between different DPD particles can be chosen according to Eq. (3):

$$a_{ij}(T) = 25 + 3.497 \cdot \chi_{ij}(T) \tag{3}$$

where a_{ij} (repulsion parameter between particles of different bead types) are linearly related to the Flory–Huggins interaction parameter χ [2].

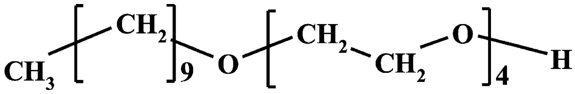
The Flory–Huggins parameter χ is defined in Eq. (4) [6]:

$$\chi = \frac{V_{\text{seg}} \cdot Z \cdot \Delta E_{12}}{RT} \tag{4}$$

where Z is the coordination number, and ΔE_{12} is the differential pair interaction energy [7] defined in Eq. (5):

$$\Delta E_{12} = 12(E_{12} + E_{21}) - 12(E_{11} + E_{22}) \tag{5}$$

The coordination number and the differential pair interaction energy were obtained by Monte Carlo simulations [6].



Scheme 1 Structure of C10E4 (**1**)

All calculations were carried out by using the COMPASS force field (condensed-phase optimized molecular potentials for atomistic simulation studies) [8], which is especially parameterized to model fluids.

Results and discussion

C10E4 in water and *n*-decane

In the present work we study the phase behavior of C10E4 (**1**) (Scheme 1) in water (**2**) and *n*-decane (**3**) at different surfactant concentrations.

Scheme 2 shows the DPD particles (beads) for the investigated system. Water (**2**) is always represented by one bead (W_1), and the oil (**3**) by three beads (D_1–C_2). The surfactant (**1**) is divided into two parts, the hydrophobic and the hydrophilic chains, which are themselves represented by several beads (C_3–B_4–A_1).

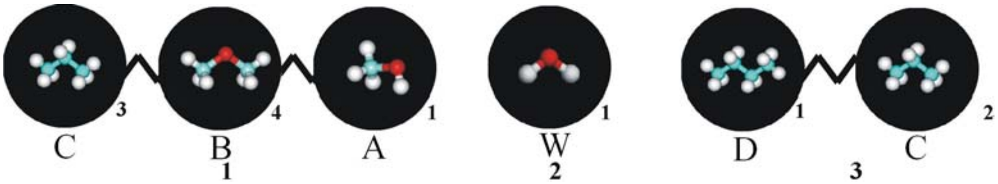
The experimental phase diagram of such a surfactant/water/oil mixture, as shown in Scheme 3, shows four different phases at equal volume fractions of water and oil and an increasing surfactant concentration [5]. The water/oil ratio in this phase diagram (α) is 0.422, as calculated with Eq. (6):

$$\alpha = \frac{m_{n\text{ - decane}}}{m_{n\text{ - decane}} + m_{\text{water}}} \tag{6}$$

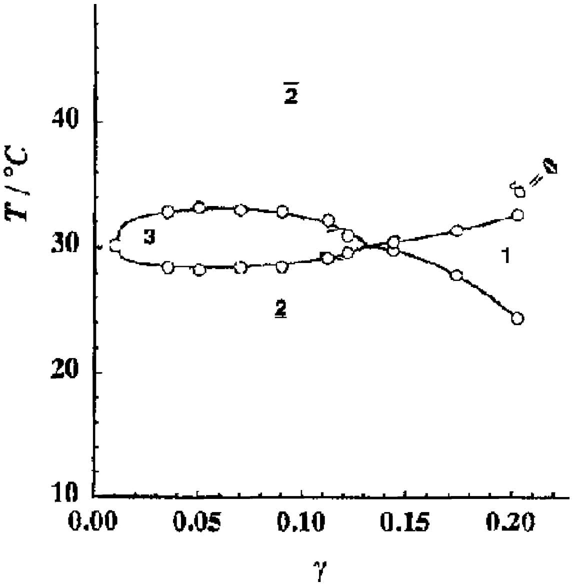
where $m_{n\text{-decane}}$ is the mass of the oil and m_{water} the mass of water.

