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Controlled polymerizations with constrained geometries

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This short review focuses on recent advances in controlled polymerization and macromolecular architectonics by means of a variety of organized media with constrained geometries.

Introduction

In nature, macromolecules are essential materials for the diversity of life. Plants synthesize cellulose from sugars to support their body, and of course, proteins, polymers of amino acids, exist universally as primary materials for structuring, molecular recognition, electron and energy transfers, catalysis, and so forth. In biological systems, short- and long-range interactions are operative to allow multi-level ordering of macromolecules, which is essential for biological events. Formation of macromolecules in biological systems occurs also in such constrained, organized media, resulting in rigorous control of primary and even higher-ordered structures. On the other hand, chemical synthesis of macromolecules, which is usually conducted in homogeneous, non-constrained media, simply follows statistics of numerous elementary reaction steps, leading to the formation of macromolecules with poorly controlled architectures. In this respect, utilization of constrained media for artificial macromolecular synthesis is an interesting subject, which possibly allows spatial control of the primary structures of polymers and even their two- and three-dimensional multi-level structuring.

This short review focuses on recent advances in controlled polymerization and macromolecular architectonics by means of a variety of organized media with constrained geometries.

Overview

The present article describes some historical background and recent studies on controlled polymerizations in constrained media such as (1) micelles, (2) lipid bilayers, (3) liquid crystals, (4) organic crystals, (5) inclusion complexes, (6) microporous zeolites, and (7) mesoporous materials (Fig. 1), which are arranged in the order of increasing the rigidity of the media (Fig. 2).[1]

For the polymerization with constrained media, there are principally two approaches. One is to conduct polymerization of ordinary monomers in confined spaces of the media, while the other is to polymerize monomers which themselves are organized or co-organized to form constrained media. Studies on the polymerization in inclusion complexes, microporous zeolites, and mesoporous materials include examples only from the former approach. On the other hand, although both approaches are possible in the polymerization with micelles, lipid bilayers, liquid crystals, and organic crystals, this article focuses mostly on recent examples from the latter approach. The review article also focuses on several attempts to stabilize such organized media by polymerization, in order to fabricate well defined two- and three-dimensional macromolecular objects and hybridized materials.

Polymerization in micelles

Amphiphilic molecules having both hydrophobic long alkyl chains and hydrophilic groups are known to form micelles in aqueous media, where the alkyl chains are aggregated to form the core, while the hydrophilic head groups are exposed to water on the exterior surface to minimize the interfacial energy. In general, micelles are spherically shaped with a diameter of 3–4 nm, while under certain conditions rod-like micelles are formed, which have a cylindrical shape with a diameter of the cross section similar to the above. As for the polymerization of surfactant monomers, free radical polymerization has mostly been studied, since it is tolerant to water. In the polymerization in micelles, the chain growth is often affected by the structure and properties of the micelle. Furthermore, micelles are not static but dynamic. Therefore, a rapid exchange of the surfactant monomers between the micellar phase and the aqueous phase takes place during the polymerization (Fig. 3). The average time taken for surfactant molecules to leave a micelle is in the range 10^{-5}–10^{-9} s, which is much shorter than that for the growing radical to propagate (10^{-2}–10^{-6} s).[2–4] Hence, micelles are considered to be more or less soft media for polymerization.

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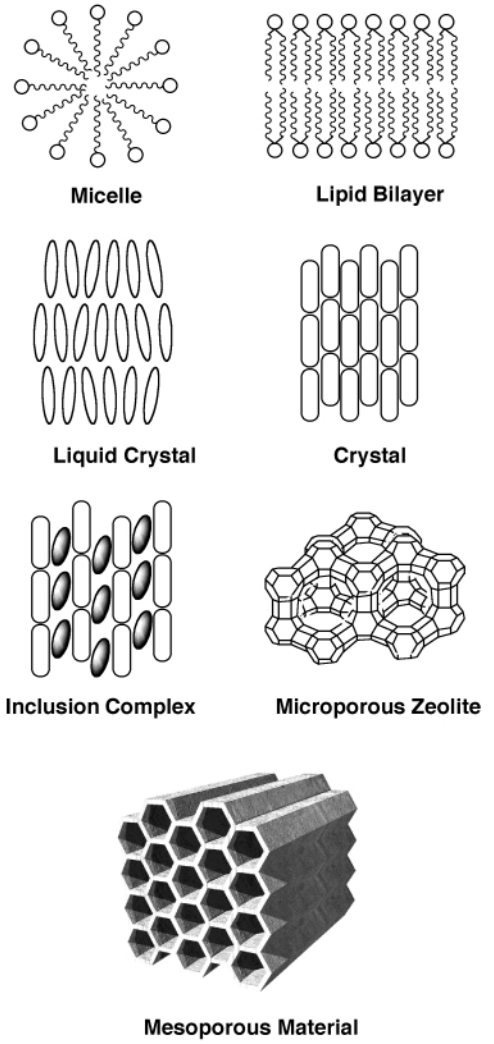


Fig. 1 Schematic representation for constrained media for polymerization.

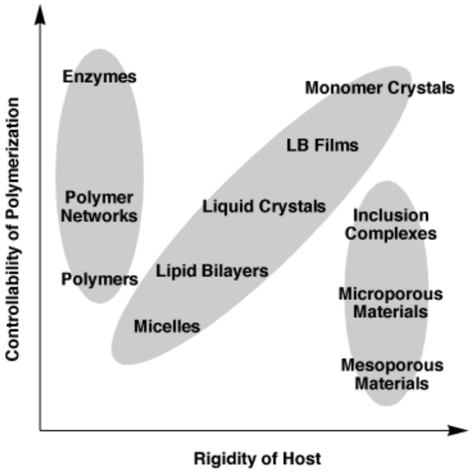


Fig. 2 Rough relationships between host rigidity and controllability of polymerization.

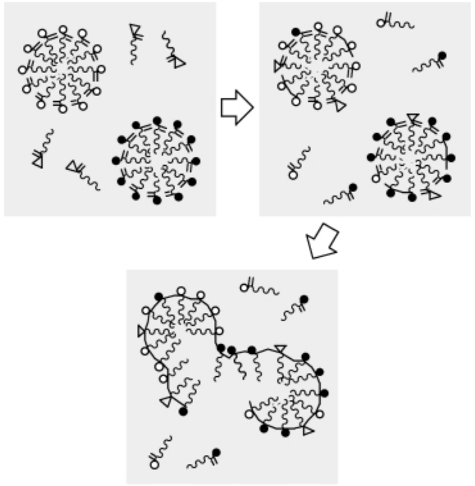
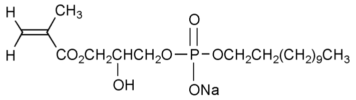


Fig. 3 Dynamical features of polymerization in micelles.

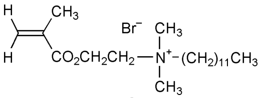
A typical phenomenon in free radical polymerization of surfactant monomers is that the propagation reaction above critical micelle concentration (c.m.c.) can be accelerated by ‘condensation effect of monomer’. Examples include polymerization of anionic,[5] cationic,[6] and nonionic[7] surfactant monomers. In some cases, surfactant monomers in micelles spontaneously undergo radical polymerization without externally added initiators.[8,9] For example, the polymerization of sodium dodecyl 2-hydroxy-3-methacryloyloxypropyl phosphate **1** in water at a concentration above the c.m.c (*ca.* 10^{-3} mol L^{-1}) takes place even at room temperature (35 °C) without initiator, to attain 100% monomer conversion.[8] In contrast, in methanol where **1** does not aggregate to form micelles, no polymerization occurs unless radical initiators are added. The spontaneous polymerization may also be accounted for by ‘condensation effect of monomer’. That is, the methacryloyl group of **1** is condensed at the core of the micelle, where the local monomer concentration must be as high as that in bulk.



$H_2C=C(CH_3)CO_2CH_2CH(OH)CH_2O-P(=O)(ONa)-OCH_2CH_2(CH_2)_9CH_3$

1

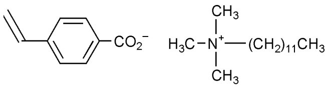
Control of molecular weight of polymer by the size of micelle is a challenging subject. However, owing to the dynamic characteristics of micelles, monomer reactivity, rather than micelle size, is the predominant factor for determining the molecular weight. On the other hand, the synthesis of stereoregular polymers in micelles is also an interesting subject, considering possible orientations of polymerizable groups in micelles. However, successful examples are only very limited.[10,11] For example, Dais and coworkers have reported that the polymerization of dodecyl-2-methacryloyloxyethyldimethylammonium bromide **2** initiated by γ-rays at a monomer concentration above the c.m.c. leads to a polymer consisting exclusively of syndiotactic sequences at 25 °C.[11] In contrast, when a radical initiator such as 2,2′-azobisisobutyronitrile (AIBN) is used in place of γ-rays for initiating the polymerization, the tacticity of the resulting polymer at 50 °C is not directed but almost comparable to that of a polymer formed under homogeneous conditions.[10]



$H_2C=C(CH_3)CO_2CH_2CH_2-N^+(CH_3)_2-(CH_2)_{11}CH_3\ Br^-$

2

Polymerized micelles with an enhanced physical stability can be formed by free radical polymerization of surfactant monomers but only under very restrictive conditions owing to dynamic characteristics of micelles. For example, a rod-like micelle consisting of cetyltrimethylammonium 4-vinylbenzoate **3** is stabilized by radical polymerization of the vinylic group of the counter anion.[12] The resulting polymer micelle, as observed by small-angle neutron scattering, is likely to retain its original rod-like architecture, which shows an enhanced thermal stability and no longer dissociates upon dilution.



