

ARCHITECTURE OF LADDER, TUBULAR AND SIEVE-PLATE POLYMERS PREPARED BY STEPWISE COUPLING POLYMERIZATION

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Abstract “Stepwise-coupling polymerization” (SCP) is a very useful approach for preparing microstructure-controllable ordered network polymers, including soluble one-dimensional ladderlike polymers (LP) and tubular polymers (TP), and two-dimensional sieve-plate polymers. The novel reactive LPs are important precursors of micro-structure controllable polymers such as “fishbone-” or “rowboat-”like mesomorphic polymers and their metal complexes as well as tubular polymers (TPs). They are full of great potential for use as advanced materials.

Keywords Stepwise coupling polymerization, Ladder polysiloxane, Tubular polymers

INTRODUCTION OF STEPWISE COUPLING POLYMERIZATION (SCP)

SCP has been explored and gradually improved by our research group since 1984^[1, 2]. Now, SCP has become a powerful method for preparing microstructure-controllable polymers. As shown in Fig. 1, the first step of SCP is that a silicon monomer, tetrafunctional silane, reacts with the first coupler $X-X$ to form a coupled intermediate. Then it reacts with the second coupler $Y-Y$ to form a ladder polymer (LP). If the LP has *cis*-isotactic configuration it can further react with the third coupler $Z-Z$ to form a tubular polymer (TP). TP also can be formed from two different reactive LPs by reacting with each other. If the LP has a non-*cis*-isotactic (e.g. *cis*-syndiotactic or *trans*-syndiotactic) configuration it reacts with the fourth coupler $Z'-Z'$ to form a sieve-plate polymer (SP). Besides, the LP can also be grafted with organic groups including some mesogenic or non-mesogenic groups to form the mesomorphic ladder polymer (MLP). One could observe from this scheme that by proper choice of different silicon monomers and different couplers the pore size, pore shape and the affinity of LP, TP and SP can be adjusted. And the LP also plays an important role as a prefabricated part for further constructing TP, SP and MLP. In other words, the LP can determine which kind of TP or SP will be formed.

LADDER POLYMERS (LP)

Ladder Polysilsesquioxane

The first ladderlike polyphenylsilsesquioxane (Ph-T) was prepared by Brown via thermal equilibrium polycondensation as early as 1960^[3]. But, Brown's method can not be applied to synthesize other LPs except Ph-T due to the harsh reaction conditions. Fifteen years ago, our group developed a preaminolysis method^[4-6], as shown in Fig. 2, which is one kind of SCP.

The first step involves the reaction of trichlorosilane with the first coupler, phenylenediamine (PDA), to form an isolatable coupled intermediate, which is then hydrolyzed with the second coupler, water, to form a silanol, PDA-bridged tetrahydroxydisilane, it is then self-assembled through H-bonding to form a ladder oligomer. Next, the PDA bridge is removed by hydrolysis to form the H-bonding bridged oligomer, which is finally poly-condensed to generate the title LP. According to this scheme, we can make the following remarks: PDA acts as a template and the H-bonding assisted self-assembly can facilitate the formation of ladder oligomer

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and polymer. Because this reaction proceeds under very mild conditions, so it can be used to prepare reactive LP. Moreover, in consideration of the tetrahedral configuration of the silicon atom and the assistance of H-bonding, the LP prepared by this method usually possesses *cis*-isotactic configuration. In order to confirm the proposed mechanism it is necessary to identify the coupled intermediate and to prove the *cis*-isotactic configuration of LP. So far we have successfully isolated the intermediates although these coupled intermediates are very air-sensitive. Concerning the stereo-tacticity, by a combination of fluorescence spectroscopy, XRD, AFM, ^{29}Si -NMR, molecular simulation and so on we have confirmed that the LP has a *cis*-isotactic configuration. This provides an important prerequisite for the further formation of tubular polymers.

Until now, we have synthesized a series of LPs including non-reactive and reactive ladder polysilsesquioxanes^[4-12] as shown in Fig. 3.

