Table I. Normalized SH Intensities of LB films Containing Compounds 1–4 (Thickness, 10 Double Layers)

composition of LB film	$I^{2\omega a}$	composition of LB film	$I^{2\omega a}$
1	1	**2**/**3** (2:1)	5×10^{-5b}
2	1×10^{-3b}	**2**/**4** (2:1)	no effect obsd

[a] Experimental values are normalized to $I^{2\omega}$ of 10 double layers of 1. Nonlinear optical susceptibilities of **1**: $d_{333} = 6.8 \pm 1.2$ pm/V, $d_{311} = 0.9 \pm 0.2$ pm/V.[2] [b] No differences were found prior and subsequent to UV polymerization of **2**.

tical density due to the progressive polymer formation in the sample. In the mixed film, the increase is faster and the integral optical density reached after prolonged UV exposure is higher, indicating a more rapid polymerization and a higher conversion to polymer than in films of pure **2**. In mixture I, this can originate from a polymerization of either compound, whereas in mixture II the high photoreactivity must be due to another molecular packing of **2**. According to a previous study on mixed LB films of diacetylenes,[9] the occurrence of the photopolymerization is a strong indication for a phase separation of the individual compounds in the mixed film.

As indicated by small-angle X-ray scattering (SAXS), the LB films containing either pure **2** or a 1:1 mixture of **2** and **3** exhibit bilayer spacings of 3.99 and 5.16 (±0.04) nm, respectively. Since the maximum length of **2** in the fully extended conformation is shorter than the observed layer spacing, a head-to-tail (X- or Z-type) structure can be ruled out. Instead it must be concluded that the LB films are Y-structured, the molecules being tilted with regard to the layer plane. The different layer spacings observed for either the pure or mixed films most likely originate from different molecular arrangements, which may be similar to those in monolayers at the air–water interface (Figure 2).

Optical second harmonic generation (SHG) was studied on pure and mixed LB films containing **2** as monomer and polymer. A Q-switched Nd:YAG laser beam (BMI 501 DNS: wavelength $\lambda = 1064$ nm, pulse width $\tau = 25$ ns, repetition rate $f = 30$ Hz) was focused perpendicularly onto the sample. The second harmonic (SH) signal was detected as described previously.[10] In Table I the SH intensities $I^{2\omega}$ are listed. Data are normalized to the SH intensity of a corresponding LB film of pure **1** for both fundamental and SH wave polarized parallel to the dipping direction. As shown by the table, **2** exhibits a much lower SH intensity than **1**. In mixed films of **2** and the cadmium salt of **3**, nonlinear optical effects are even further diminished. Since in these cases the intensity was very close to the damage threshold of the glass, damage mechanisms may also have caused the nonlinearity. In mixed films of **2** and the cadmium salt of **4** nonlinear optical effects have not been observed. In the active films, the SH signal is always strongly polarized in the dipping direction, indicating a preferential alignment of the aromatic headgroups along this direction. The alignment is known to occur during LB-type transfer of the monolayers onto the substrate.[11]

Since the LB films are highly ordered, it can be inferred that the optical nonlinearity is a property of the film and most likely originates from a polar Y-structure (Figure 1).[1-3] The poor SH intensity observed for the mixed LB films is likely due to a more upright position of **2**, giving rise to a less polar structure. In addition, the SH intensity can be diminished by a more random orientation of the herringbone domains of **2** in the phase-separated mixed film.

In conclusion, we prepared a novel polymerizable amphiphile and observed optical second harmonic generation in Langmuir–Blodgett films of this material. Unfortunately, LB films based on this compound exhibit either a high photoreactivity and poor optical SHG or vice versa but not both effects at the same time.

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Organo Clay Assemblies for Triphase Catalysis

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Triphase catalyst systems for organic nucleophilic displacement reactions consist of a dispersed solid phase and two immiscible liquid phases that contain the electrophilic and nucleophilic reagents.[1] Reaction occurs by transfer of the reagents from the liquid phases to the solid phase. Normally, the triphase catalyst is a functionalized organic polymer[1-6] or inorganic support[7-10] that contains immobilized organo cations, including quaternary ammonium ions analogous to those used for conventional liquid–liquid phase-transfer catalysts.[11]

Although triphase catalysis greatly simplifies the recovery of the catalyst and provides opportunities for selective chemical conversions based on substrate size or polarity, the technique is not without limitations.[12-14] Polymer-supported triphase catalysts have yet to find industrial applications, in part because of their diffusion limitations and mechanical or chemical instability.[14] Several inorganic supports, including metal oxides,[7] clays,[8,9] and zeolites,[10] have been used in place of polymers, but these generally suffer similar disadvantages of low reactivity or structural instability under sustained reaction conditions. Thus, new materials for improved triphase catalysis are desirable.

