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SHORT COMMUNICATION

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Polymerisation in supported bilayers

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Abstract The intercalation of the twin-tailed amphiphilic dioctadecyldimethylammonium (DODA) ions in smectite clay minerals provides a well-defined supported bilayer system. Polymerisation of styrene in these robust model bilayers allows one to focus on the effect of the constrained medium on the polymerisation process and the polymer. Small-angle X-ray scattering analysis and differential scanning calorimetry data indicated that the polymerisation of styrene in DODA–montmorillonite leads to phase separation between polystyrene and the surfactant matrix.

Key words Organically modified clay minerals · Polymerisation · Supported bilayers · Dioctadecyldimethylammonium bromide

Introduction

During the last decades, processes were developed to disperse different types of organically modified clay minerals (OMC) in a large variety of polymers, leading to polymer–silicate nanocomposites [1–3]. The OMCs are typically obtained by insertion of amphiplilic molecules (classical surfactants or block copolymers) between the layers of clay materials such as montmorillonites [4–7]. The dispersion of the inorganic material in the polymer could be achieved either by melt extrusion of the polymer with the inorganic compound or by polymerisation in the presence of the inorganic compound. Owing to the growing commercial interest in these organic–inorganic hybrid materials, this field has become a rapidly expanding research area of materials chemistry. However, most of the work deals with the engineering aspects and the properties of the materials obtained and only lately has the model character of these systems for confined polymers been realised. Our interest in this subject is motivated by the model character of the OMC systems to polymerisations in surfactant bilayer systems investigated earlier and to confined environments for polymerisations in general [1]. Our synthetic concept to study polymerisations in stabilised bilayer environments is rather simple: First, we provide a supported or stiffened bilayer system by fixing the amphiphilic twin-tailed dioctadecyldimethylammonium (DODA) cations between montmorillonite layers by cation exchange. The hydrophobic bilayer adsolubilises hydrophobic molecules such as styrene [8–10]. Polymerisation of the adsolubilised monomer molecules provides a thin two-dimensional polymer film. Conceptually, the process (Fig. 1) is analogous to the polymerisation process in other bilayer systems, for instance, vesicles or lyotropic liquid-crystalline phases which we investigated earlier [11]. Our main result from these previous studies on polymerisation in bilayers was that the generation of a polymer immediately induces a phase separation between the polymer and the surfactant matrix owing to the incompatibility between these two compounds. Hence, the concept of polymerisation in bilayers to produce thin films is frustrated by the unfavourable thermodynamics of the system. Using

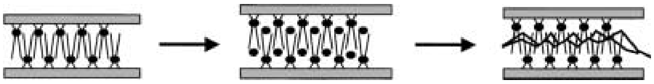

Fig. 1 The concept of polymerisation in organically modified clay minerals (*OMC*). Preparation of the OMC by intercalation of dioctadecyldimethylammonium (*DODA*) in the gallery of smectite clays (*left*); adsolubilisation of monomer (*dark spots*) in the bilayer (*middle*); polymerisation of the inserted monomer (*right*)

supported bilayers as a "matrix" for the polymerisation of inserted monomers we want to focus on the question whether the phase separation between polymer and bilayer can be overcome in a mechanically stabilised bilayer system. Related to that, we investigate the influence of the polymer on the state of the bilayer.

Similar experiments on polymerisation in supported surfactant layers were reported by several research groups. Wu et al. [12, 13] used surfactant bilayers adsorbed on alumina as two-dimensional reaction solvents to perform polymerisation of adsolubilised styrene. This approach to thin films was also applied by Sakhalkar and Hirt [14] for the preparation of polystyrene films on glass fibres. These authors observed that polymerisation was not restricted to the admicelles on the fibres but that it also occurred in the supernatant. Meguro et al. [15] reported the encapsulation of inorganic pigments by polymerisation of adsolubilised monomers. Zirkzee [16] investigated the polymerisation of styrene adsolubilised in DODA bilayers which were adsorbed on silica particles. He concluded that the encapsulation of silica with a polystyrene layer was possible in principle.

Our present study is divided into three stages: First, we study the DODA-exchanged clay mineral, then we investigate the adsolubilisation of monomer in the bilayers before we finally focus on the polymerisation step.

Experimental

Materials

Dioctadecyldimethylammonium bromide (DODAB, Acros) and sodium montmorillonite (EXM 757, Süd Chemie) were used as received. Styrene (Merck, purity above 99%) was distilled under reduced pressure and stored at −18′°C. Super-Q water (Millipore) was used to prepare the dispersions. The oil-soluble photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA, Aldrich, 98%), the water-soluble azo initiator 2,2′-azobis(2-methylpropionamidine)dihydrochloride (V50, Aldrich, 97%) and the oil-soluble azo initiator α,α'-azoisobutyronitrile (AIBN, Fluka) were used as received.

