the effective size of a molecule, which is defined as the end-to-end distance projected on the center line of the channel. Figure 3 shows the distribution of this distance for a large (AET) and optimal pore size (AFI). In the large-pore structure we observe for the linear isomer a very broad distribution, reflecting all possible conformations (curled and stretched) of this isomer. Hence, the effective size of the linear and branched isomer is nearly identical. If we reduce the size of the channel, this distribution is dominated by the stretched conformations, which increases the effective size of the linear isomers. Because the effective size of the linear isomer is large, these molecules are expelled at *high* pressure.

An important difference between the concept of inverse shape selectivity and our entropic explanation is the role of the zeolite. Inverse shape selectivity indicates that one should look at those zeolites, which have an optimal "match" for the branched isomer. In our mechanism the role of the zeolite is to provide an environment in which the length differences between the linear and branched isomers are maximum, which translates into an optimal pore diameter. For a given pressure, the maximum selectivity is determined by the relative effective sizes of the alkane molecules. The details of the channel structure are in this mechanism of secondary importance. This situation suggests that we can "optimize" any zeolite structure by tuning its diameter. In Figure 4 we have performed this optimization for several known zeolite structures by changing the pore diameters by a simple scaling factor. Of course, such an optimization cannot be performed in practice, but does illustrate our point that irrespective of the details of the zeolite a similar optimal selectivity is obtained for nearly identical channel dimensions. At lower temperatures or higher pressures the entropy effect is more pronounced and a better selectivity could be expected. The results shown in Figure 4 are at lower temperatures than those in Figure 1 (403 K versus 577 K). The data at these lower temperatures give significantly higher selectivities. A similar effect can be expected from an increase of the pressure.

Two conclusions of practical importance can be drawn from our work. We have shown that there is a thermodynamic limit to the maximum selectivity that can be obtained for these types of reactions. This limit implies that any novel zeolite structures will have a selectivity towards branched paraffins which is at best similar to the selectivity of MAZ and AFI. A more successful approach to increase the selectivity would be to operate at higher pressure or lower temperatures, since the entropy effect is more pronounced at these conditions.

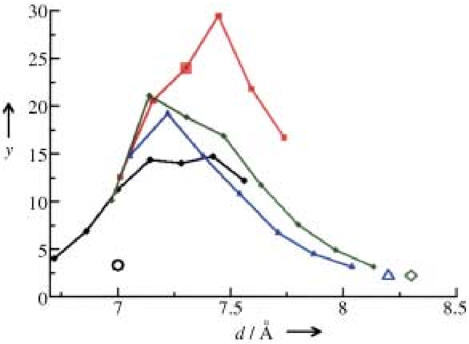

Figure 4. Normalized 2,2-DMB/n-C_6 yield ratios (with respect to the FAU selectivity) for some "optimized" pore structures at $T = 403$ K and $P = 1000$ kPa. The size of MOR- (black, pore too small), AFI- (red, optimal), AET- (green, too wide), and DON-type (blue, too wide) channels was adjusted by scaling the coordinates. The open symbols represent the zeolite structures before resizing. MOR was first made circular before the scaling was applied.

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Reaction Principles and Crystal Structure Design for the Topochemical Polymerization of 1,3-Dienes

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Crystal engineering is the planning of the properties and functions of crystalline materials by using preorganized molecules.[1] This process involves the control of crystal