We report here a promising new family of triphase catalytic materials based on alkylammonium exchange

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Table I. Alkylammonium Hectorites as Triphase Catalysts for the Cyanation of n-$C_5H_{11}Br$[a]

exchange cation	d_{001},[b] Å	k_{obs}, h^{-1}
$[(n\text{-}C_{14}H_{29})NMe_3]^+$	17.0	0.14 (0.07)[c]
$[(n\text{-}C_{16}H_{33})NMe_3]^+$	18.0	0.16 (0.07)
$[(n\text{-}C_{14}H_{29})NMe_2(CH_2C_6H_5)]^+$	18.1	0.16 (0.38)
$[(n\text{-}C_{16}H_{33})NMe_2(CH_2C_6H_5)]^+$	18.3	0.16 (0.37)
$[(n\text{-}C_{18}H_{37})NMe_2(CH_2C_6H_5)]^+$	18.3	0.16 (0.42)
$[(n\text{-}C_{12}H_{25})_2NMe_2]^+$	20.1	0.16 (0.54)
$[(n\text{-}C_8H_{17})_3NMe]^+$	21.0	0.18 (1.10)

[a] All reactions were carried out at 90 °C under the following stoichiometric conditions: 2.0 mmol of 1-bromopentane in 6.0 mL of toluene; 20 mmol of KCN in 3.0 mL of water; 0.073 mol of clay-bound quaternary ammonium ion. [b] X-ray basal spacing of the organo clay under air-dried conditions. [c] Values in parentheses are the k_{obs} values obtained under equivalent biphasic reaction conditions using the same stoichiometric quantity of unsupported alkylammonium ion.

forms of smectite clays. These intercalation compounds are efficient, stable, and recyclable catalysts for a variety of organic chemical conversions. Unlike previous triphase catalysts, organo clays can form thin, membranelike assemblies of platelets at the liquid–liquid interface of an oil/water type of emulsion. The reagents in the emulsified liquid phases are readily transferred to the interface of the clay assemblies for facile reaction. The emulsion, however, can easily be broken by gravity, low-speed centrifugation, or filtration, thus allowing for the convenient recovery of the catalyst and the reaction products.

The cyanation of 1-bromopentane was selected as a convenient nucleophilic displacement reaction to demonstrate the effectiveness of organo clay assemblies as triphase catalysts. Hectorite, with an idealized anhydrous unit cell formula of $Na_{0.67}[Li_{0.67}Mg_{5.33}]Si_{8.00}O_{20}(OH,F)_4$ served as a representative smectite clay. The native mineral was converted quantitatively to homoionic, quaternary alkylammonium exchange forms by aqueous ion exchange at room temperature. The products then were washed free of excess onium salt and air-dried before use as triphase catalysts.

Table I provides the pseudo-first-order rate constants (k_{obs}) for the conversion of 1-bromopentane to the corresponding nitrile under triphase reaction conditions using several quaternary ammonium ion exchange forms of hectorite as the triphase catalyst. Included in the table are the basal spacings for the organo clay and, for comparison purposes, the k_{obs} values obtained for the same alkylammonium ions under equivalent *biphasic* reaction conditions in the absence of the clay support. For each triphase system, catalytic reaction ceased ($k_{obs} < 0.001\ h^{-1}$) when the organo clay was filtered from the reaction mixture. Under the reaction conditions specified in the table, no change in k_{obs} was observed with increasing stirring rate, indicating that mass transfer was not rate limiting. Also, the clay catalysts retained their structural integrity after reaction, as judged by X-ray diffraction.

For each reaction system in Table I, the organo clay formed a thin, membranelike film at the interface of a toluene-in-water emulsion. Neither emulsion formation nor catalytic activity was observed for the pristine Na^+ hectorite. Significantly, the triphasic k_{obs} values were independent of the quaternary ammonium ion in these emulsion-forming systems. An average value of $k_{obs} = 0.16 \pm 0.01\ h^{-1}$ was obtained for the seven related organo hectorites. Both $[(n\text{-}C_{14}H_{29})NMe_3]^+$– and $[(n\text{-}C_{16}H_{33})NMe_3]^+$–hectorite exhibited a 2-fold increase in reactivity relative to the corresponding biphasic systems; the five remaining organo hectorites were 2.3–6.1 times less reactive than the biphasic analogues.