The o/w microemulsion ($\underline{2}$) with excess oil, where oil droplets are covered with the surfactant and dissolved in the large water phase is found at temperatures lower than 28°C. The opposite, a w/o microemulsion ($\bar{2}$) with water droplets dissolved in the large oil phase and excess of water is found at temperatures higher than 32°C. At temperatures between 28°C and 32°C, a three-phase region (3) occurs, an excess of water as well as oil and a microemulsion. With increasing surfactant concentration the excess water and oil become less, and at a C10E4 concentration of 13.2 wt% just one microemulsion phase (1) is visible.

All simulations were carried out at 300 K and a box side length of about 35 nm with a DPD density (ρ_{DPD}) of 3, which equals a normal density of $\rho = 1$. The oil/water ratio was for all calculations (α) 0.422. All



Scheme 2 Schematic representation of the simulation model for C10E4 (**1**), water (**2**), and *n*-decane (**3**)



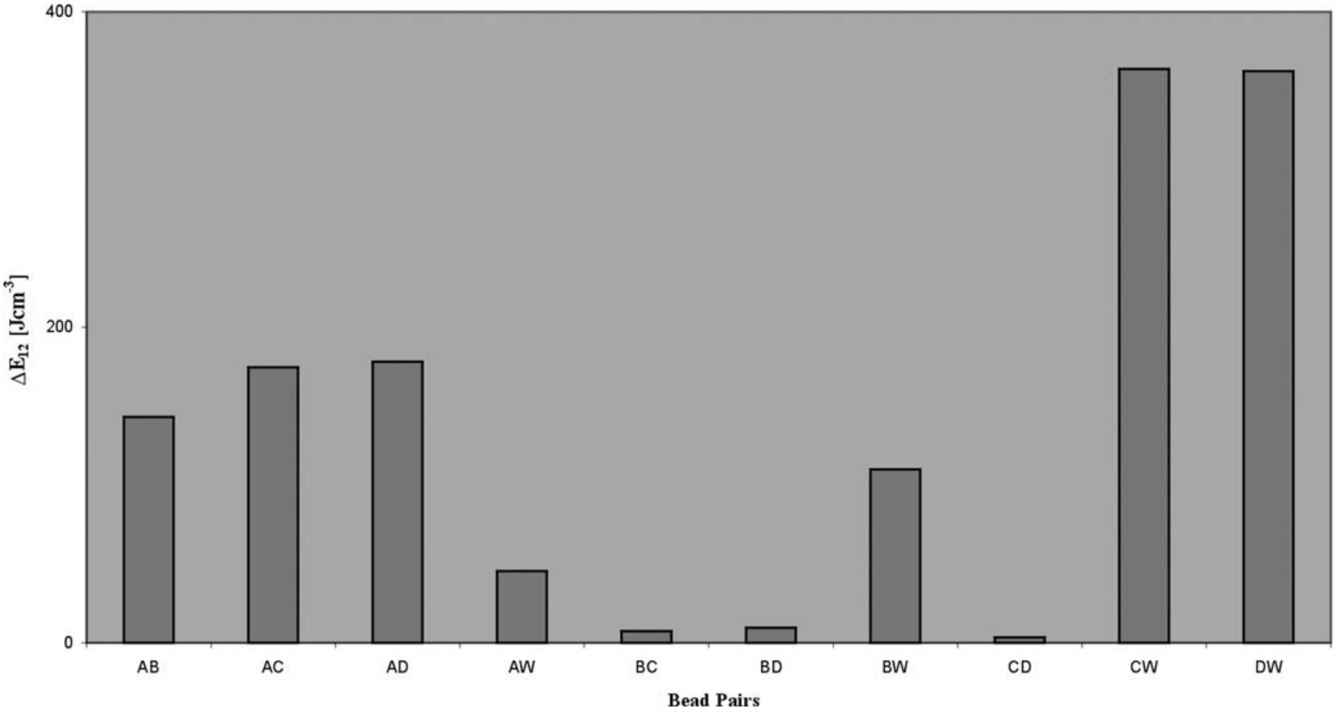
Scheme 3 Experimental phase diagram of C10E4 in water and *n*-decane [5]