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packing based on information from the chemical structure of the molecules and is required to clarify the correlation between the structure and functions. Topochemical polymerization, which is one of the most important functions of crystalline materials, is the specific crystal-to-crystal reaction to give a unique chain structure and a polymer single crystal that cannot be manufactured by solution polymerization or by recrystallization of a preformed polymer from its solution or melt. This technique is very useful in developing nanomaterials and devices in constrained media including layers, channels, and solid surfaces.[2] It is well known that some limited diyne and olefin monomers undergo topochemical polymerization,[3–7] but other monomers have long been believed not to polymerize in a topochemical manner. In fact, no designer crystal has been reported for the 1,3-diene monomers, despite the pioneering work by Tieke et al. reported in the 1980s regarding the radiation polymerization of several layered compounds in the crystalline state.[8] In recent years we have studied the solid-state photopolymerization of various 1,3-diene monomers, including the esters and alkylammonium salts of the (*Z*,*Z*)- and (*E*,*E*)-muconic and sorbic acids, which proceeds by means of a topochemical reaction mechanism.[9–13] The polymer crystals obtained were characterized as organic intercalation materials.[1d, 9]

Here we propose principles for the topochemical polymerization of 1,3-diene monomers to predict the polymerization reactivity and design crystalline polymer materials. Currently, topochemical polymerization is opened not only to the diyne library, but also to the larger and more popular diene library. This is a first step in the rational design for the topochemical polymerization of diene monomers, moving away from the trial-and-error approach. Diene polymerization has potential for the construction of advanced organic materials in the solid state, because the topochemical polymerization of diyne and diene monomers provides different types of polymers, that is, conjugate and nonconjugate polymers, respectively, which could be used as molecular devices for optics and optoelectronics.

We have investigated the molecular packing in the crystals of many diene monomers that can or cannot undergo topochemical polymerization. All the muconic and sorbic acid derivatives with *Z*,*Z* and *E*,*E* configurations (**1**–**4**, Scheme 1) have similar molecular conformations in the crystalline state, that is, they are s-*trans* dienes with a highly planar structure.[14] The stacking structure of the monomers was evaluated by using the following parameters (Figure 1):[15] the intermolecular distance between carbon atoms that react to make a new bond during the topochemical polymerization (d_{cc}), the stacking distance along the column (d_s), and the angles between the stacking direction and the molecular plane in orthogonally different directions (θ_1 and θ_2). The values of the parameters determined for the monomers **1**–**4** are summarized in Table 1.[16]

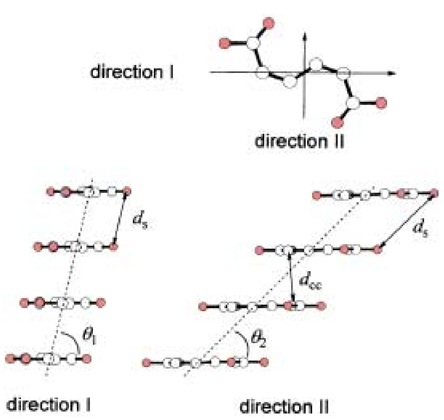
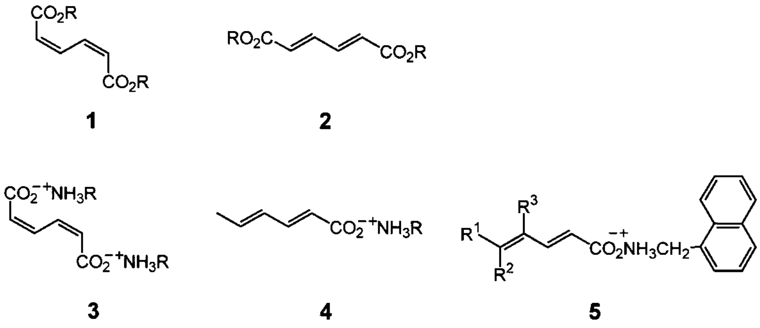


Figure 1. Definition of stacking parameters used for the prediction of the topochemical polymerization reactivity. d_{cc} is the intermolecular distance between the 2 and 5′ carbon atoms. d_s is the stacking distance between the adjacent monomers in a column. θ_1 and θ_2 are the angles between the stacking direction and the molecular plane in orthogonally different directions. The view from direction I is parallel to a vector through the 2 and 5 carbon atoms of the diene moieties.



Scheme 1. Diene monomers examined in this study.