A decrease in catalytic efficiency upon onium ion immobilization is a general feature of triphase catalysis. Thus, the enhanced reactivity for $[(n\text{-}C_{14}H_{29})NMe_3]^+$– and $[(n\text{-}C_{16}H_{33})NMe_3]^+$–hectorite is an unusual and unexpected benefit of immobilization. The decrease in reactivity for the remaining organo hectorites is more typical of inorganic support systems and comparable to the loss in activity observed for onium ions immobilized on silica and alumina.[7] Although organo-functionalized silicas and aluminas can exhibit catalytic reactivities similar to our organo clays, they require relatively elaborate preparative procedures that involve the use of silane coupling agents to covalently bind the onium ion to the oxide surface. In contrast, our clay assemblies are readily prepared by simple ion-exchange reactions. Also, clays offer the possibility of improved catalytic longevity. For instance, we have recycled $[(n\text{-}C_{16}H_{33})NMe_3]^+$–hectorite through multiple catalytic cycles of 1-bromopentane cyanation at 90 °C. More than 70 mol of product was formed per mole of clay-immobilized quaternary ammonium ion before k_{obs} decreased to half its initial value.[15]

Organo cation exchange forms of smectite clays have been observed previously to function as triphase catalysts.[8,9] The earlier work of Cornēlius and Laszlo[9] is particularly relevant as these workers first utilized a commercially available quaternary ammonium montmorillonite (Thixogel VP[16]) to catalyze the formation of symmetrical formaldehyde acetals from dichloromethanes, alcohols, and aqueous NaOH. Almost any organo clay may be expected to function as a phase-transfer catalyst owing to the general hydrophobicity of these materials and their ability to bind ion pairs. However, we find that triphase catalytic activity depends greatly on the ability of the clay to assemble at the organic liquid–aqueous liquid interface of the emulsion. Emulsion formation by certain quaternary ammonium clays has been recognized previously in the use of these materials as oil well drilling fluids,[17] but little is known concerning mechanism.

Our results suggest that the orientation of the exchange cations on the clay surfaces plays an important role in emulsion formation. If the alkylammonium chains are sufficiently short to lie completely flat on the clay basal surfaces, then the clay layers do not assemble as part of an emulsion, and the triphasic rate constants are reduced by an order of magnitude. This latter conditions arises for $[(n\text{-}C_4H_9)_4N]^+$–hectorite where the basal spacing ($d_{001} = 14.7$ Å) corresponds to a gallery height of ~5.1 Å. Thus, even though $[(n\text{-}C_4H_9)_4N]^+$ is a very good biphasic catalyst for 1-bromopentane cyanation ($k_{obs} = 0.56\ h^{-1}$), the corresponding organo hectorite is a relatively poor triphase catalyst. For the organo hectorites listed in Table I, however, the basal spacings are substantially larger than 14.7 Å and indicative of the longer hydrocarbon chains being kinked with part of the chain tilted away from the clay basal surface.[18,19] Chain kinking and tilting may prove to be important for the wetting of the clay surface by the organic liquid interface, as well as by the aqueous interface of the emulsion.

In addition to being effective catalysts for cyanations, organo hectorite assemblies also are useful catalysts for a wide variety of other organic chemical conversions. For instance, in the presence of $[(n\text{-}C_8H_{17})_3NMe]^+$–hectorite 1-bromopentane can be converted to the corresponding

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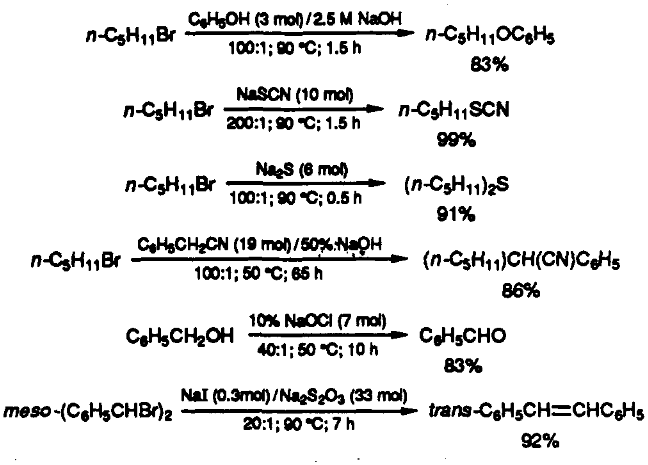
Scheme I



ether, thiocyanate, and sulfide derivatives at the substrate: catalyst molar ratios, temperatures, and reaction times shown in Scheme I. The C-alkylation of a nitrile, oxidation of an alcohol, and dehalogenation of a *vic*-dibromide represent additional facile conversions, as also shown in the scheme.