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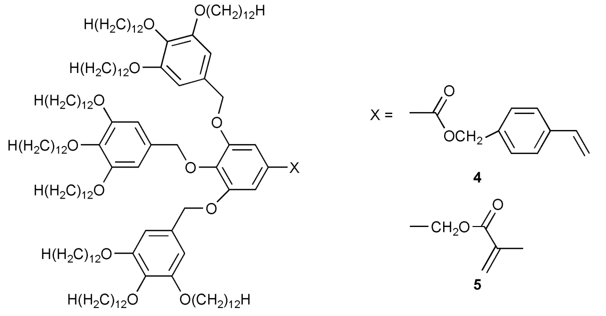
Dendrimers can also provide constrained media for polymerization. Percec *et al.* have recently reported an interesting phenomenon in free radical polymerization of self-assembled dendritic monomers. Dendritic monomers **4** and **5** are self-organized at a concentration above 0.20 mol L^{-1} to form spherical micellar aggregates in benzene.[13] In the interior of the aggregate, the polymerizable groups are condensed, so that the polymerization by a free radical initiator is considerably accelerated. As the polymerization proceeds, the interior of the aggregate becomes more constrained and thus protected from invasion of further initiator molecules. Consequently, the polymerization takes place in a 'living' fashion, to give a polymer with a narrow molecular weight distribution (MWD). Of further interest, the shape of the resulting macromolecule depends on the degree of polymerization (D_p) (Fig. 4). When D_p is lower than 20, the polymer remains spherical. On the other hand, when D_p exceeds 20, the polymer becomes cylindrical, as directly observed by atomic force microscopy (AFM). As an extension of the present study, the living ring-opening metathesis polymerization of dendritic monomers having at the focal point a 7-oxanorbornene unit **6** has been reported.[14] Interestingly, the rate constant of propagation is increased discontinuously at a certain monomer conversion where D_p exceeds a critical value for the shape transition from a densely packed, spherical architecture to a more accessible, cylindrical one (Fig. 5).



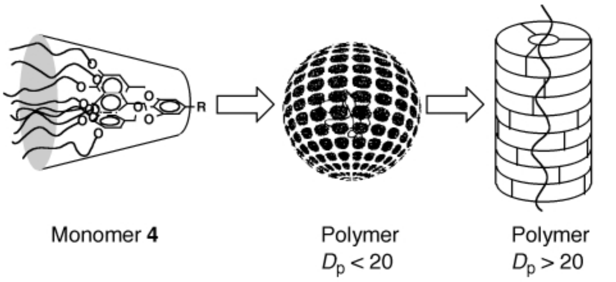
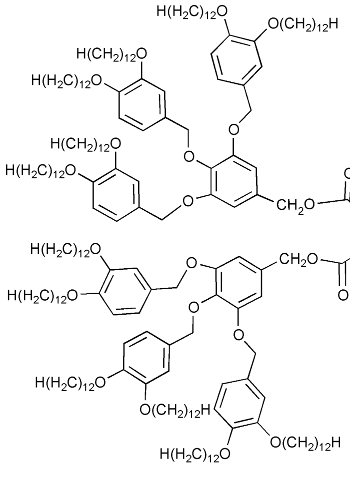


Fig. 4 Illustration for shape transition in free radical polymerization of self-organized dendritic monomers **4** and **5**.

Polymerization in lipid bilayers

Certain amphiphilic molecules such as lipids are known to form vesicles, *i.e.* liposome-like bilayer assemblies, which have been actively studied as synthetic analogues of biological membranes. In vesicles, the hydrophobic alkyl chains of lipids form two-dimensional (2-D) aggregates, while the hydrophilic head groups form ionic surfaces to contact water. Vesicles are larger than micelles and have a much smaller surface curvature. Although a lateral diffusion of lipid molecules within a layer can occur, exchange of the lipid molecules among vesicles is slow. At a given temperature (T_m), vesicles show a main phase transition, which is attributed to a conformational change of the alkyl chains. At temperatures below T_m, the lipid molecules are in a solid-like state with a low mobility, where the alkyl chains adopt a *trans* conformation. On the other hand, at temperatures above T_m, they are in a liquid crystalline state with greater diffusibility, where the alkyl chains adopt a *gauche* conformation.[15] Since the pioneering works by Ringsdorf *et al.* on the formation of polymerized vesicles,[16] extensive studies have been made on free radical and photo-initiated polymerizations of synthetic bilayers.[17] In contrast to micelles, vesicles are stabilized easily through polymerization to give macromolecular containers which can be used for a variety of applications such as drug delivery.



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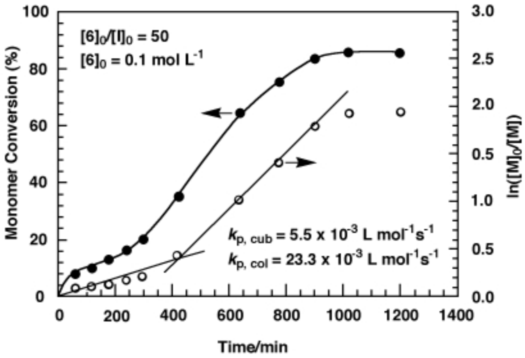
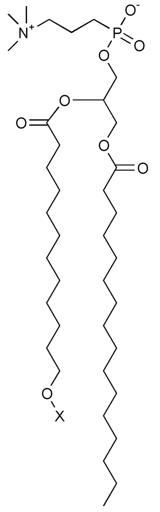


Fig. 5 Self-acceleration characteristics in ring-opening metathesis polymerization of a dendritic monomer **6**; $k_{p,\,cub}$, $k_{p,\,col}$: rate constants of propagation in cubic and columnar phases, respectively.

Free radical polymerization of lipid monomers in bilayer membranes shows significantly different kinetics from those in the bulk phase.[18–20] For example, in the polymerization of a vesicle consisting of a phosphatidylcholine derivative having an acryloyl (**7**), methacryloyl (**8**), or sorbyl group (**9**) at the hydrophobic chain end, the degree of polymerization (D_p) is proportional to $[M]^2$ and $[I]^{-1}$ at a high monomer conversion ([M] and [I] are concentrations of monomer and initiator, respectively). In contrast, in bulk under otherwise identical conditions to the above, D_p is proportional to [M] and $[I]^{-0.5}$. These contrasting trends indicate that the polymerization of the lipid monomers in the bilayer state is terminated mostly by recombination of the growing polymer radical with a fragment radical of the initiator, rather than self-recombination of the



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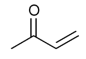

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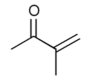

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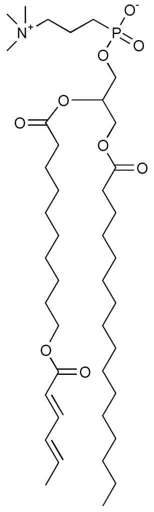

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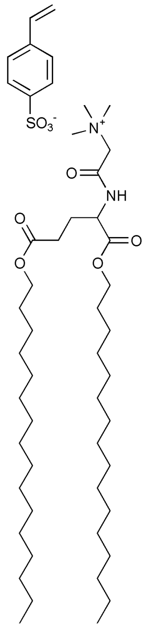

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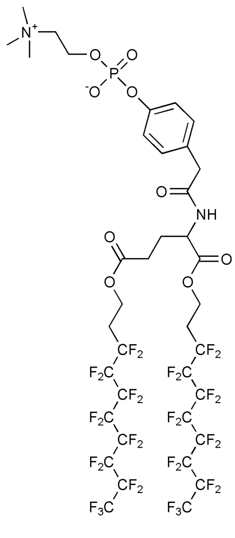


11

growing polymer radicals.[21] This is likely due to a reduced mobility of long polymer chains in bilayer media.

Phase transitions of bilayer membranes also affect polymerization kinetics. For example, in free radical polymerization of lipid monomer **9**, the activation free energy E_a and frequency factor A, obtained in a temperature range below the phase transition temperature T_m, are 10 kcal mol^{-1} and 10^7, respectively (Fig. 6).[22] On the other hand, at temperatures higher than T_m, they are 24 kcal mol^{-1} and 10^{16}, respectively. Such discontinuous changes in kinetic parameters upon phase transition indicate a large effect of the lateral diffusibility of **9** on the polymerization kinetics.