Table 1. Stacking structure of the topochemically polymerizable muconic and sorbic acid derivatives in the crystals.

Monomer	R	d_{cc} [Å]	d_s [Å]	θ_1 [°]	θ_2 [°]
1	ethyl	3.79	4.93	79	49
1	4-chlorobenzyl	3.57	5.12	82	44
3	benzyl	4.24	4.86	67	55
3	2-chlorobenzyl	4.19	4.94	62	52
4	2-methylbenzyl	5.35	5.00	28	60
4	4-methylbenzyl	5.43	4.93	24	61
4	1-naphthylmethyl	5.37	4.99	29	61
4	−R− = *p*-xylylene	5.47	4.99	25	60
Lithium sorbate	–	5.69[a]	5.04[a]	7[a]	32[a]
5a	$R^1 = R^2 = R^3 = H$	5.31	4.95	29	61
5d	$R^1 = R^2 = CH_3$, $R^3 = H$	3.30	4.90	87	42

[a] Calculated from the crystal structure reported in [ref. 22].

The polymerizable monomer crystals exhibit d_{cc} values in the range between 3.6 and 5.7 Å, and the distance increases in the order of monomer species **1** < **3** < **4**. The θ_1 and θ_2 values are also dependent on the monomer structure. In contrast, all the d_s values are in an exclusively limited region of 4.9–5.1 Å. Figure 2 shows the relationship between the d_s and θ_2 values. The blue curve is calculated for the closest packing of the planar molecules with a thickness of 3.5 Å and θ_1 of 90°. For esters **1** and **2**, the plots are situated near the calculated curve because of the closest packing of the planar molecules in the crystals. In contrast, the ammonium derivatives often favor structures other than the columnar structure which results in the scattered points far from the calculated curve. This is caused by the diversity in the hydrogen bond pattern including one-dimensional ladders and two-dimensional sheets, depend-

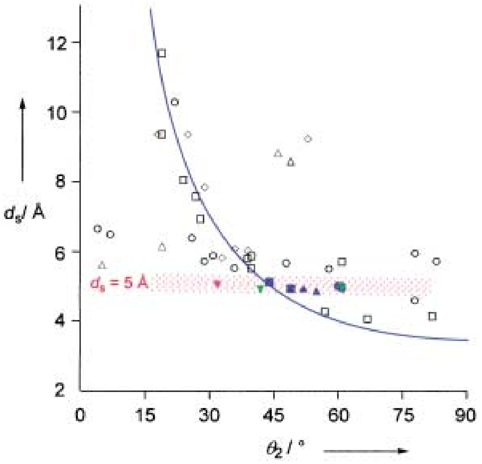


Figure 2. Relationship between the d_s and θ_2 values for the 1,3-diene monomers in the crystals. (□) **1**, (◇) **2**, (△) **3**, (○) **4**, and (▼) **5**; data for lithium sorbate (▼) reported by Schlitter and Beck.[22] Closed and open symbols represent polymerizable and nonpolymerizable monomers, respectively.

ing on the structure of the N-substituted groups. Several monomers have smaller d_{cc} and d_s values, and although this appears to be advantageous for the polymerization, they are actually nonpolymerizable (see also Supporting Information). For example, the diethyl ester of **1** has an alternative crystal structure at a low temperature as a result of the first-order phase transition,[17] which seriously affects the polymerization reactivity; this monomer polymerizes quite rapidly at room temperature, but not at all below −45 °C. The stacking parameters of **1** (R = Et) determined at a low temperature (d_{cc} = 3.88 Å, d_s = 4.25 Å, θ_1 = 80°, and θ_2 = 57°) are very similar to those given in Table 1 for the polymerizable structure. In this way, a slight change in the d_s value from 4.93 to 4.25 Å or a deviation from the shaded red zone in Figure 2 diminishes the polymerization reactivity of the diethyl ester of **1**.