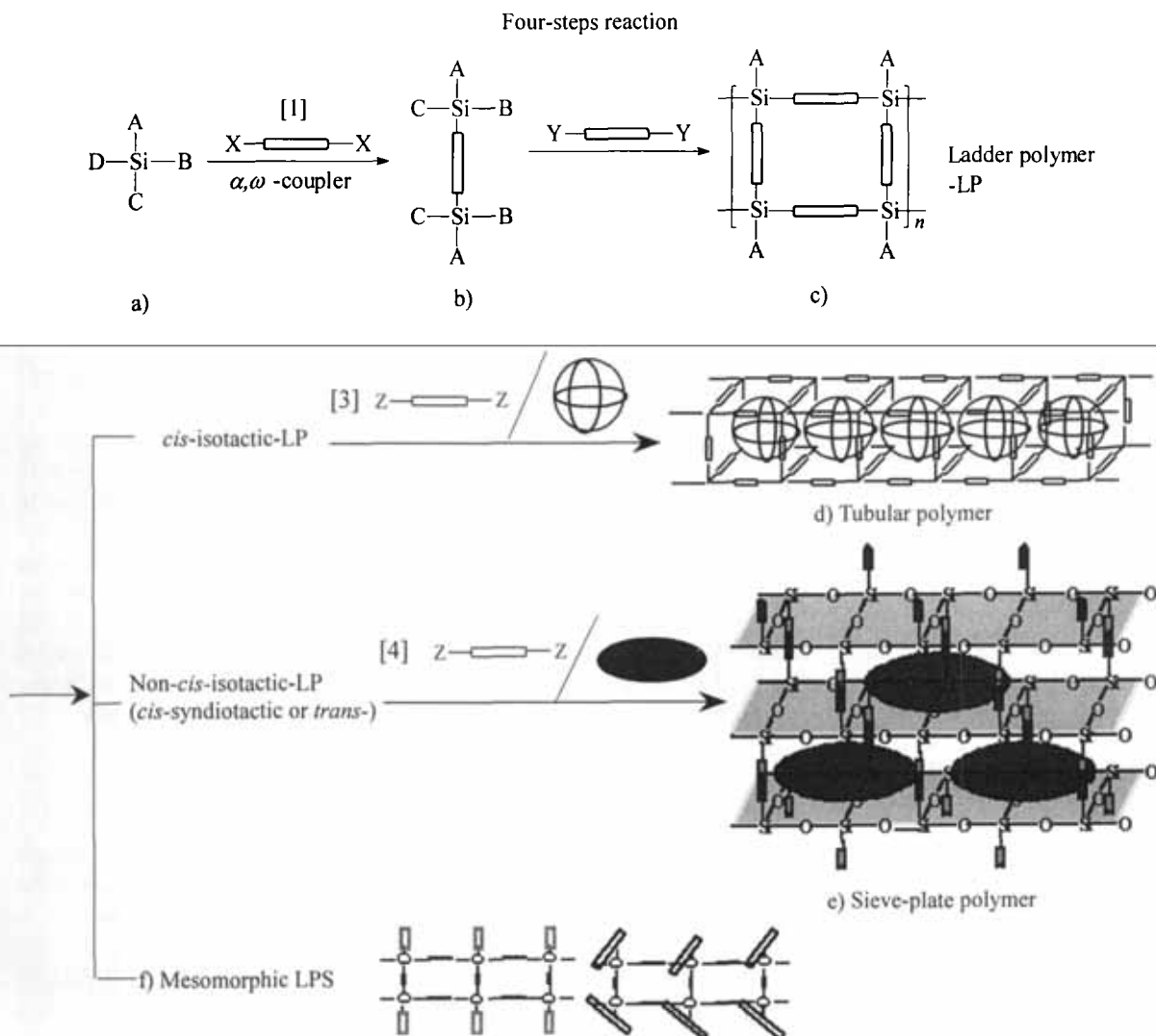


Fig. 1 Schematic representation for stepwise coupling polymerization (SCP)