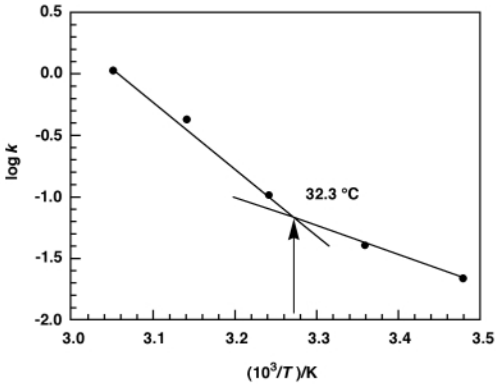


Fig. 6 Effect of phase transition on propagation rate constant in free radical polymerization in a bilayer membrane of a lipid monomer **9**.

Control of molecular weight of the polymer in bilayer membranes is also an interesting subject, and numerous attempts have been made by, *e.g.* changing monomer/initiator mole ratio, phase separation, and addition of chain transfer agents.[19,23] For example, a mixture of a hydrocarbon lipid monomer **10** and a non-polymerizable fluorocarbon lipid **11** forms a phase-separated bilayer membrane (Fig. 7), since fluorocarbons are poorly miscible with hydrocarbons.[23] In this phase-separated system, the molecular weight of the resulting polymer becomes lower as the content of **10** in the membrane (≈ size of the monomer domain) is decreased.

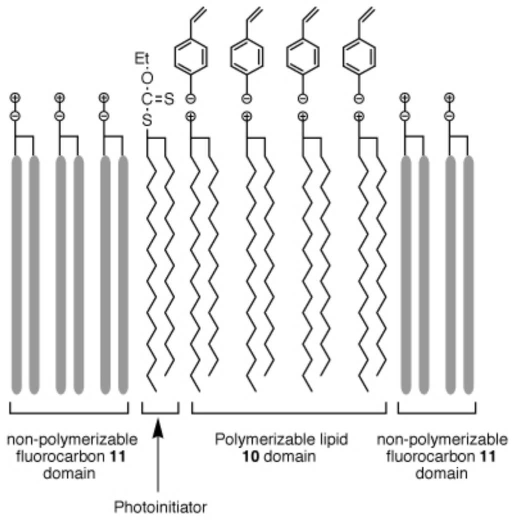
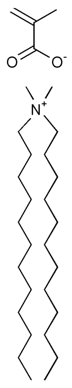


Fig. 7 Illustration for photoinduced polymerization in a phase-separated bilayer membrane of a mixture of a lipid monomer **10** and a non-polymerizable fluorocarbon lipid **11**.

As bilayer membranes are not stiff enough to fix the orientation of polymerizable groups for steric control, only limited examples of stereospecific polymerization in bilayer media have been reported. An old but interesting example is the polymerization of a vesicle consisting of dioctadecyldimethylammonium methacrylate **12**.[24] Upon irradiation of the vesicle, the methacrylate anion on the surface of the vesicle is polymerized to give a highly syndiotactic poly(methacrylate) anion. In contrast, under homogeneous conditions in ethanol, no polymerization occurs under otherwise identical conditions.

Vesicles can be used as templates for the synthesis of topologically unique polymers.[16] Recent examples include selective polymerization of a heterobifunctional lipid monomer **13** containing diene and dienoyl groups at the hydrophobic and hydrophilic termini of its alkyl chain, respectively.[25] O'Brien and coworkers have reported that photoirradiation of vesicles of **13** results in the polymerization of the dienoyl group exclusively, while radical initiation with AIBN gives rise to the selective polymerization of the diene group. Of interest, a simultaneous or a sequential polymerization of both the dienoyl and diene groups of **13** in the vesicular state results in the formation of a novel ladder polymer **14** and not a 2-D cross-



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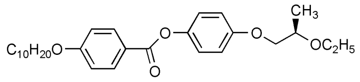

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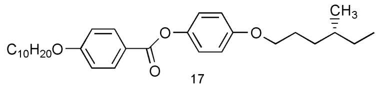

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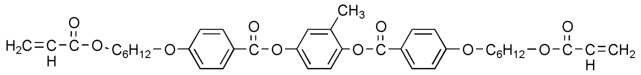

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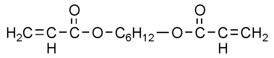

$H_2C{=}\underset{H}{C}-\overset{O}{\overset{\|}{C}}-O-C_6H_{12}-O-\overset{O}{\overset{\|}{C}}-\underset{H}{C}{=}CH_2$

19

linked network **15** (Fig. 8). Addition of a surfactant molecule to polymer **14** in water results in destruction of its vesicular assembly, as observed by light scattering, whereas polymer **15** with a cross-linked architecture is robust under similar conditions. These contrasting trends suggest that polymer **14** is not cross-linked but a ladder.

Polymerization in liquid crystals

Liquid crystals have been utilized for optical materials such as LCDs. Depending on the manner of molecular orientation, several different LC phases such as nematic, smectic, and cholesteric phases are formed. LC media are more constrained than micellar and even bilayer media, and therefore attractive for control of polymerization.

Molecular orientation of monomers considerably affects the polymerization kinetics in LC media. A mixture of **16** and **17** forms a smectic C* (SC*) LC phase at room temperature, which becomes isotropic when heated to 70 °C. Bowman and coworkers have found that free radical polymerization of mesogenic monomer **18** in the SC* LC phase at 25 °C, as observed by differential scanning calorimetry (DSC), proceeds with much higher propagation and termination rates than in the isotropic phase at 70 °C.[26] In contrast, when non-mesogenic monomer **19** is polymerized in the SC* phase (35 °C), the propagation rate is not much different from that under isotropic conditions, but the termination is considerably slower. According to polarized IR spectroscopy, mesogenic and non-mesogenic monomers **18** and **19** are oriented normal and parallel to the smectic layer of the LC phase, respectively. Since addition of **18** to the LC phase does not affect the *d* value, mesogenic **18** most likely exists in the smectic layer (Fig. 9a). In contrast, non-mesogenic monomer **19** is possibly intercalated between the smectic layers, as the *d*-value of the LC phase becomes larger upon addition of **19** (Fig. 9b). This work provides a clear demonstration that the polymerization kinetics depend considerably upon spatial segregation and orientation of monomers in LC media.

In the polymerization in LC media, structural characteristics of the LC phase may give rise to unique organized structures of produced polymers. Recently, Akagi and Shirakawa *et al.* have reported an interesting observation that the polymerization of acetylene in a chiral LC phase leads to helical fibers of polyacetylene.[27] An optically active binaphthol derivative **20** having mesogenic units combined with a 1 : 1 mixture of **21** and **22** forms a chiral nematic LC phase, where the polymerization of acetylene with a homogeneous Ziegler–Natta catalyst ($Ti(OBu^n)_4/Et_3Al$) proceeds to give single-handed helical fibers of polyacetylene, as observed by scanning electron microscopy (SEM). The helical sense of the fibers can be controlled by the absolute configuration of the LC solvent. For example, in the nematic phase of the (*R*)-binaphthol derivative **20**, helical fibers with an anticlockwise sense result (Fig. 10). Circular dichroism spectroscopy of the fibers also shows a clear Cotton effect in the region of a π–π* transition of the conjugated backbone. In this case, the twisted molecular packing of **20** in the chiral nematic

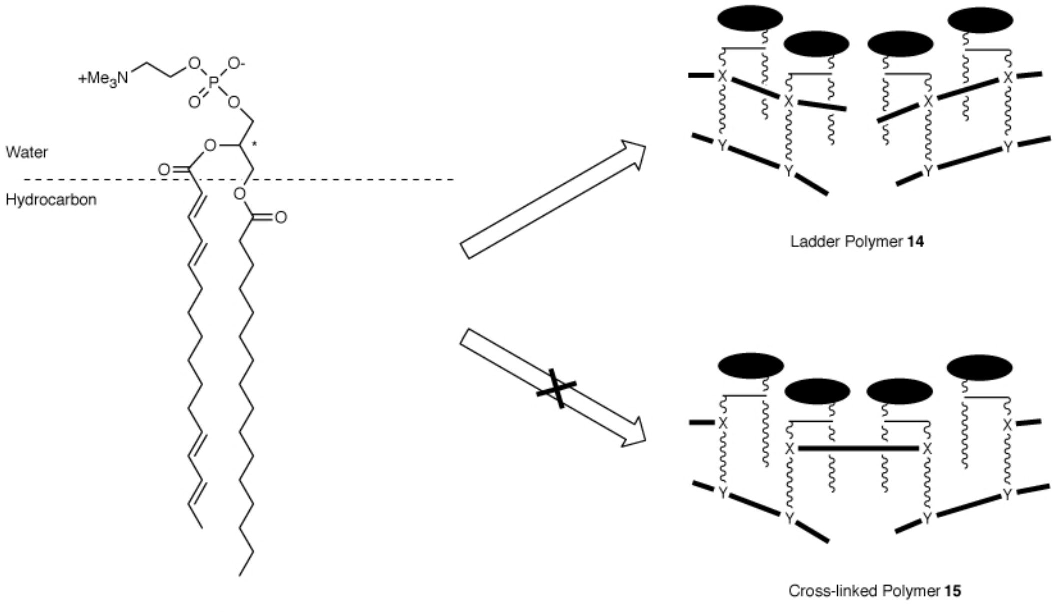

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Fig. 8 Illustration for different modes of polymerization in a bilayer membrane of a lipid monomer **13**.