Preparation of the ion-exchanged montmorillonite

The montmorillonite (cation exchange capacity = 0.95 mEq/g) and DODAB (mass ratio 1:0.66) were dispersed in water (5%wt), heated to 60 °C and stirred overnight. The ion-exchanged montmorillonite was filtered, washed several times with water and either freeze-dried or used directly as an aqueous dispersion.

Swelling of the ion-exchanged montmorillonite

A known mass of the DODA–montmorillonite composite was stored in a saturated styrene atmosphere at room temperature. The take-up of monomer was weighed, and typically after 2 days a constant weight was attained.

A simpler way to transport the monomer into the bilayer was by dispersing 10–20%wt DODA–montmorillonite in styrene. Alternatively, a known amount of ion-exchanged montmorillonite was dispersed in water and a calculated amount of styrene was injected into the dispersion.

Polymerisation

Polymerisation was carried out in several ways. In dispersions of 10–20%wt DODA–montmorillonite in styrene, the polymerisation was initiated thermally after addition of AIBN (5%wt based on monomer) and heating to 70 or 140 °C in a sealed vial. Alternatively, the polymerisation was initiated photochemically by DMPA (5%wt based on monomer) and exposure to UV radiation (Philips HPR 125 lamp) at room temperature.

The polymerisation of styrene in aqueous dispersions (10%wt, [DODA]:[styrene] = 1:5.5) was initiated thermally, using a water-soluble azo initiator (V50, 5%wt based on monomer) and by heating to 70 °C in a sealed flask.

Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) analysis was carried out using a Perkin–Elmer Pyris 1 calorimeter (heating/cooling rate 10 K/min).

X-ray scattering measurements

Synchrotron X-ray scattering experiments were performed at the A2 beamline at Hasylab, Hamburg. Details concerning the measurements were described previously.

Results and discussion

The ion-exchanged montmorillonite

The hydrated sodium ions of the montmorillonite were exchanged by the amphiphilic double-tailed cation DODA, the exchange capacity of this montmorillonite being 0.95 mEq/g [5, 6, 17]. The interlayer spacing, as measured by small-angle X-ray scattering (SAXS), after cation exchange and extensive drying in vacuo increased from 1.26 to 3.7 nm i.e. the thickness of the amphiphile layer amounts to 2.7 nm as the thickness of the inorganic layer itself is 1 nm [4, 18][1]. Considering the length of an extended DODA ion of 2.6 nm, it is evident that the alkyl chains are either strongly tilted to the layer normal by an angle of 31° or, alternatively, that the

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[1] Note that 0.26 nm is the thickness of the counterion layer, while 1 nm is the thickness of the unit layer.

DODA ions are almost fully interdigitated. From the present data it cannot be decided what the structure of the DODA–montmorillonite actually looks like.

A typical feature of the intercalated alkyl chains is that they adopt an ordered structure at low temperatures when the trans conformations prevail and a more liquidlike behaviour at higher temperatures when the gauche conformations are attained [6, 19]. It is therefore not surprising to find a transition between these two states which can be determined by DSC measurements to be at 44.3 °C in the present case (Fig. 4). Note that this phase-transition temperature is very similar to the phase-transition temperature of the DODAB vesicle bilayers [11], possibly suggesting that the chain packing density in the vesicles and the exchanged mineral is comparable. Any attempts to discern the chain crystallinity from the wide-angle X-ray scattering (WAXS) pattern failed as the clay mineral spacings dominate the pattern with peaks at 0.52 and 0.47 nm. This WAXS spectrum does not change above the transition temperature, whereas the interlayer distance extended by 0.23 nm with increasing temperatures owing to the conformational freedom of the alkyl chains (Fig. 2, Table 1). Interestingly, a decrease in lamellar spacing upon heating was observed by Lagaly [6] for several OMCs that could be ascribed to the occurrence of more gauche conformations at elevated temperatures.

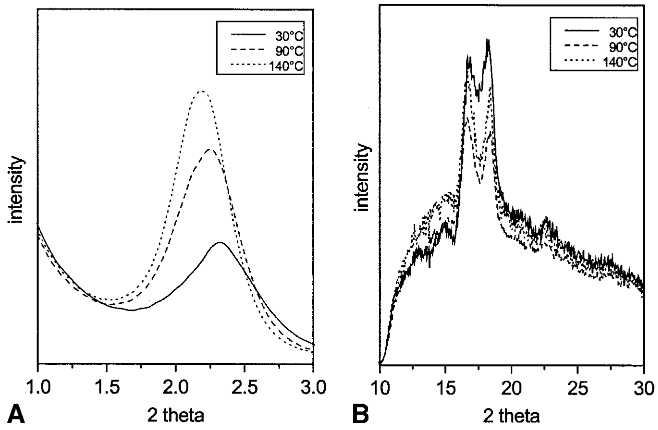

Fig. 2 **a** Small-angle X-ray scattering (*SAXS*) and **b** wide-angle X-ray scattering patterns of the DODA–montmorillonite as a function of temperature