simulations were carried out with a starting geometry of an arbitrary bead distribution in the box. For all bead pairs, a coordination number of 6.5 was estimated by using Monte Carlo simulations [6]. The differential pair interaction energies ΔE_{12} were obtained by Monte Carlo simulations [6] and are represented in Fig. 1, where the *x*-coordinate shows the different bead pairs and the *y*-coordinate shows the energy ΔE_{12} (in J cm^{-3}). The energies for pairs of equal beads were very close to 0 and therefore estimated as such. Figure 1 makes the differences in the behavior of different bead pairs visible. All hydrophobic beads (C,D) have high positive values with water (W) due to their repulsive behavior. The hydrophilic beads (A, B) have lower interaction energies and therefore mix better with water.

The experimental phase diagram (Scheme 3) shows that the three-phase region changes to the one-phase region at a concentration of **1** of 13.2 wt%. The simulation results did not reproduce the three-phase region, but showed a simple phase separation of water (**2**) and oil (**3**). The differences between the simulation and the experimental result from the diverse system sizes. The experimentally found three phases are macroscopic, while the phase separation occurs in a "nano-box" and therefore cannot be compared directly. Figure 2 shows the simulation result at a surfactant (alkyl chain beads–green, ethylene oxide beads–red) (**1**) concentration of 7.5 wt% (a) and 12 wt% (b) at the interface of the water (blue) and *n*-decane (white).

Figure 2 makes visible how the shape of the interface between oil (**3**) and water (**2**) changes with increasing surfactant concentration. While the interface at a C10E4 concentration of 7.5 wt% (Fig. 2a) is still almost a plane it changes with increasing surfactant concentration to a

Fig. 1 Pair interaction energies ΔE_{12} (in J cm^{-3}) for all bead pairs of the C10E4/*n*-decane/water system



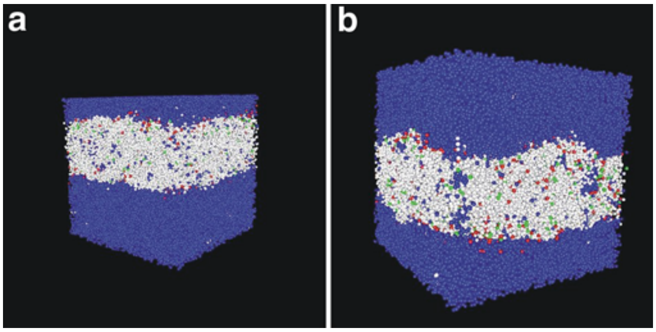


Fig. 2a,b Phase separation of water and *n*-decane at a C10E4 concentration of 7.5 wt% (**a**) and 12.5 wt% (**b**)

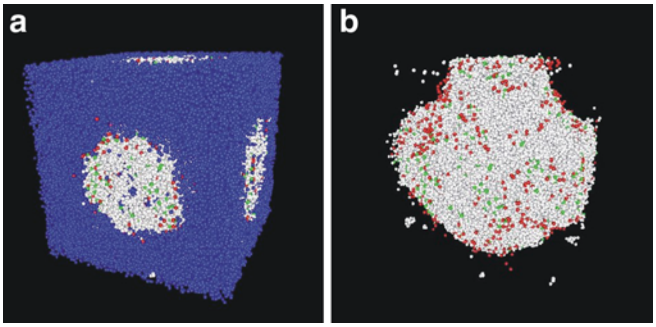


Fig. 3a,b Bicontinuous phase at a polymer concentration of 15 wt%: **a** shows the L_3 phase with water and **b** without

convoluted interface as visible in Fig. 2b at a surfactant concentration of 12.5 wt%.