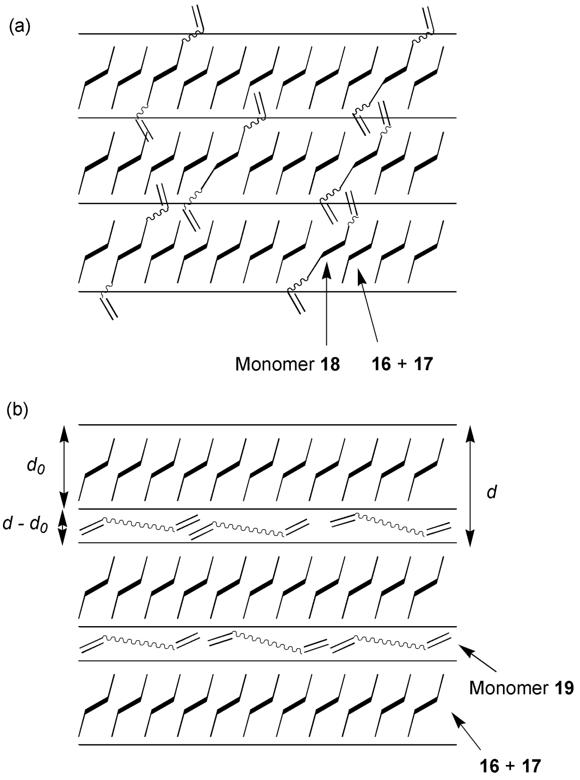
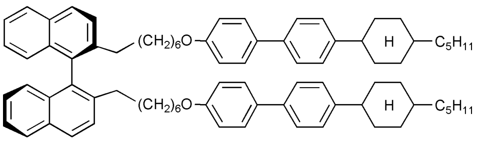


Fig. 9 Proposed models for photoinduced polymerizations of mesogenic and non-mesogenic monomers (**18**, **19**) in a smectic C* liquid crystal.



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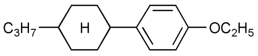

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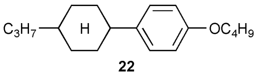

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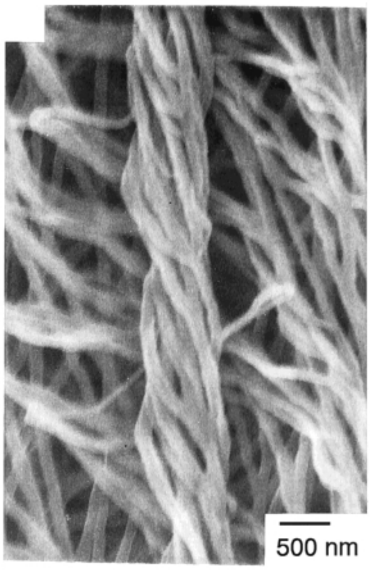


Fig. 10 A SEM micrograph of helical polyacetylene fibers formed with a homogeneous Ziegler–Natta catalyst in a chiral nematic phase of a mesogenic (*R*)-binaphthol derivative **20**. Reprinted in part with permission from: *Science*, 1998, **282**, 1683 (Copyright © 1998, the American Association for the Advancement of Science).

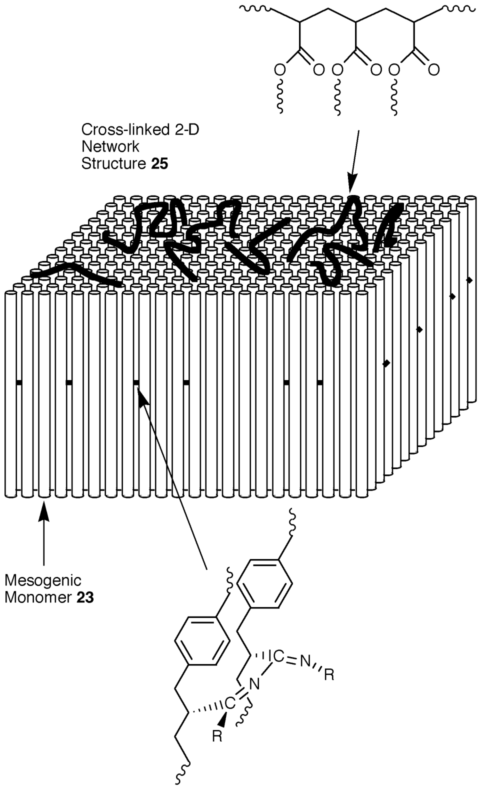
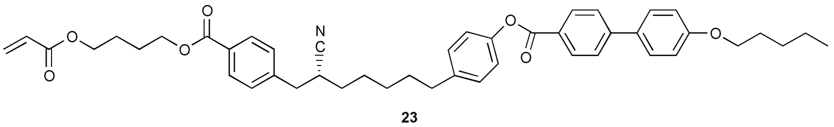


Fig. 11 Illustration for thermal-induced polymerization in a smectic liquid crystalline phase of a mesogenic monomer **23**.

phase is likely to serve as a template for the formation of helical polyacetylene fibers.

Much attention has also been paid to the polymerization of LC monomers for obtaining polymeric materials with predictable structures from their LC phases. Stupp *et al.* have reported the synthesis of a conceptually new two-dimensional (2-D) polymer by the polymerization of a mesogenic monomer in a smectic LC phase (Fig. 11).[28] Monomer **23** has an acrylic group at a terminus, a nitrile group in the middle, and a mesogenic group at the other terminus. **23** is organized to form a smectic LC phase **24** (non-polymerized form of **25**) by a π–π interaction among the mesogenic groups and a homochiral interaction among the chiral nitrile groups. The acrylic and nitrile groups in the LC state are polymerized by heating, to give a cross-linked 2-D network structure **25**, which still shows certain characteristics of the original LC phase. Although the polymer is soluble in chloroform, it most likely retains a sheet-like structure originating from the smectic phase even in solution. Analysis by gel permeation chromatography (GPC) indicates that the polymer has an ultrahigh molecular weight (17 000 000) with a broad molecular weight distribution, suggesting that the polymer is a nanometer-sized 2-D object. According to transmission electron microscopy (TEM), this polymer can be spread over a glycerin surface upon casting from its dilute



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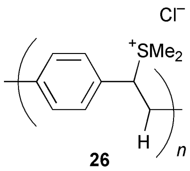
chloroform solution, to give a single-layered polymeric film with a thickness of < 100 Å. Along the line of this study, a triblock molecule having a relatively large coiled head group with crosslinkable oligobutadiene units anchored by a rigid mesogenic tail has been synthesized. Owing to the relatively large head group, this rod-coil molecule self-assembles to form a 'mushroom-shaped' cluster of limited size rather than an infinite 2-D sheet as in the case of **23**. Annealing of this molecule in a LC phase at 250 °C resulted in crosslinking of the oligobutadiene domains to form a soluble polymeric nanoscale object with a molecular weight of *ca.* 70 000 ($M_w/M_n = 1.11$). Although extended annealing promotes the crosslinking and enhances the yield, no substantial increase in molecular weight results. Therefore, the crosslinking occurs within individual clusters to fix the mushroom shape.[29] This is an interesting 2-D approach to the template synthesis of nanoscale polymeric objects.

Not only thermotropic LCs but also lyotropic LCs can be stabilized by polymerization. Gin and co-workers have reported an interesting example of the stabilization of a lyotropic LC phase by polymerization.[30] When a water-soluble polymeric precursor of poly(*p*-phenylenevinylene) (PPV) **26** is mixed with amphiphilic acrylate monomer **27** in aqueous media, an inverse hexagonal lyotropic LC phase is formed, in which **26** is likely to be threaded into the hexagonal column and oriented parallel to its *c*-axis (Fig. 12). Subsequently, the acrylate group of **27** is polymerized by photo-irradiation, and the resulting mixture is heated to promote the removal of dimethyl sulfide and HCl to convert **26** to fluorescing PPV. Interestingly, the fluorescence of PPV from the resulting hybrid material is much stronger than that of bulk PPV, suggesting that the hybridized PPV chains are spatially isolated from one another and protected from self-quenching of the excited state. The present self-assembling/polymerization approach is unique, and can be applied not only to the design of anisotropic optical materials but also to the fabrication of new silica/polymer hybrids[31] and polymer-supported transition metal catalysts.[32]



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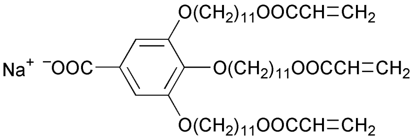

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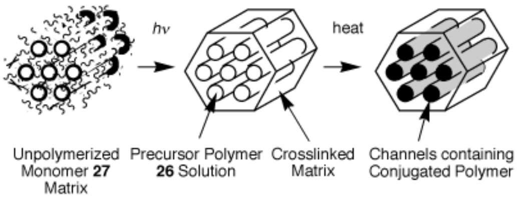
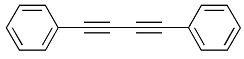


Fig. 12 Illustration for photoinduced polymerization of an amphiphilic acrylate monomer **27** in a lyotropic liquid crystalline phase and subsequent thermal transformation of the precursor polymer **26** into poly(phenylenevinylene).