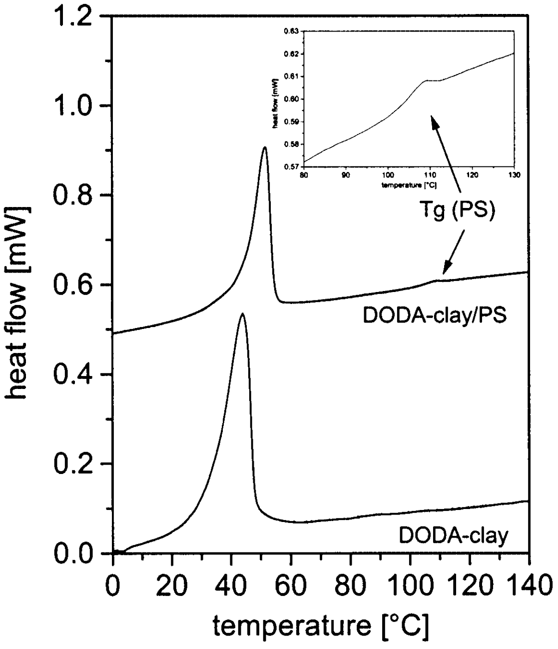

Fig. 3 SAXS patterns of the DODA–montmorillonite material before and after addition of styrene and after polymerisation. The measurements were performed at 30 °C

Swelling of the ion-exchanged montmorillonite

The hydrophobic DODA interlayers have a considerable swelling capacity for oil-soluble monomers. The organically modified montmorillonite adsorbed about 35% of its own mass at room temperature, which corresponds to a molar ratio [DODA]:[styrene] = 1:5.5. SAXS measurements (Fig. 3) show that the intercalation increased the basal spacing by more than 1 nm, i.e. a volume increase of 39%. Alternative methods to swell the DODA–clay mineral by dispersion in styrene (20%wt OMC) or dispersion in styrene-saturated water (10%wt OMC) led to identical results. This increase in interlayer spacing compares to the expansion of cetyltrimethylammonium–vermiculite in toluene [10] and the values determined by Regdon et al. [20] for the swelling of dodecylammonium–vermiculite in butanol.

Any attempts to asses the effect of the inserted styrene on the thermal behaviour of the interlayer by DSC measurements failed as a consequence of a shift in baseline caused by the premature loss of styrene.

Table 1 Small-angle X-ray scattering data of dioctadecyldimethylammonium (*DODA*)–montmorillonite systems in a dried state before and after polymerisation and after saturation swelling with styrene. Δ*d* refers to the reference state DODA–montmorillonite at 30 °C

System	T (°C)	*d* (nm)	Δ*d* (nm)
DODA–montmorillonite	30	3.70	0
DODA–montmorillonite	90	3.82	0.12
DODA–montmorillonite	140	3.93	0.23
DODA–montmorillonite/styrene	30	4.75	1.05
DODA–montmorillonite/polystyrene	30	3.80	0.10
DODA–montmorillonite/polystyrene	90	4.11	0.41
DODA–montmorillonite/polystyrene	140	4.11	0.41

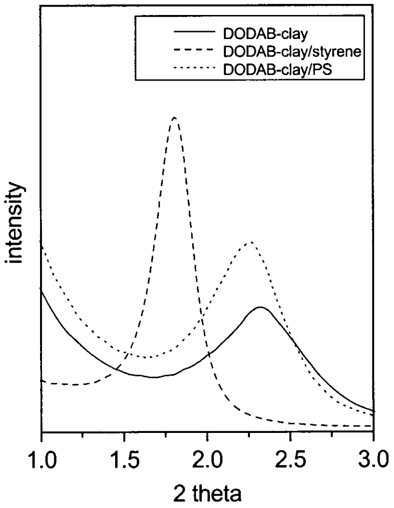

Fig. 4 Differential scanning calorimetry measurements of the pure DODA–montmorillonite and after the polymerisation of styrene