At concentrations even higher than 14 wt%, the simple phase separation changes to a bicontinuous phase. In Fig. 3 the structure of a bicontinuous L_3 phase is shown, which appears first at a C10E4 concentration of 15 wt%.

The sponge-like structure as shown in Scheme 6b is reproduced even though not completely visible. The box-size limits the view of the bicontinuous phase because of the comparatively small dimensions.

The theoretically found transition concentration from the three- to the one-phase region is 15 wt%, which is in remarkable agreement with the experimental value of 13.2 wt% C10E4.

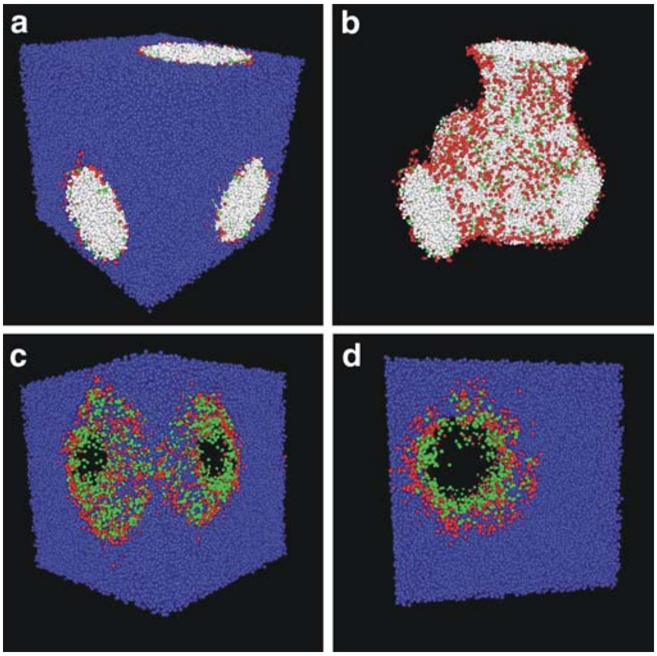


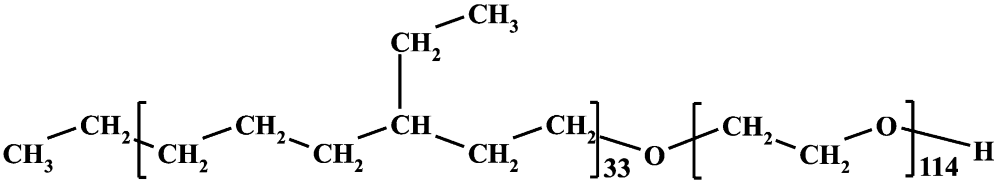
Fig. 4a–d Bicontinuous phase at a polymer concentration of 20 wt%: **a** shows the L_3 phase with water and oil and **b** with water masked and **c** and **d** with oil masked

At even higher concentrations of **1** the formation of the sponge-like structure is even more distinct. Figure 4 shows the L_3 phase at a surfactant concentration of 20 wt%. Figure 4b points out the tube-like oil phase with the water masked. In Figs. 4c and 4d the oil is masked and the tubes in the water phase are visible.