Polymerization in organic crystals

In the crystalline state, the arrangement and orientation of molecules are strictly determined by crystal packing. Topochemical polymerization, in which the polymerization of a crystallized monomer occurs without changing the symmetry of the crystal lattice, has been well known since the 1960s. Representative examples include topochemical polymerization of diacetylenic monomers in the crystalline state, which occurs upon exposure to UV light or γ-rays.[33] [2 + 2] Photopolymerization of diolefinic monomers in the crystalline state has also been studied extensively.[34] In general, topochemical polymerization is highly sensitive to the crystal structure of monomers. If the crystal packing of monomers is not suited for the active growing end to propagate, no polymerization occurs. For example, for diacetylenic monomers to polymerize topochemically, monomer molecules in the crystalline state are required to adopt a tilted molecular stacking with a distance between the diacetylene centers of *ca.* 4.7–5.2 Å and an angle between the molecular stacking axes of *ca.* 45°. On the other hand, for topochemical polymerization of diolefinic monomers, a center-to-center distance of 3.5–4.2 Å between the polymerizable units is required.

Although crystal engineering of organic molecules has been greatly advanced in recent years, 'crystal design' for topochemical polymerization has not been established yet. A general approach to the 'design' of monomer crystals for topochemical polymerization makes use of some directional forces such as hydrogen-bonding and π–π interactions for suitable alignment of monomer molecules in the crystalline state. For example, Grubbs and coworkers have attempted to prepare polymerizable crystals of diacetylene[35] and diolefin[36] derivatives by using π-stacking interactions. To achieve a suitable orientation of the polymerizable groups, monomers having phenyl and perfluorophenyl groups in proximity to the polymerizable units are co-crystallized. X-Ray crystallography of the co-crystal of **28** and **29** shows a face-to-face stacking of the monomers, where the distance between the polymerizable units is short enough for the topochemical polymerization to occur (Fig. 13). In fact, the co-crystals undergo topochemical polymerization upon irradiation with UV light, whereas no polymerization occurs when



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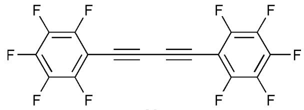

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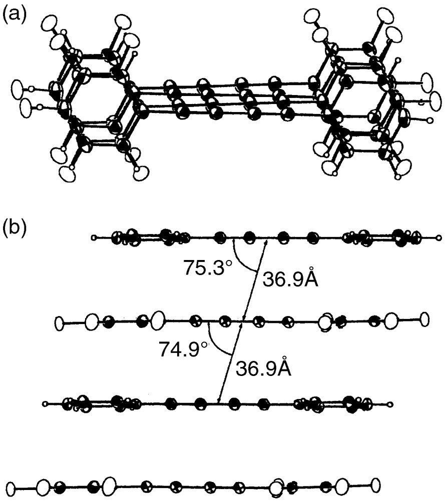


Fig. 13 Crystal packing views of a co-crystal of phenyl- and perfluorophenyl-substituted diacetylenic monomers (**28**, **29**). Reprinted in part with permission from: *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 248 (© 1997, WILEY-VCH Verlag GmbH).

unimolecular crystals of **28** and **29** are irradiated under the same conditions.

Stereochemical aspects of topochemical polymerization are also interesting. Single crystals of diethyl (*Z*,*Z*)-hexa-2,4-diene-1,6-dioate **30** have been reported to undergo photoinduced polymerization without change of crystal shape.[37–40] In contrast, methyl, butyl and isopropyl esters of (*Z*,*Z*)-hexa-2,4-diene-1,6-dioic acid in the crystalline state are not polymerized under the same conditions. Interestingly, the topochemical polymerization of **30** is highly stereospecific. When **30** is polymerized by a radical initiator in bulk or solution, a polymer consisting of a mixture of *trans*-1,4- (four possible stereo sequences), *cis*-1,4-, and 1,2-sequences is formed (Fig. 14). On the other hand, in the crystalline state, an ultrahigh molecular weight polymer consisting exclusively of a *trans*-1,4-*meso*-diisotactic sequence is formed. This perfect steric regulation demonstrates a large effect of crystal packing on the stereochemical course of the polymerization. As observed by X-ray crystallography, the polymer chains are completely oriented along the longer axis of the monomer crystal. Thus, if no structural defect exists in the monomer crystal, the molecular weight of the polymer may be controlled by the length of the longer crystal axis.[41] In relation to this study, Nakanishi and coworkers have reported a novel crystallization method for controlling the size of diacetylene crystals for topochemical polymerization for application to non-linear optics.[42,43]

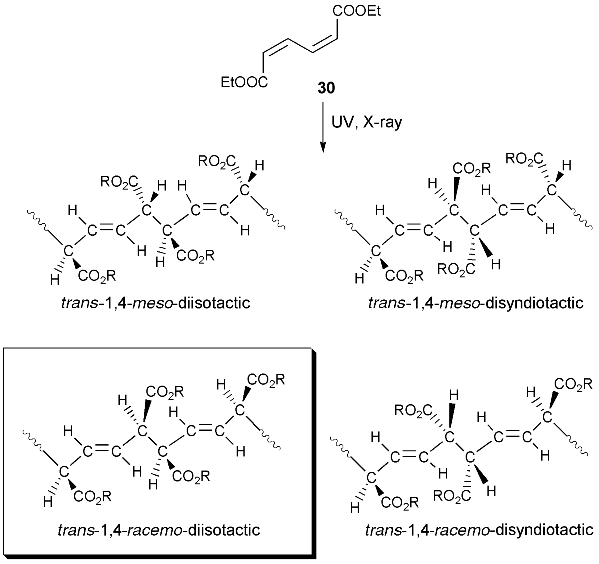
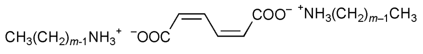


Fig. 14 Schematic representation for stereospecific polymerization in a crystal of diethyl (*Z*,*Z*)-hexa-2,4-dienedioate **30** by UV light.

More recently, topochemical polymerization of long-chain alkylammonium (*Z*,*Z*)-hexa-2,4-diene-1,6-dioates **31** has been reported to produce layered polymer crystals.[44,45] During the polymerization, the alkylammonium group of **31** is intercalated between the crystalline layers of poly(muconic acid) (Fig. 15). The interlayer spacing *d* is increased linearly with the carbon number of the alkylamino group. The intercalated alkylammonium group can be removed from the polymer crystal by stirring in acidified methanol at room temperature, to leave a layered crystal of poly(muconic acid). Interestingly, when crystals thus obtained are exposed to alkylamine, re-intercalation of the amine into the crystalline layers occurs. Thus, this material can be considered as an organic clay, and may be useful for molecular recognition, separation and catalysis.



m = 10-18

31

Although successful examples include only a narrow range of monomers, topochemical polymerization in the crystalline state has a high potential for controlling the locus of polymerization and polymer architectures.

Polymerization in inclusion complexes

It is well known that host molecules such as urea, thiourea, and perhydrotriphenylene are crystallized, in the presence of guest molecules, to form inclusion complexes. In many cases, inclusion complexes consist of one-dimensional columnar channels of crystalline host molecules, which are filled with guest molecules. If the included guest molecules are loosely packed, they can eventually be exchanged with other molecules of similar structures. When the guest molecules have polymer-

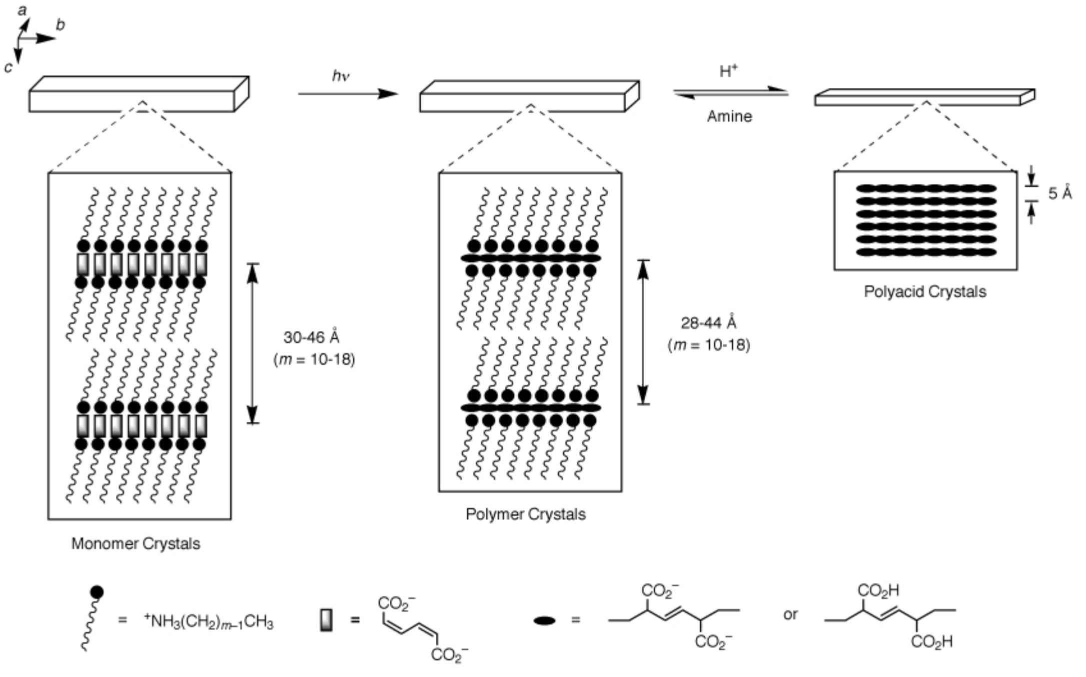


Fig. 15 Proposed models for topochemical polymerization in a crystal of a long-chain alkylammonium (*Z*,*Z*)-hexa-2,4-dienedioate **31** and subsequent transformation into a layered crystal of poly(muconic acid).