Which factor determines the polymerization reactivity? We emphasize the importance of the d_s value for the topochemical polymerization process. Namely, the stacking distances of the polymerizable monomers are close to the values of the repeating unit, that is, a fiber period of polymer chains with a fully stretched conformation, produced along with a crystallographic axis in the crystals. The fiber period for the ethyl ester polymer of **1** was determined to be 4.84 Å from the X-ray diffraction data gathered for the polymer single crystal.[10] If the polymerization proceeds for monomers with d_s values greater or smaller than 5 Å, then the monomer molecules have to translate along the stacking axis during the polymerization. When d_s is close to the fiber period of the resulting polymer, monomer molecules rotate with the minimum translational movement and make a bond between the 2 and 5′ carbon atoms.

The principles of diene polymerization seem to be similar to those for diynes, which are already well established,[4] but the former are more sensitive to structural changes in the monomer crystals. This results from the difference in the planar and linear molecular shapes of dienes and diynes, respectively, that is, the direction of the π orbital of the reacting moieties. Because the structural factors of diene polymerization in the crystalline state are not as straightforward as those for diyne polymerization, the discovery and generalization of the former has lagged behind.

The next question is how to make a suitable stacking distance of 5 Å for the polymerization in the crystals of the diene monomers. Some "supramolecular synthons"[19] are available for the topochemical polymerization of the ammonium and ester derivatives of the 1,3-diene carboxylic acids: two-dimensional hydrogen bond networks, aromatic ring stacking, and CH/π or halogen–halogen interactions (Figure 3). It is noteworthy that a naphthylmethylammonium counterion enforces a robust layer structure in which diene carboxylic acid molecules are arranged in a fashion appropriate for the polymerization. These crystals show the synergetic effects of the two-dimensional hydrogen bond network, aromatic stacking, and CH/π interaction.[20, 21] Furthermore, we tested the polymerization reactivity of several diene carboxylic acids other than the muconic and sorbic acids. All the substituted diene monomers **5a**–**5e** (Scheme 1 and Table 2) polymerized by means of a topochemical polymerization mechanism to give the corresponding stereoregular polymers under photoirradiation in the crystalline state. The crystal structures and molecular packing (**5a** and **5d** in Table 1) were again similar to those of other polymerizable sorbate and muconate monomers which indicates that the polymerization principles are valid for a variety of diene monomers.

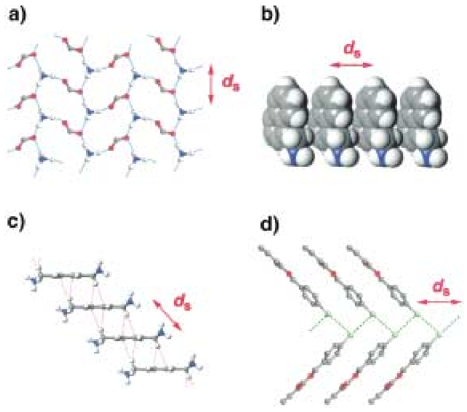


Figure 3. Supramolecular synthons for the molecular stacking with a 5 Å distance, which is appropriate for the topochemical polymerization of the 1,3-diene monomers. a) Two-dimensional hydrogen bond network formed between primary ammonium and carboxylate groups, which act as triple hydrogen bond donors and acceptors, respectively. b) Aromatic ring stacking. The benzyl and naphthylmethyl moieties are packed in the crystals with a herringbone or γ-type structure. c) CH/π interaction between aromatic and benzyl groups. In the naphthylmethylammonium crystals, interactions between the π and aromatic or benzylic hydrogen atoms are observed. In the crystals of benzylammonium, 4-methylbenzylammonium, and *p*-xylylenediammonium crystals, an interaction of π-electrons with the benzylic hydrogen atoms is important. d) Halogen–halogen zigzag chains. The validity of this interaction has been proved by the chlorine atom substitution of the benzyl ester of **1**.[23] Similar halogen chains are also observed in the crystals of the chloro-substituted benzylammonium salts of **3**.