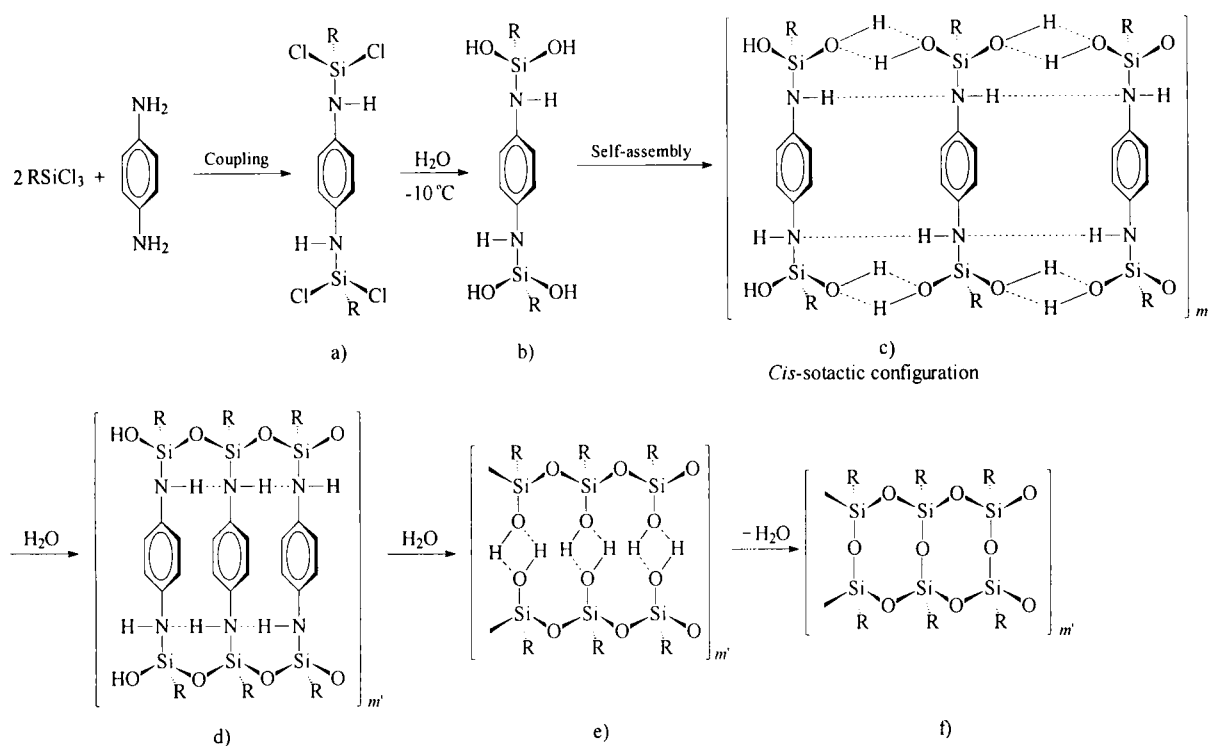


Fig. 2 Preparation process of ladderlike polysiloxane (LP) by pre-aminolysis

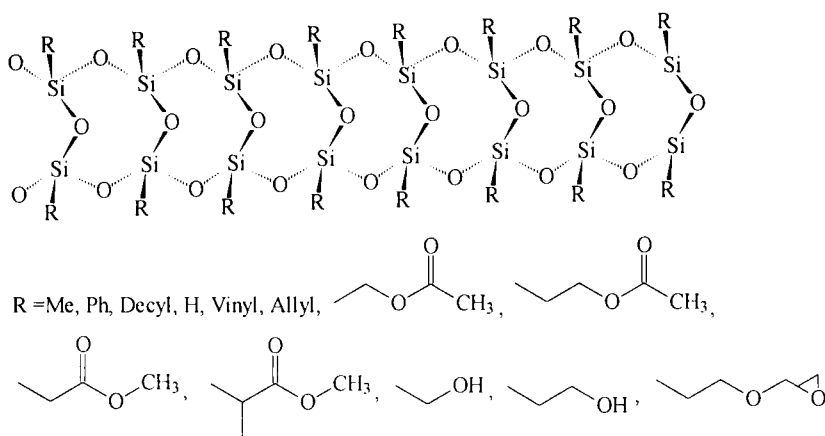


Fig. 3 Various ladderlike polysiloxanes

Ladder Poly-Organo-Bridged-Siloxane

The first poly-organo-bridged-siloxanes including poly-phenylene-bridged-siloxane and poly-biphenylene-bridged-siloxane were synthesized by SCP in 1992^[13]. The purpose of this preparation is to enlarge the pore size and change the pore shape and the chemical affinity of the tubular polymers derived from them. So far we have synthesized a series of non-reactive and reactive poly-organo-bridged-siloxanes as shown in Fig. 4.

MESOMORPHIC LADDER POLYMER (MLP)

The first comb-like liquid crystalline polymer (LCP) based on a single main chain polysiloxane was synthesized by Finkelmann in 1980^[14]. However, so far the comb-like LCP has not been widely commercialized. One reason for that is its poor mechanical properties and low liquid crystallinity. Fortunately, the ladder polysilsesquioxane

(LP) possesses excellent comprehensive properties such as fair mechanical properties, high thermal stability and film-forming ability and so on, which stem from its originally combined inorganic ladderlike backbone and organic side groups. During the last decade we have successfully synthesized a series of mesomorphic ladder polymers (MLP) by linking the mesogenic groups to the ladder main chain, which show a remarkably improved liquid crystallinity.