izable groups, one can polymerize these monomers in confined spaces of the crystalline channels. This is denoted 'inclusion polymerization'.

Historically, extensive studies on inclusion polymerization have been made in the 1960s–1980s. Farina and coworkers have reported the inclusion polymerization of various diene and triene monomers in the crystalline channels of perhydrotriphenylene **32** with an average diameter of *ca.* 5.5 Å.[46] For example, when an inclusion compound of **32** with *trans*-penta-1,3-diene as the guest is irradiated with γ-rays, a highly isotactic polymer consisting exclusively of 1,4-*trans* sequences is formed, indicating a strong spatial demand of the crystalline channel for the chain growth. Asymmetric synthesis of poly(*trans*-penta-1,3-diene) is also possible by the polymerization of the same monomer in the crystalline channels of optically resolved perhydrotriphenylene. Takemoto and Miyata *et al.* have made systematic studies on inclusion polymerization with crystalline channels of cholic acid derivatives by taking advantage of their high ability to include a variety of monomers (Table 1).[47] As the result, the size of the channel has been found to affect kinetics and specificity of the polymerization. For example, *trans*-2,4-dimethylpenta-1,3-diene can be polymerized in the crystalline channels of apocholic acid **33** at ambient temperatures, but no polymerization occurs even at 100 °C in slightly smaller crystalline channels (4 × 6 Å) of deoxycholic acid **34**. According to electron paramagnetic resonance (EPR) spectroscopy, the propagating radicals are included tightly in the channel of **34**, while loosely held by the channel of **33**. Furthermore, when *trans*-penta-1,3-diene is polymerized within the channels of **34**, a polymer with a 99% 1,4-*trans* structure is formed, whereas the selectivity is lower by 10% when the slightly larger channel of **33** is utilized. Cyclophosphazene **35** also forms inclusion compounds with a channel diameter of 5 Å, which have been extensively studied by Allcock *et al.* for the polymerization of various vinyl monomers[48] and dienes.[49] For example, a γ-ray induced polymerization of methacrylonitrile included in the channel of **35** gives a highly isotactic polymer soluble in THF. This is in contrast with a γ-ray induced bulk polymerization of methacrylonitrile, which affords an insoluble, cross-linked polymeric mass.[48]

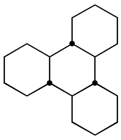

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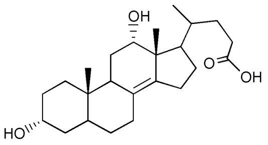
Table 1 Space size effects on the radical polymerization in inclusion complexes

Cavity size of host	Motion of propagating radicals	Polymerization rate	Selectivity of reaction
Large ↕ Small	Unrestricted ↕ Restricted	Fast ↕ Slow	Low ↕ High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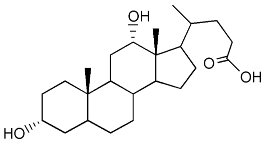
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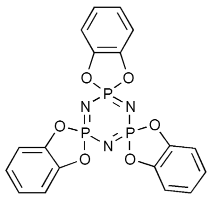
Recently, α,ω-amino acids and α-cyclodextrin **36** have been found to form inclusion complexes, where the cyclodextrin acts as the host for the amino acids to form crystalline channels.[50] Upon heating, polycondensation of the included amino acids takes place to give polyamides in the solid state (Fig. 16).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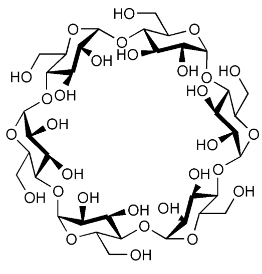
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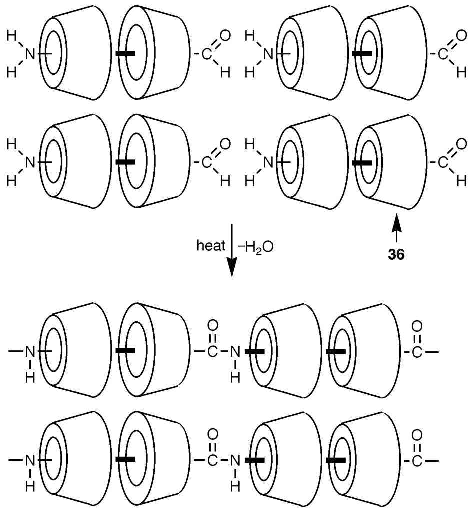

Fig. 16 A proposed scheme for solid state polycondensation of α,ω-amino acid in the presence of α-cyclodextrin **36** to form a polyrotaxane.

Interestingly, the polymerization mixtures are water-soluble, although the polyamides alone are insoluble in water owing to strong intermolecular hydrogen bonding interactions. This observation indicates a high coverage of the polyamide chains by α-cyclodextrin, *i.e.* formation of a polyrotaxane.

Polymerization in microporous zeolites

Microporous zeolites are porous inorganic crystalline materials with a pore diameter of 3–10 Å and possess ion exchangeable sites on the internal surface. Similarly to inclusion complexes, microporous materials can provide confined spaces for controlled polymerization. Historically, radical polymerization of polar vinyl monomers has most extensively been studied with microporous zeolites, by focusing attention on (1) possible elongation effects on the lifetime of growing radicals[51] and (2) possible steric effects on the chain growth step.[52]

Recently, microporous zeolites have been used as catalyst supports for the polymerization of olefins, in which, however, spatial effects of the microporous cavities are not very clear. For example, in the polymerization of ethylene with supported zirconocenes by microporous zeolites, coupled with methylalumoxane (MAO) as cocatalyst, the activity is not related to the internal surface area of the zeolite, but the external surface area and the content of aluminium in the silicate framework appear to be more important.[53]

In view of fabrication of organized hybrid materials, polymerization in microporous zeolites is attractive but somewhat limited, as their pores are too narrow to allow guest molecules to be packed continuously. However, synthesis of nanowires of conducting polymers such as poly(methylacetylenes),[54] polypyrroles[55] and polyanilines[56] has been reported. For example, when a pyrrole vapor is diffused into Cu^{II}-doped zeolite channels, the polymerization occurs with a color change, to give a polypyrrole/zeolite hybridized material (Fig. 17), which however does not show any significant electronic conductivity.

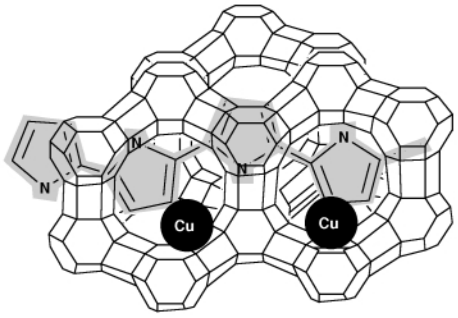

Fig. 17 A proposed model for Cu^{II}-catalyzed oxidative polymerization of pyrrole in zeolite-Y to form a conducting hybrid material.

In relation to microporous zeolites, inorganic materials with layered architectures have been synthesized, which are able to change the interlayer distance upon intercalation of guest molecules. Polymerization with such layered inorganic materials as the reaction media has also been investigated,[57] mainly for the synthesis of functional polymer/inorganic hybridized materials. For example, oxidation polymerization of aniline[58] and pyrrole derivatives[59] within the interlayer spaces gives electroactive composite materials (Fig. 18a). From a more practical point of view, certain clays with layered architectures have also been utilized for the ring-opening polymerization of heterocyclic monomers such as lactams,[60] lactones[61] and cyclic carbonates,[62] and coordination polymerization of olefins,[63] where the monomers intercalated between the 2-D inorganic sheets are polymerized to give nanocomposite materials. Because of a uniform dispersion of the clay 2-D sheets at the molecular level in polymer matrices, the hybrid materials exhibit excellent mechanical properties and unique gas barrier characteristics (Fig. 18b).