Here we have proposed reaction principles for the topochemical polymerization of 1,3-diene monomers in the crystalline state. In the crystals of polymerizable monomers,

Table 2. Topochemical polymerization of **5** under UV irradiation for 8 h in the crystalline state.

Monomer	R^1	R^2	R^3	Yield [%]
5a	H	H	H	88
5b	$(CH_2)_2CH_3$	H	H	20
5c	$(CH_2)_5CH_3$	H	H	24
5d	CH_3	CH_3	H	67
5e	CH_3	H	CH_3	11
4	CH_3	H	H	98

diene molecules stack in a columnar structure with an exclusively limited stacking distance of 5 Å, a value close to the repeating distance of the monomer units in the resulting polymer chain and appropriate for the polymerization by a topochemical reaction mechanism. We have also identified supramolecular synthons for constructing the desired monomer stacking in the crystals by using weak intermolecular interactions such as the two-dimensional hydrogen bond networks, aromatic ring stacking, and CH/π or halogen–halogen interactions.

Experimental Section

The muconic and sorbic acid derivatives used in this work were prepared by the methods described in previous papers.[9, 11, 12] The reaction of malonic acid and acrolein was used to prepare *trans*-2,4-pentadienoic acid;[24] subsequent reaction with 1-naphthylmethylamine gave **5a** quantitatively. Precursor carboxylic acids for **5b**–**5e** were synthesized by the reaction of triethylphosphonoacetate with the corresponding unsaturated aldehydes followed by hydrolysis.

Typical procedure: To NaH (1.42 g, 0.036 mmol) in dry THF was added triethylphosphonoacetate (7.1 mL, 0.036 mmol), and then 3-methyl-2-butenal (3.0 g, 0.036 mmol) in THF was added dropwise over 1 h. The reaction mixture was stirred overnight. Silica gel column chromatography (hexane/ethyl acetate 10:1) provided ethyl 2-*trans*-5-methyl-2,4-hexadienoate. After hydrolysis with KOH, 2-*trans*-5-methyl-2,4-hexadienoic acid was isolated as a yellowish powder. Yield 2.65 g (60 %). The quantitative reaction with 1-naphthylmethylamine provided **5b**, which was recrystallized from methanol.

Photoirradiation was carried out with a high-pressure Hg lamp (Toshiba SHL-100-2, 100 W) at a distance of 10 cm through a Pyrex filter. The polymer yield was determined gravimetrically after any unreacted monomer had been removed with methanol or chloroform. Single-crystal X-ray data were collected on a Rigaku RAXIS RAPID diffractometer or Nonius Kappa CCD system with $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) or $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) and a graphite monochromator. The structures were solved by direct methods with the programs SIR88 and SIR92 and refined by using full-matrix least-squares procedures. All the calculations were performed with the CrystalStructure crystallographic software package of Molecular Structure Corporation or maXus of Mac Science, Japan.

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[14] We do not have sufficient crystal data for the *E*,*Z* monomers to discuss at the present because of the difficult isolation of pure isomers and single crystals.

[15] In the previous papers θ_1 and θ_2 were defined in an alternative way. Formerly, direction I was parallel to a vector through the 2 and 3 carbon atoms (4 and 5 carbon atoms) for the *Z*,*Z* monomers and the 2 and 4 carbon atoms (3 and 5 carbon atoms) for the *E*,*E* monomers. However, it was not convenient for nonplanar molecules. Therefore, the values of θ_1 and θ_2 in this study are different from the previously reported values for some monomers. The present method is unambiguous and valid even for nonplanar 1,3-butadiene derivatives.

[16] In Table 1 the data for the topochemically polymerizable monomers are shown. Supporting information is available for the nonpolymerizable monomers; see also, refs. [11], [17], [18], and [23].

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