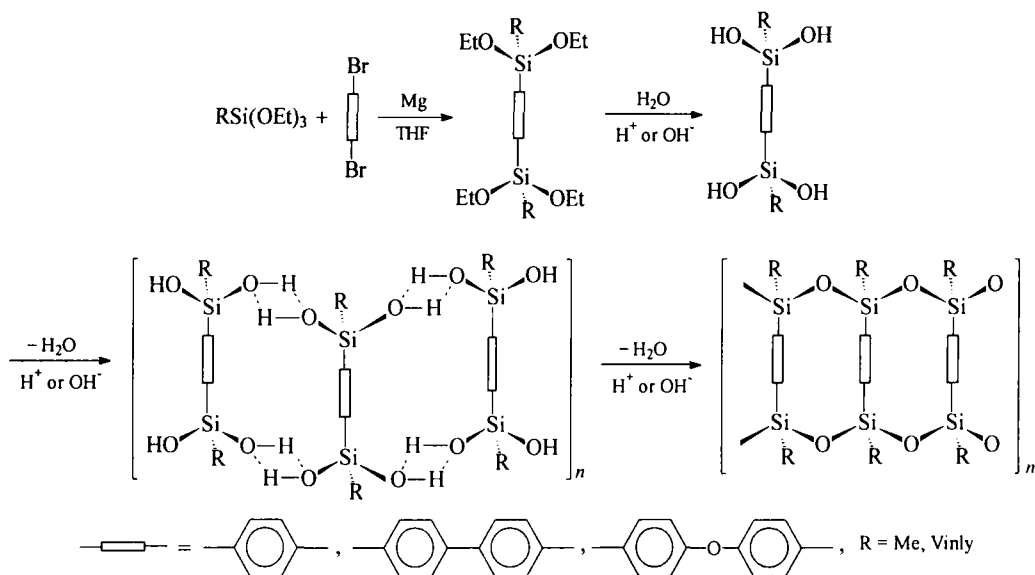


Fig. 4 Synthetic route of organo-bridged ladderlike polysiloxanes

There are two types of MLP as illustrated in Fig. 5. The so-called fishbone-like liquid crystalline polymer (FBLCP) and its metal complex in which the mesogenic groups are end-on fixed to the ladder main chain and the so-called rowboat-like liquid crystalline polymer (RBLCP) in which the mesogenic groups are side-on fixed to one side of the ladder main chain.

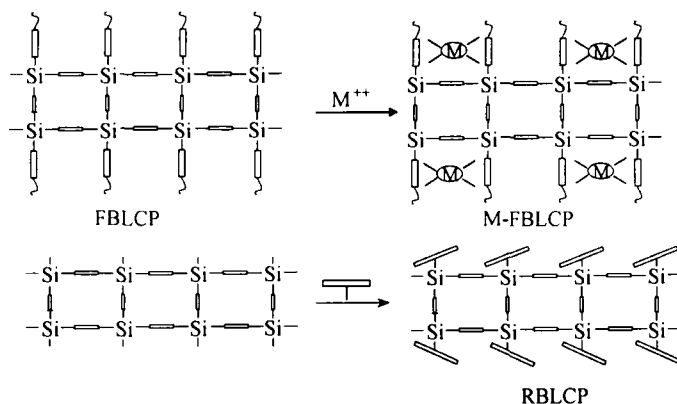


Fig. 5 Schematic representation of three-kinds of mesomorphic ladderlike polymers

Fishbone-Like Liquid Crystalline Polysilsesquioxane (FBLCP) and Its Metal Complex^[15-30]

Table 1 indicates the comparative results of mesomorphic properties for a single main chain LCP and the mesomorphic ladder main chain polymers. It can be seen that the mesophase range of fishbone-like FBLCP is much wider than that of the single main chain LCP by ca. 200°C. The metal complexes also show a similar trend but the values are not so significant because the complexes decompose before the clearing point. Generally speaking, the ladder main chain is conducive to improving the liquid crystallinity of the polymer.

Interesting potential applications of FBLCP include highly stable photo-driven command surfaces and pretilt-controllable alignment layers; they are expected to be used for advanced liquid crystalline display (LCD).