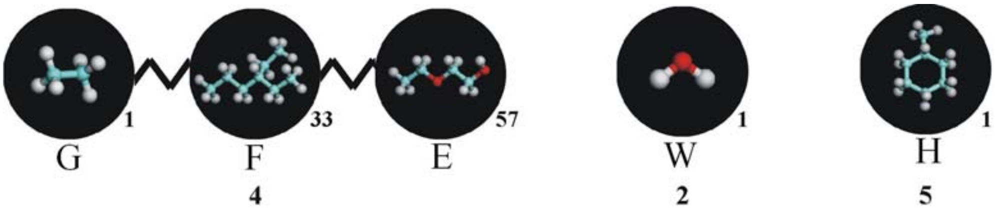
Poly(ethylene butylene)–poly(ethylene oxide) in water and methylcyclohexane

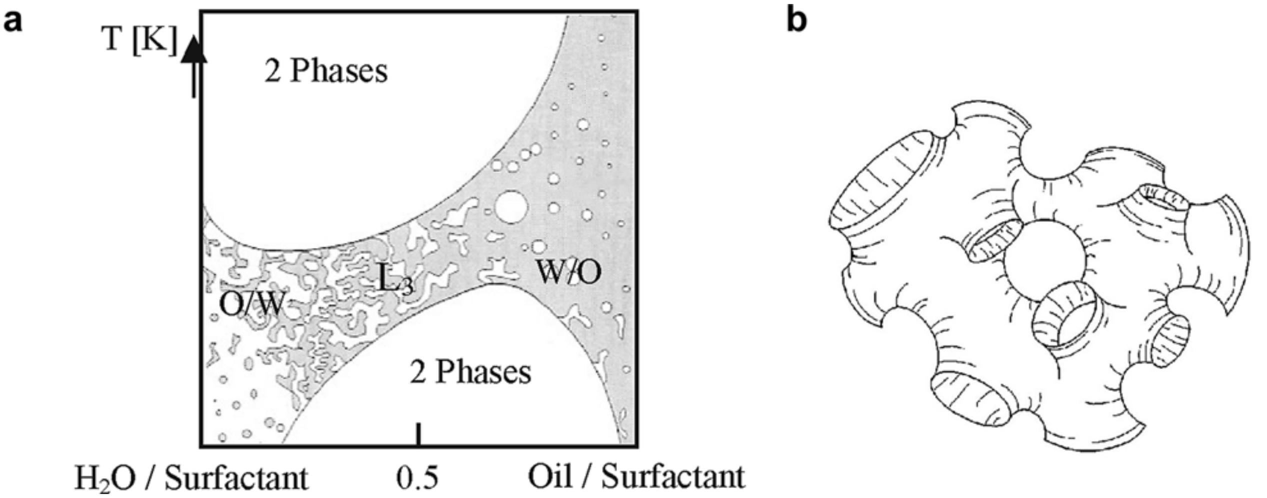
The simulation results of the microemulsion formation of C10E4 in *n*-decane and water were in exceptional agreement with the experiment. It was experimentally difficult to investigate microemulsions of the system poly(ethylene butylene)–poly(ethylene oxide) diblock copolymer (**4**) in water (**2**) and methylcyclohexane (**5**). Therefore, a theoretical study of the phase behavior was carried out to determine if microemulsion formation

Scheme 4 Poly(ethylene butylene)–poly(ethylene oxide) (**4**) with 67 ethylene, 33 butylene, and 114 ethylene oxide units



Scheme 5 Schematic representation of the simulation model





Scheme 6a,b Model phase behavior of a polymer/water/oil mixture (**a**) and the schematic bicontinuous L_3 phase (**b**) [9]

with such a polymer is in principle possible. The experimental problems could be the effect of insufficient kinetics in the formation process.

The diblock copolymer contains an alkyl chain with a molar mass of 3,800 g mol^{-1}, includes 67 ethylene and 33 butylene units statistically distributed, whereas the hydrophilic ethylene oxide part of this polymer contains 114 ethylene oxide units and has a molar mass of 5,000 g mol^{-1} (Scheme 4).

Scheme 5 shows the DPD particles (beads) for the investigated system. Water (**2**) as well as the oil methylcyclohexane (**5**) are always represented by one bead (W_1) and (H_1). The polymer is divided into two parts, the hydrophobic and the hydrophilic chains, which are themselves represented by several beads (G_1–F_{33}–E_{57}).

