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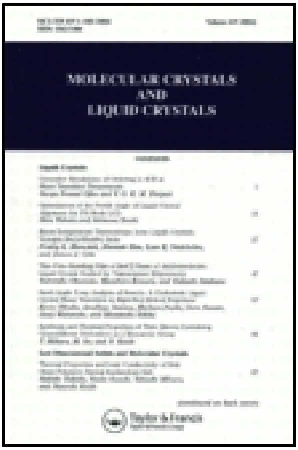

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Polymerization of Diene and Diyne Monomers in Deoxycholic and Apocholic Acid Inclusion Compounds

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POLYMERIZATION OF DIENE AND DIYNE MONOMERS IN DEOXYCHOLIC AND APOCHOLIC ACID INCLUSION COMPOUNDS

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Abstract One-dimensional polymerization of conjugated diene and diyne monomers in channels of deoxycholic and apocholic acid inclusion compounds is discussed. The polymerization exhibited the following remarkable features on the basis of a one-dimensional character of the molecular assemblies, in contrast to that in solution or the solid state: (i)stabilized propagating radicals, (ii)decreased reaction rates, and (iii) an efficient induction of regiospecificity and stereospecificity.

INTRODUCTION

The chemistry of lattice-type inclusion compounds is of great current interest.[1] Some of the compounds have channels which accomodate guest molecules with translational and rotational motions differing from those in solution or the solid state.[2] The guests are known to undergo some novel reactions in the channels.[3] However, no attention was given to the phenomenon that the guest molecules in the channels constitute one-dimensional molecular assemblies, which may bring about characteristic chemical reactions. We describe here a striking example of such a one-dimensional assembly.

We studied assemblies of conjugated diene and diyne monomers and their polymerization reaction (termed inclusion polymerization[4]) in channels of the lattice-type inclusion compounds of deoxycholic acid and apocholic acid (Figures 1 and 2).

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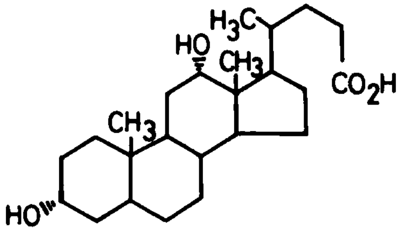

FIGURE 1 Deoxycholic acid

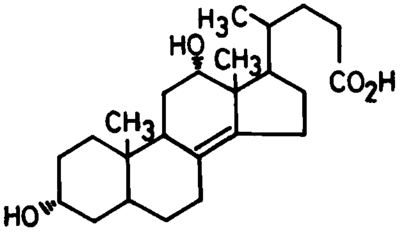

FIGURE 2 Apocholic acid

FEASIBILITY FOR USE OF A COMPREHENSIVE LIST OF MONOMERS

The extensive inclusion ability[5] of the hosts enabled us to polymerize a great variety of diene monomers having polar and/or bulky substituents.[6] Applicable monomers are listed in Table 1 and compared with those in the case of other hosts so far employed. The result indicates that the inclusion method using apocholic acid has potential usefulness with over one hundred different diene monomers having various combinations of substituents, whereas the conventional use of urea, thiourea or perhydrotriphenylene has been applied only to a restricted number of monomers.[4] Thus, inclusion polymerization has now been developed for widespread one-dimensional polymerization, starting from a preliminary report by Clasen in 1956[7] and the full reports by Brown and White in 1960.[8]

TABLE 1 Polymerizable monomers in channels.

Host	Monomer					
Urea						
Thiourea						
Perhydro- triphenylene						
Deoxycholic acid					 CO_2CH_3	 CN
Apocholic acid					 CO_2CH_3  CO_2CH_3	 CN  CN

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STABILIZED PROPAGATING RADICALS

One reason for our successful development lies in thermal stability of the steroidal hosts in addition to their extensive inclusion abilities. Another comes from a mechanistic consideration. The polymerization proceeded very slowly at lower temperature after γ-ray irradiation, suggesting the existence of thermally stable intermediates of the living-type. ESR studies gave direct evidence for the existence of such allylic propagating radicals for all the monomers employed. Figure 3 shows a typical example of the ESR spectrum observed at room temperature, which was practically identical to that of the propagating radicals observed at -120°C in frozen benzonitrile.[9] The spectrum in the inclusion state changed neither by raising the temperature up to 100°C, nor by standing at room temperature over two months, whereas it disappeared at -80°C in benzonitrile.[9] The concentration of the radicals in the channels amounted to about 10^{-3} mol per one kg of the host, which exceeds in that for a usual solution polymerization by a factor of 10,000. These observations indicate very long life times for radicals in the one-dimensional molecular assemblies. This may be explained by the fact that a propagating radical in a channel can not couple with other ones in other neighboring channels owing to the complete isolation by the walls consisting of the host molecules. Figure 3 shows the situation schematically. This leads to a remarkable suppression of the termination reaction. Thus, we can observe ESR spectra of the propagating radicals in the inclusion state very readily,[10] in contrast with the difficulty in solution or in the solid state[11].