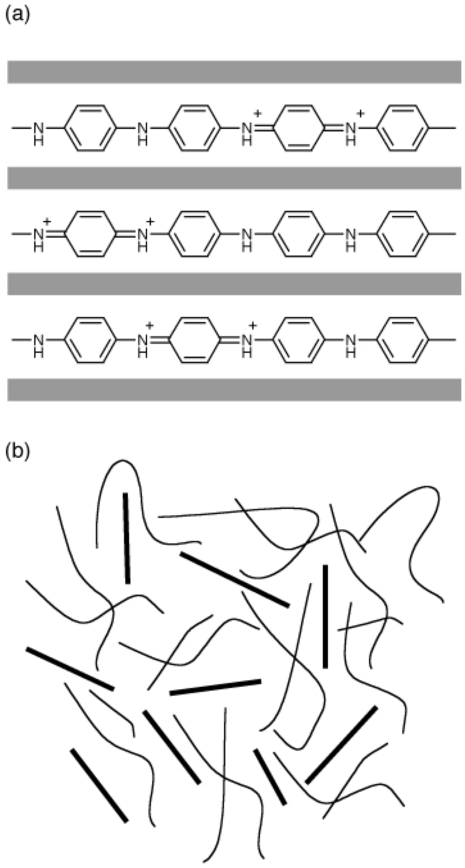

Fig. 18 Proposed structures of (a) an electroactive composite material of polyaniline with a layered inorganic material and (b) a composite material containing uniformly dispersed clay 2-D sheets in a polymer matrix.

Polymerization in mesoporous materials

Since the first report on mesoporous silicate MCM-41 in 1992, a variety of mesoporous silicate materials have been developed.[64] These inorganic materials are prepared by using rod-like micelles as templates, and have an ordered hexagonal or cubic array of uniformly sized mesoscopic channels with a pore diameter variable from 15 to 100 Å. Mesoporous materials have an advantage over microporous zeolites for the inclusion of large molecules. A comprehensive review of the inclusion chemistry with mesoporous materials has been reported.[65] Although mesoscopic pores are large enough for the inclusion of ordinary polymers, the included polymer chains may retain their freedom of conformational change. Thus, mesoporous materials are more attractive than microporous materials not only in view of the control of polymerization locus but also for fabrication of polymeric materials.

Recently, several studies on macromolecular synthesis with mesoporous materials have been reported. For example, Aida and coworkers have utilized MCM-41 for the radical polymerization of methyl methacrylate (MMA) with benzoyl peroxide as initiator, and obtained a polymer (PMMA) with a much higher molecular weight than that formed in solution under otherwise identical conditions.[66] Electron paramagnetic resonance study (EPR) has shown the formation of long-lived propagating polymer radicals within the mesoscopic channels, where *ca.* 25% of the initial intensity of the EPR signal remains even after a month (Fig. 19). Furthermore, molecular weight of the polymer can be controlled over a wide range $M_n = (1.3–3.0) \times 10^5$ ($M_w/M_n = 2.5$) by changing initial molar ratio of MMA to BPO (Fig. 20). On the other hand, the tacticity of the polymer is not particular but almost identical with that of PMMAs obtained by a free radical polymerization in solution.[67] Thus, the mesoscopic pores of MCM-41 are not small enough to affect the stereochemical course of the chain growth. Bein and coworkers have also investigated free radical polymerization of MMA with MCM-41, and reported that PMMA formed within the mesoscopic channels shows no glass transition probably because of a strong interaction between the polymer chain and the internal surface of the mesopore.[68]

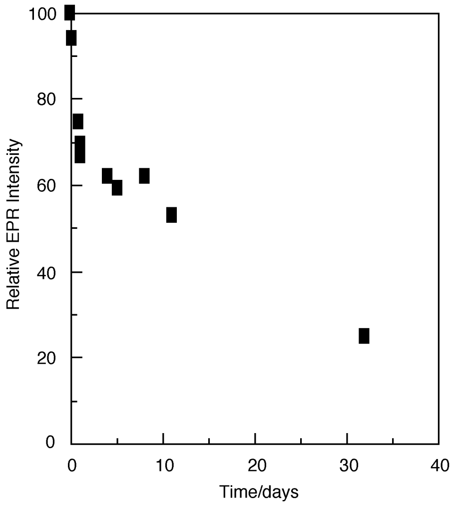

Fig. 19 An electron paramagnetic resonance (EPR) trace of free radical polymerization of methyl methacrylate (MMA) by 2,2′-azobisisobutyronitrile (AIBN) in mesoscopic channels of MCM-41.

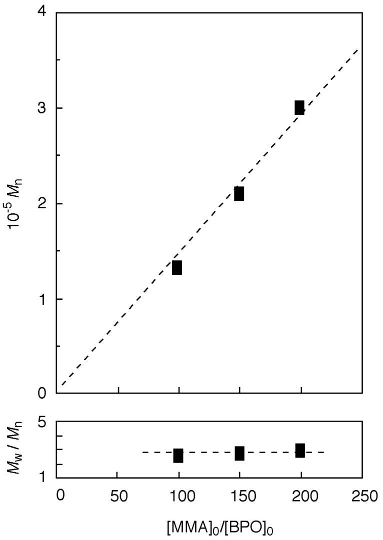

Fig. 20 Molecular weight control in free radical polymerization of methyl methacrylate (MMA) by benzoyl peroxide (BPO) in mesoscopic channels of MCM-41.

Chemical properties of the mesopore surface can be tuned by the introduction of aluminium, titanium, and some other transition metal ions to the silicate framework. For example, a highly Lewis acidic mesoporous silica (Al-MCM-41) can be prepared by doping aluminium in the silicate framework. Aida and coworkers have found that lactones are polymerized in a living manner in the presence of Al-MCM-41 and an alcohol at 50 °C, to give polyesters with narrow molecular weight distribution (MWD).[69] By changing the mole ratio monomer/alcohol, the molecular weight of the polymer can be controlled over a rather wide range. A sequential polymerization of two different lactone monomers with an Al-MCM-41/alcohol system gives the corresponding block copolymer with narrow MWD. Furthermore, Al-MCM-41 is easily separated from the polymerization mixture by filtration, and can be used again for the polymerization. NMR studies have indicated that the alcohol is incorporated into the polymer terminus at the initiation step of the polymerization. In contrast with the case using Al-MCM-41, no polymerization occurs in the presence of a pure silicate MCM-41 or modified MCM-41 with methylated silanol functionalities under otherwise identical conditions to the above. Furthermore, use of a microporous aluminosilicate zeolite-Y (pore diameter = 8 Å), in place of Al-MCM-41, results in no polymerization. These observations suggest that the large pore size as well as the Lewis acidic character of the surface is essential for the polymerization. The postulated mechanism of polymerization is shown in Fig. 21, in which the monomer is activated by a possible cooperation of Lewis acidic aluminium sites and Brønsted acidic silanol functionalities.

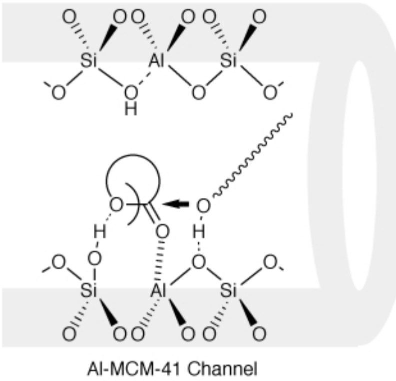

Fig. 21 A proposed mechanism for activation of lactone on the interior wall of Al-MCM-41 for ring-opening polymerization with alcohol.

Mesoporous silicates have been used as inorganic supports for metallocene catalysts for the polymerization of olefins.[70] However, only limited examples have been reported that indicate some spatial effects of mesoscopic pores on the polymerization. For example, co-oligomerization of ethylene and propylene with an MCM-41-supported zirconocene compound, in conjunction with methylalumoxane (MAO) as cocatalyst, has been investigated,[71] where the pore size has been claimed to affect the molecular weight of the resulting co-oligomer. When MCM-41 prepared with a C_{16} surfactant is used as the support, a co-oligomer with M_n of 1280 is formed. On the other hand, when the support is MCM-41 prepared with a shorter-chain C_{14} surfactant, a co-oligomer with M_n of 1730 is formed.