The model phase diagram of such a polymer/water/oil mixture as shown in Scheme 6 shows three regions of distinguishable phases [9]: the o/w microemulsion, in which oil droplets are covered with the polymer and dissolved in the large water phase; the opposite, a w/o microemulsion with water droplets dissolved in the large oil phase; and the bicontinuous phase (L_3) at equal fractions of water and oil.

The simulations with dissipative particle dynamics reproduce the model phase behavior with remarkable agreement. All simulations were carried out at 300 K and a box side length of about 35 nm with a DPD density (ρ_{DPD}) of 3, which equals a normal density of $\rho = 1$. Simulations of all water/oil ratios at a certain polymer concentration of 0.12 mol% were achieved. All simulations were carried out with an arbitrary bead distribution in the box. For all bead pairs, a coordination number of 6.5 was estimated by using Monte Carlo simulations [6]. The differential pair interaction energies ΔE_{12} were obtained by Monte Carlo simulations [6] and are represented in Fig. 5, in which the x-coordinate shows the different bead pairs and the y-coordinate shows the energy ΔE_{12} (in J cm^{-3}). The energies for pairs of equal beads were very close to 0 and therefore estimated as such. Figure 5 makes the differences in the behavior of different bead pairs visible. All hydrophobic beads (F,G,H) have high positive values with water (W) due to their repulsive behavior. The hydrophilic beads (E) have lower positive interaction energies and therefore mix better with water. In contrast, the hydrophobic beads of the polymer (G, F) have slightly negative energies with the oil beads (H). The fact that the ethylene oxide bead (E) has a slightly higher interaction energy with water than with oil seems to be inconsistent with its hydrophilic behavior. However, the interaction energies of the hydrophobic part (F,G) with water (W) is dimensions higher and causes a strong repulsion, while the interaction of the ethylene oxide (E) with water (W) and oil (H) is of a similar magnitude.