Finally, we note that organo clays are members of a much larger class of layered materials capable of being intercalated by alkylammonium ions.[19] Onium ion exchange forms of layered phosphates, titanates, vanadates, and niobates, for instances, might also form interfacial assemblies and exhibit useful triphase catalytic properties.

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Formation of Ultrathin Metal Island Particulate Films by the Transfer of Monolayers of Reversed Micelle Entrapped Colloidal Particles to Solid Supports

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Molecular organization of ultrasmall colloidal particles is an intensively active, current area of research.[4-6] The assembly of individual molecules to small clusters, size-quantized particles, and larger crystallites having solid-state properties is inherently interesting and provides an entry to novel materials that have desirable chemical, mechanical, electrical, and electrooptical properties. Molecular beam epitaxy has been used primarily to construct desired structures by atomic, layer-by-layer deposition in ultrahigh vacuum.[6] An alternative "wet" colloid chemical approach was launched in our laboratories some years ago. Surfactant vesicles, bilayer lipid membranes, monolayers, and Langmuir–Blodgett films have been used as templates in the in situ generation of nanosized semiconductor and magnetic particles.[4] These organized assemblies have not only provided a passive size and dimensionality control but, by virtue of electrostatic and hydrophobic interactions, have profoundly influenced the physical and chemical behavior of the given system. We report here that silver particles, in situ formed in the aqueous pools of reversed micelles, can be transferred as a "monolayer" of metal-island particulate films onto solid substrates.

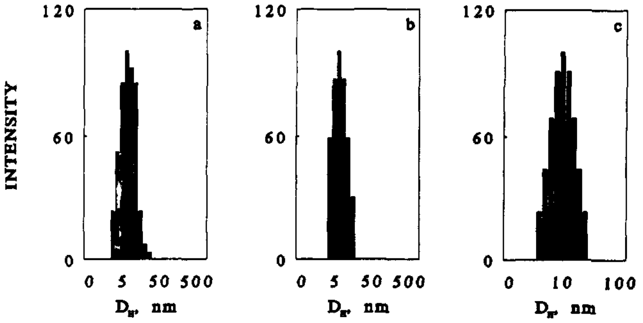

Figure 1. Hydrodynamic diameters, presented in terms of size distributions, or reversed micelles prepared from 1.0×10^{-2} M AOT and 1.0×10^{-2} M H_2O ($w = 20$) in heptane in the absence (a) and in the presence of 7.3×10^{-3} M Ag^+ (b) prior (a and b) and subsequent to exposing sample b to 60 min of repetitive laser pulses (c).

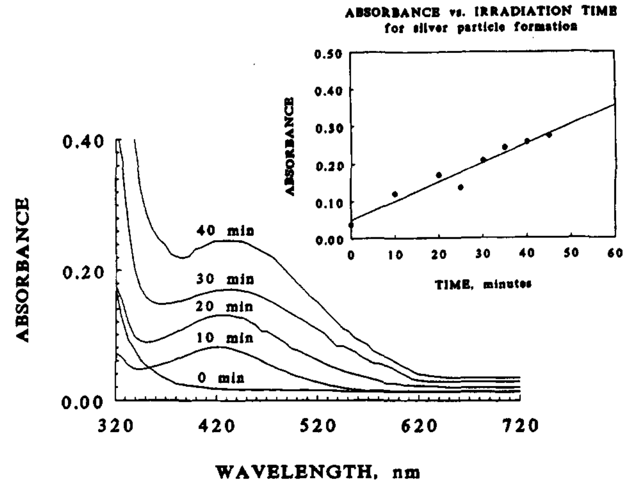

Figure 2. Absorption spectra of reversed micelles prepared from 1.0×10^{-2} M AOT and 1.0×10^{-1} M H_2O ($w = 10$) in heptane in the presence of 7.3×10^{-3} M Ag^+ prior and subsequent to exposure to increasing times of laser pulses. A plot of absorbance at 450 nm vs irradiation is shown in the insert.

Sodium bis(2-ethylhexyl)sulfosuccinate, aerosol-OT or AOT (Aldrich), and calcium alkylarylsulfonate surfactant, 1 (Texaco),[7] was used to prepare reversed-micelle solutions in heptane in the absence and in the presence of appropriate concentrations of aqueous silver nitrates (Matheson, Coleman and Bell Co.). Heptane (Aldrich, HPLC grade) was used as received. Water was purified by using a

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