Recently, Aida and Kageyama *et al.* have found that a titanocene complex supported by a particular type of mesoporous silicate denoted mesoporous silica fiber (MSF, pore diameter = 27 Å),[72] in conjunction with MAO, produces crystalline nanofibers of ultrahigh molecular weight (M_n = 6 200 000) linear polyethylene.[73] The polyethylene is obtained as a cocoon-like white mass with a low bulk density. Scanning electron microscopy (SEM) shows that the fibers are 30–50 nm in diameter (Fig. 22), and the crystalline density is close to a theoretical upper limit for polyethylene. Unlike ordinary high-density polyethylenes consisting of folded-chain crystals, the polyethylene fibers thus obtained consist exclusively of extended chain crystals, according to small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). For the formation of crystalline nanofibers of polyethylene, the ‘extrusion polymerization’ mechanism, which mimics biological formation of natural fibers such as crystalline cellulose fibers, has been postulated, where the polymer chains, formed at the activated titanocene sites within the individual mesopores, are extruded into the solvent phase and assembled to form extended-chain crystals (Fig. 23). Thus, the mesoscopic pore in this particular case serves as a template, which can suppress the kinetically favored chain folding process, since the pore diameter (27 Å) is almost one-order of magnitude smaller than the lamellar thickness (270 Å) of the folded-chain crystals of ordinary polyethylenes. Since most studies on precision polymerization have focused on the control of primary structures of polymers, the present finding, which enables control of a

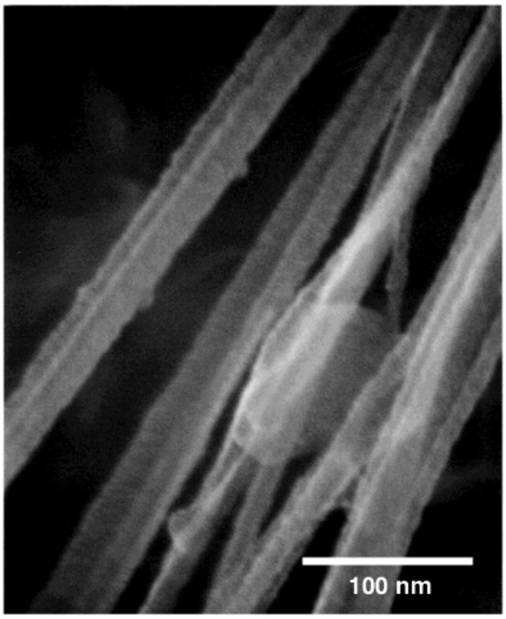

Fig. 22 A SEM micrograph of crystalline polyethylene fibers formed by polymerization with a supported titanocene by mesoporous silica fiber (MSF) in conjunction with methylalumoxane (MAO). Reprinted in part with permission from: *Science*, 1999, **285**, 2113 (Copyright © 1999, the American Association for the Advancement of Science).

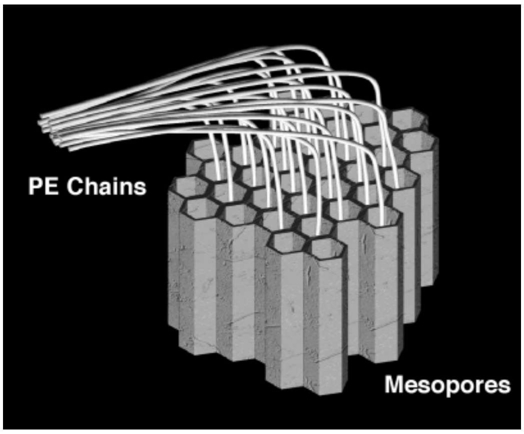

Fig. 23 A proposed mechanism for the formation of fibrous polyethylene with titanocene-mounted mesoporous silica fiber (MSF).

ternary structure, is unique and may have a high potential for the fabrication of novel polymer materials from specialty as well as commodity monomers. Along the line of this study, a novel hybridized thin film of polyethylene and silica (Fig. 24) has been synthesized[74] by the polymerization of ethylene on a mesoporous silica film[75] doped with titanocene.

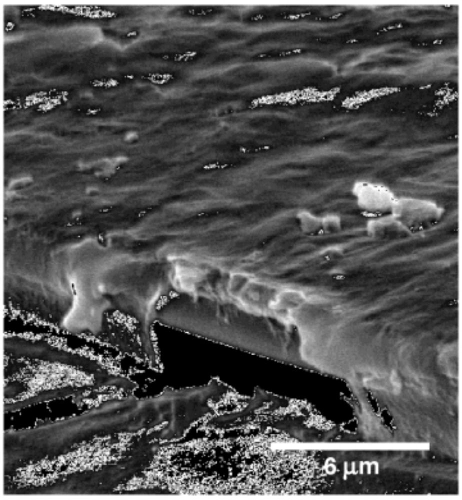

Fig. 24 A SEM micrograph of a polyethylene/silica/mica hybridized thin film formed by polymerization of ethylene on a titanocene-mounted mesoporous silica film in conjunction with methylalumoxane (MAO). Reprinted in part with permission from: *J. Polym. Sci. Part A: Polym. Chem. Ed.*, 2000, in press (© 2000, John Wiley & Sons, Inc.).

In relation to the above study, Mallouk and Ozin and coworkers have utilized MCM-41 as a mold for the fabrication of a fibrous poly(phenolformaldehyde) resin.[76] When an acid-catalyzed polyaddition/condensation of phenol and formaldehyde is carried out within the mesoscopic channels of MCM-41, and then the silicate framework is destroyed by HF, mesofibers of poly(phenolformaldehyde) with a diameter of *ca.* 20 Å and an aspect ratio of more than 10^3 is obtained (Fig. 25). In contrast, when the polymerization is conducted in the presence of non-porous silica Cab-O-Sil, only a non-fibrous, agglomerated polymeric mass results.

Fig. 25 A TEM micrograph of polymer mesofibers formed by polyaddition/condensation of phenol and formaldehyde within the mesoscopic channels of MCM-41. Reprinted in part with permission from: *J. Mater. Chem.*, 1998, **8**, 13 (© 1998, The Royal Society of Chemistry).

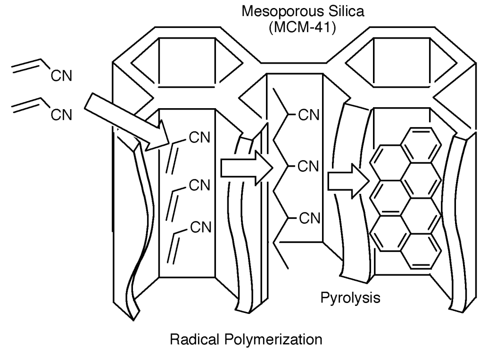

Fig. 26 Illustration for free radical polymerization of acrylonitrile within the mesoscopic channels of MCM-41 and subsequent pyrolysis to form a conducting carbon nanowire.

Since polymer chains included in individual mesoscopic pores are isolated from one another and oriented parallel to the pore axis, fabrication of photo-conducting materials with mesoporous silica has attracted attention. For example, Wu and Bein have reported the synthesis of a graphite-type conducting carbon wire by the polymerization of acrylonitrile within the mesoscopic channels of MCM-41 and its subsequent pyrolysis (Fig. 26).[77] The graphite/MCM-41 adduct, obtained by pyrolysis at 1000 °C, shows a notable microwave conductivity of 0.1 S cm^{-1}. A polyaniline wire encapsulated within the mesoscopic silicate channel has also been synthesized, which however shows only a low microwave conductivity (0.0014 S cm^{-1}).[78] Variation of the pore diameter of the mesoscopic channel would make it possible to tune the conducting properties of the hybridized material. Similarly, Ozin and co-workers have reported ring-opening polymerization of [1]sila-ferrocenophane **37**.[79] Compound **37** is incorporated into the hexagonal channels of MCM-41 by sublimation under vacuum, and then the adduct is heated at 140 °C, whereupon the polymerization occurs to give a poly(ferrocenylsilane)/MCM-41 hybrid (Fig. 27). When the hybrid is pyrolyzed at 900 °C under nitrogen, the included polymer is decomposed to leave iron nanoparticles with an average particle size of 20 ± 5 Å. The magnetic properties of the pyrolyzed product indicate that the iron nanoclusters in the interior are supermagnetic.

Concluding remarks

Template-assisted polymerization, *i.e.* polymerization of pre-organized monomers or in constrained media, has a long history, but is still growing even more rapidly. This is not only from a continuous interest in short- and long-range information transfers in the molecular world but also for a strong demand

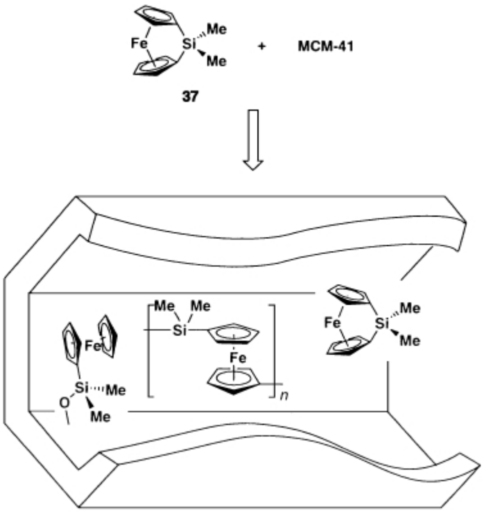

Fig. 27 Illustration for ring-opening polymerization of [1]silaferrocenophane **37** within the mesoscopic channels of MCM-41.

from the next-generation material design for fabrication of well defined nanostructures. Bringing together knowledge about biology and physics as well as organic, inorganic, supramolecular, and macromolecular chemisty into this area will lead to further breakthroughs in science and technology.

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