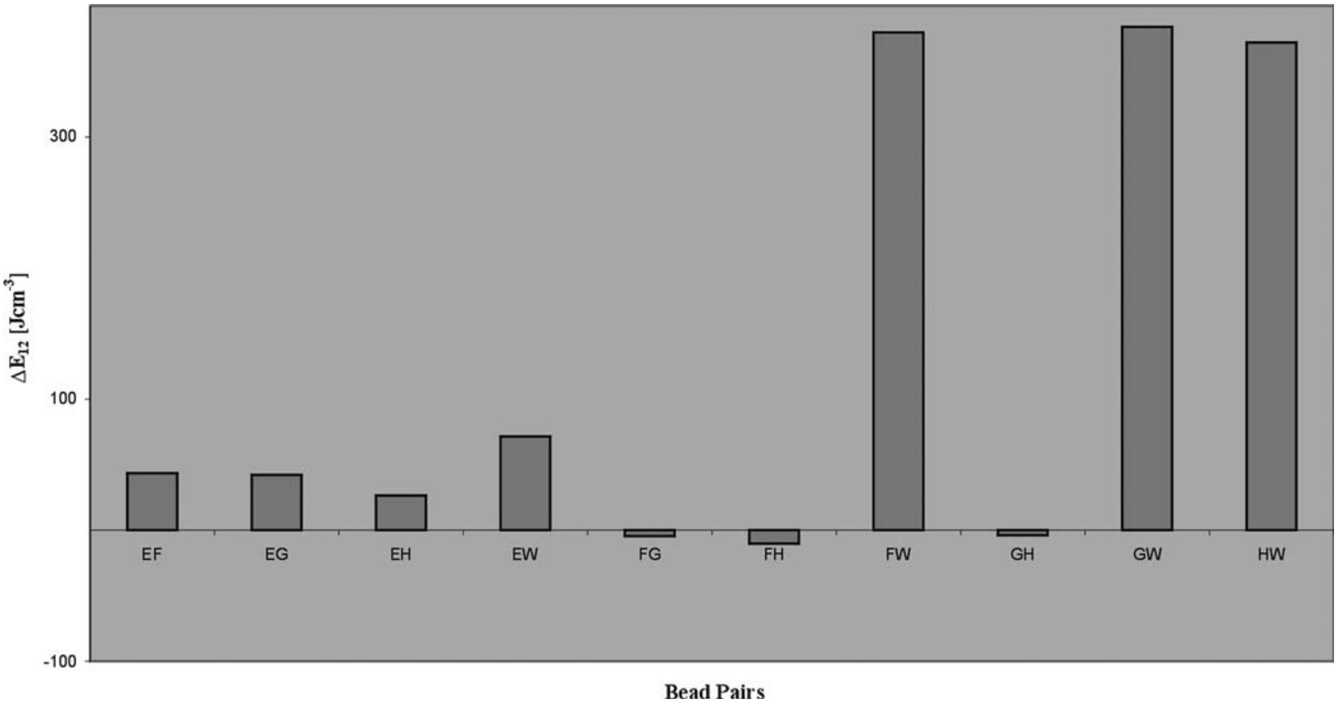


Fig. 5 Pair interaction energies ΔE_{12} (in J cm^{-3}) for all bead pairs of the poly(ethylene butylene)–poly(ethylene oxide)/ methylcyclohexane/water system

Figure 6 shows the result of the simulation carried out at a water/oil ratio of 8:1. At this ratio, oil droplets (methylcyclohexane beads–white) form in the water phase (water beads–blue) with the polymer (alkyl chain beads–purple, ethylene oxide beads–yellow) at the interface. In Fig. 6b, where the water was removed in the visualization, the differences in the behavior of the alkyl chain and the ethylene oxide chain is visible. While the alkyl chain is sprawled out into the oil, the ethylene oxide chain remains at the interface.

As shown in the model phase diagram as well as in Fig. 7, a w/o-type emulsion is formed at an excess of oil. In Fig. 7a the simulation result with a polymer concentration of 0.12 mol% and a water/oil ratio of 1:8 is visualized with all components. In Fig. 7b the oil was made invisible and it shows, as mentioned, before the sprawled alkyl chain, whereas the ethylene oxide remains at the interface and builds a rim around the water droplet.

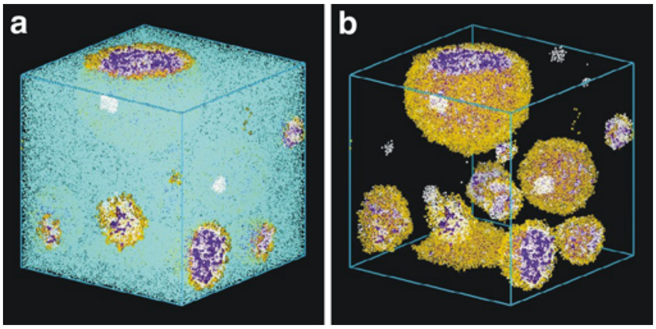


Fig. 6 a,b O/W emulsion at a polymer concentration of 0.12 mol% and a water/oil ratio of 8:1

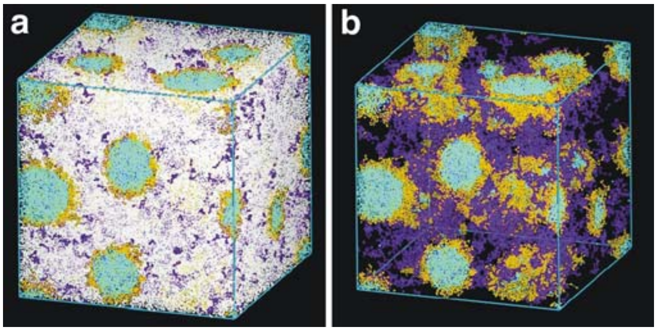


Fig. 7 a,b W/O emulsion at a polymer concentration of 0.12 mol% and a water/oil ratio of 1:8