DECREASED REACTION RATES

The rate constants of the elementary reaction of the inclusion polymerization were not determined so far. We successfully determined the values in case of the inclusion polymerization of 1-chloro-1,3-butadiene in channels of deoxycholic acid.[12]

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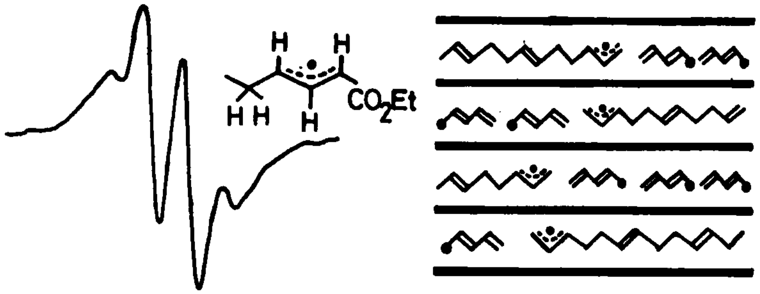

FIGURE 3 ESR spectrum of propagating radicals in channels of apocholic acid (left) ; Schematic representation of one-dimensional polymerization which proceeds by propagating radicals stabilized in channels (right).

At the initial stage of the polymerization, the conversion increased with increasing postpolymerization time, and the number average molecular weight of the resulting polymers increased with increasing conversion. The polymerization may be classified as a stationary successive polymerization with a rapid initiation. We employed a graphical evaluation for the rate constants of the elementary reactions of the polymerization. Table 2 shows the estimated values together with those for usual solution polymerizations. The rate constant of the propagation (k_p) is less than 10^{-3} of that for the solution. This may be explained by the fact that molecular motions are substantially hindered in the channels as compared with those in solution. Another remarkable thing is that the termination rate constant is decreased drastically in the channels. Therefore, the polymerization of 1-chloro-1,3-butadiene in channels of deoxycholic acid seems to be living-like.

TABLE 2 Comparison of parameters for the inclusion polymerization in channels of deoxycholic acid with those for usual solution polymerizations.

	Inclusion	Solution
k_p	$10^{-3}(\mathrm{kg \cdot mol^{-1} s^{-1}})$	$10^{0-3}(\mathrm{l \cdot mol^{-1} s^{-1}})$
k_t	$10^{-9}(\mathrm{kg \cdot mol^{-1} s^{-1}})$	$10^{7-10}(\mathrm{l \cdot mol^{-1} s^{-1}})$
$[\sim M^{\cdot}]$	$10^{-3}(\mathrm{mol \cdot kg^{-1}})$	$10^{-7 \sim -8}(\mathrm{mol \cdot l^{-1}})$
	(successive)	(chain)

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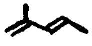
THROUGH-SPACE INDUCTION OF REGIO- AND STEREO-SPECIFICITY

The third feature of the polymerization in an efficient "through-space" induction of regiospecificity and stereospecificty due to a restraint in the one-dimensional space. Most of the resulting polymers consisted of head-to-tail, 1,4-trans structure. For example, we confirmed the complete regiospecificity of poly(methyl 1,3-pentadienoate) by use of 500 MHz ^{1}H and 125 MHz ^{13}C NMR spectroscopy. The polymerization can be characterized as α-ω, head-to-tail polymerization. Further studies have proved that the present method is of great value in case of conjugated triene monomers such as 1,3,5-heptatriene and 1,3,5-octatriene. The enlarged 125 MHz ^{13}C NMR spectrum showed about 75 % isotacticity of the poly(methyl 1,3-pentadienoate), which should be closely related to an asymmetric induction.

Asymmetric Induction

All of the resulting polymers from prochiral monomers showed the optical activities (Table 3), indicating the chiral transfer from the chiral hosts through space.[13] Thus, asymmetric inclusion polymerization has been extended to a wide variety of monomers, starting from the first communication by Farina and his coworkers in 1967.[14]

TABLE 3 Optical activities of polymers obtained by asymmetric inclusion polymerization of various prochiral butadiene monomers in channels of deoxycholic acid.

Monomer	$[\alpha]_D$	Monomer	$[\alpha]_D$
 CH_2CH_3	+8.4		+90
 Cl	-41.9		+46.4
 CN	-83.7		+55.4
 CO_2CH_3	+54.7		-22.4

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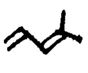
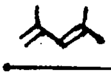
SPACE-SIZE DEPENDENCE

Another feature is a novel space-size dependence of the polymerization.[15] A pair of the hosts, deoxycholic acid and apocholic acid, provide a pair of channels suitable for the detection of the space-size effect, since the former provide a smaller channel in size than the latter.[3a] For example, 4-methyl-1,3-pentadiene polymerized in both channels as shown in Table 4, but 2,4-dimethyl-1,3-pentadiene did not. The slight changes of the monomers in size, shape and polarity introduced the drastic changes in the polymerizability in the channels. The result may be explained in terms of the relative sizes between the guests and the channels. It is considered that the polymerization will not occur when the guest molecules are too tightly included in the channels.

In conclusion, we established one-dimensional polymerization on the basis of the one-dimensional molecular assembly of the guest molecules in the channels. The described method will permit further studies of the polymerization of various conjugated polyenes. Work is continuing seeking as many examples of a one-dimensional inclusion polymerization system as possible.

TABLE 4 Inclusion polymerization of methyl-substituted butadienes in channels of deoxycholic acid and apocholic acid under various conditions.

Monomer	Host	Postpolymerization		Yield (%)
		(°C)	(days)	
	deoxycholic acid	0	2	trace
		50	1	25
	apocholic acid	0	2	23
		50	1	37
	deoxycholic acid	100	4	trace
	apocholic acid	50	1	34

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