Polymerisation in the ion-exchanged montmorillonite

Polymerisation of styrene in the DODA interlayers was accomplished in several ways. The simplest way was to disperse the DODA–derivative (10 or 20%wt) in styrene and to initiate polymerisation thermally after addition of AIBN. This required higher temperatures (70 and 140 °C). Polymerisations at lower temperatures, i.e. below the transition temperature, could be carried out by photopolymerisation at room temperature using DMPA as an effective photoinitiator or, alternatively, by irradiation with an electron beam [21]. Independent of the polymerisation temperature and independent of the mode of initiation, the polymerisation led to a yellowish-brown, brittle material that exhibited a lamellar spacing about 0.1 nm greater than that of the reference DODA–clay mineral. The large decrease in the spacing of monomer-swollen material ($\Delta d =$ 1.05 nm) compared to the polymerised material ($\Delta d =$ 0.10 nm) cannot be explained by the volume shrinkage of the polymer, typically leading to only 13% volume contraction. We assume that most of the polymer was displaced from the bilayer in the course of the polymerisation reaction. In fact, an on-line thermal polymerisation experiment at 70 °C revealed a gradual decrease in spacing with progressing conversion. Our findings are corroborated by a recent report by Doh and Cho [22], who measured an even smaller increase in spacing of $\Delta d = 0.02$ nm for the polymerisation of styrene at 50 °C in a comparable OMC.

These results are somewhat surprising since DODA–clay minerals and similar derivatives are supposed to be favourable materials for the melt intercalation of polystyrene [23]. Giannelis and coworkers reported an increase in gallery height of $\Delta d = 0.7$ nm upon intercalation of molten polystyrene ($M_w = 35{,}000$ or 400,000) into DODA–clay minerals at 165 °C. It was concluded that the intercalation of polystyrene from the melt was driven by enthalpic polymer–host interactions. The authors noted further that attempts to intercalate from solution (toluene) resulted in the intercalation of the solvent instead of the polymer as a consequence of the preferable solvent–host interactions. In the light of these results one could argue that the in situ synthesis of a clay–polymer nanocomposite, as presented here, would in some respects be similar to a solvent intercalation as there is an excess of monomer, i.e. solvent, present up to high degrees of conversion. Therefore, the solvent–surfactant interactions could cause the polymer to remain in the interlayers.

In order to circumvent the problem of an excess of monomer during the reaction we changed the experimental design. The DODA–clay mineral was dispersed in water and a calculated amount of styrene was added under stirring to saturate both the organophilic montmorillonite and the water phase. As mentioned previously, the increased spacing after swelling indicated that the monomer was transferred from the water phase into the organophilic interlayer spaces. Polymerisation was then initiated by a water-soluble azo initiator (V50) at 70 °C. After heating to 70 °C and stirring overnight, the polymerisation product was dried in vacuo for several days to yield a brown-grey powder. Again, SAXS measurements showed only an increase of 0.1 nm in the interlayer spacing, which suggested that the largest part of the polymer was not intercalated. Similar to the behaviour of the pure DODA–montmorillonite, we observed increasing basal spacings with increasing temperature (Table 1).

Thermal analysis of this material revealed two transitions: the previously observed transition related to the DODA layer, now shifted to 52 °C and the glass transition of bulk polystyrene at about 103 °C. The observation of the bulk glass transition temperature is another clear hint that the polymer is not inserted in the bilayer but resides outside the clay-mineral platelets, perhaps at the edges (Fig. 4). According to Vaia et al. [23], the glass transition in truly intercalated polymers can vanish owing to an impeded translational and rotational motion of the polymer chains. Keddie and coworkers [24–26], however, reported a clear depression of the glass-transition temperature in thin polymer films.[2] The discrepancy of our observations to the successful intercalation of polystyrene from melts in similar organoclay materials may be due to the differences in experimental conditions, particularly the reaction temperature. At temperatures above 150 °C, which

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[2] In polystyrene films as thin as 8 nm, the depression from the bulk value of T_g can amount to 35 K.

were applied for the melt intercalation, the interaction between polymer and amphiphilic alkyl chains appears to be sufficiently strong to promote diffusion of the polymer into the DODA interlayers. We assume that cooling to lower temperatures freezes the system in a metastable state.

Conclusions

We investigated the polymerisation of styrene in supported DODA bilayers with a view to studying the effect of bilayer stabilisation on the polymer formation in this constrained medium. The system seems to be similar to previously studied vesicles and lyotropic systems [11]. All systems exhibit a gel-to-liquid bilayer phase transition where the aliphatic chains change from an all-trans conformation to gauche conformations. The solubilisation behaviour towards styrene also showed similarities, although the intercalation capacity of the organically modified clay mineral is high. Polymerisation of styrene in the interlayer spaces led to polymer expulsion, i.e. phase separation between the interlayer spaces and the polymer phase – irrespective of the process conditions. Again, the incompatibility between surfactant matrix and polymer both for enthalpic and entropic reasons is in analogy to previously studied systems and does not allow the intercalation of polystyrene in these supported bilayers – at least under the circumstances investigated. According to the literature, it seems that the system DODA interlayer/polystyrene becomes miscible at higher temperatures (above 150 °C); thus, it possesses an upper critical solution temperature where one single phase is established. It would be intriguing to study the influence of the temperature on the intercalation in more detail.

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