At equal concentrations of water and oil, the simulation shows the formation of a bicontinuous phase, as shown in Fig. 8. In Fig. 8b the water was removed and the tube-like structure, as depicted in Scheme 6b, is visible. The box size is too small to show the whole structure as in Scheme 6b, but the agreement is still distinct

To the best of our knowledge and from personal communication [Venzmer J, Degussa Oligomers & Silicones, Goldschmidt AG], the experimental formation of a microemulsion could not be observed, while the formation of a bicontinuous L_3 phase with dissipative

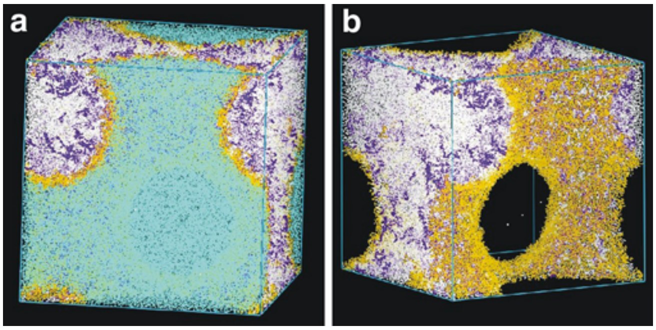


Fig. 8 a,b L_3 bicontinuous phase emulsion at a polymer concentration of 0.12 mol% and a water/oil ratio of 1:1

particle dynamics suggests that the structures found in the simulations are microemulsions. The fact that DPD is based on a thermodynamic model, which in principle should not allow the formation of a kinetically stabilized phase, supports the proposal of the existence of a microemulsion rather than an emulsion. The formation of a microemulsion in the simulation can be explained by the starting point geometry. The completely homogeneous distribution of all beads at the beginning of the calculation is energetically very unfavorable and therefore the system quickly falls into an energy minimum. This is not comparable with the experimental starting point, where the kinetics of the polymers are too slow to build a microemulsion.

Conclusions

We have successfully applied dissipative particles dynamics to simulate the self-assembly of C10E4 in water and *n*-decane as well as a poly(ethylene butylene)–poly(ethylene oxide) diblock copolymer in water and methylcyclohexane. It was possible to distinguish between the w/o, o/w, and bicontinuous emulsions just by varying the water/oil ratio. The simulation results of C10E4 in water and *n*-decane are in good agreement with the experimental phase diagram. It was also possible to calculate the experimentally unknown phase behavior of poly(ethylene butylene)–poly(ethylene oxide) diblock copolymer in water and methylcyclohexane.

Therefore, the DPD method is a reliable tool to gain a better understanding of the nanostructure of self-assemblies. The method is therefore applicable to support the often-complicated experiments and even to obtain data that has otherwise been experimentally unavailable.

References

1. Ryjkina E, Kuhn H, Rehage H, Müller F, Peggau J (2002) Angew Chem 114(6):1025
2. Espagnol P, Warren P (1995) Europhys Lett 30:191
3. Hoogerbrugge P, Koelman J (1992) Europhys Lett 19:155–160
4. Groot RD, Warren PB (1997) J Chem Phys 107:4423
5. Jakobs B, Sottmann T, Strey R, Allgaier J, Willner L, Richter D (1999) Langmuir 15:6707
6. Flory P (1953) Principles of polymer chemistry. Cornell University Press, Ithaca, New York
7. Fan C, Olafson B, Blanco M, Hsu H (1992) Macromolecules 25:3667
8. Sun H (1998) J Phys Chem 102:7338
9. Strey R in: Dörfler H-D (1994) Grenzflächen- und Kolloidchemie. VCH, Weinheim