Table 1. Comparison of the mesomorphic properties of single and double main chain LCPs and complexes

Sample	Mole ratio of Cu(II)/DK	IR data (cm ⁻¹)	Phase trans. temp. / Δ <i>H</i> by DSC (°C / J • G ⁻¹)	Δ <i>T</i> (°C)	XRD <i>d</i> (nm)	Texture
AZLCP	0	Si—O—Si:1000-1100 N=N: 1580, 1605	K-(81/22.6) S-(113/51.4) N-(138/47.7) I	57	0.42	Mosaic
Pd-AZLCP	0.42	Si—CH ₂ —: 800, 1265	K-(97/10.4) N ₁ -(159/30.0) N ₂ -(200/-)I	103		Nd
AZFBLCP	0	Si—O—Si:1000-1100 N=N: 1580, 1605	K-(72/10.4)LC ₁ -(86/6.3)LC ₂ -(101/32.2)LC ₃ -(340/-)I	267.8	21.0 4.37	Bright lines
Pd-FBAZLCP	0.45	Si—CH ₂ —: 800, 1265	K-(169/12.9)LC-330(-) Dec.	160.8	19.63 12.27 6.99	

AZLCP: Comb-like polysiloxane containing azobenzene side chains; AZFBLCP: Fishbone-like mesogenic polysiloxanecontaining azobenzene side chains; Pd-AZLCP, Pd-FBLIC: PD-complexes of AZLCP, ZAFBLCP

Rowboat-Like Polysilsesquioxane (RBLCP) ^[31-33]

Ten years ago, Leslie reported a new nonlinear optical (NLO) polysiloxane with side-on fixed stilbene-type chromophores, which shows a very good second harmonic generation nonlinear optical (SHG/NLO) susceptibility, but whose signal decays very fast due to the high flexibility of the single main chain polysiloxane^[31]. We suppose that if the stilbene group is linked to a ladder main chain the decay property might be improved. Thus, we synthesized the RBLCP in which the stilbene group was linked to the ladder main-chain of LP without a flexible spacer. Interestingly, it is a liquid crystalline polymer, but the corresponding single chain polymer is not liquid crystalline. Moreover, compared with the latter, the decay property of RBLCP is greatly improved as also shown in Fig. 6.

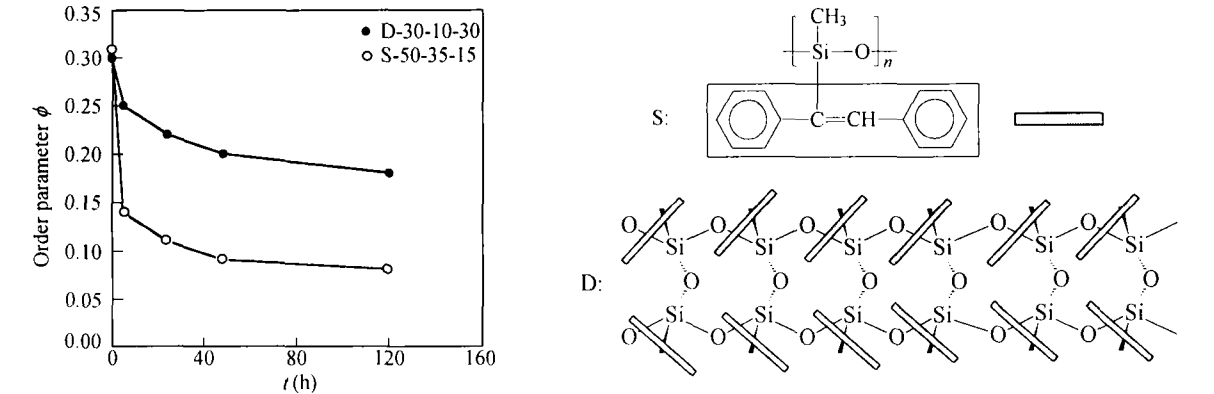


Fig. 6 Comparison on SHG decay property of poled films of single chain and double chain (ladder) polymers at 80°C

So we can say that the ladder main chain is not only helpful in improving the stability of NLO property, but also can be conducive to inducing the mesomorphic property. The IR dichroism and XRD studies confirmed that these mesogenic groups were arranged like the oars of a rowboat. So, imaginatively, we call it rowboat-like LCP.

SIEVE-PLATE POLYMER (SP) & ITS CLATHRATE ^[34-39]

As shown in Fig. 7, SP, as a host of this clathrate system, can be prepared from *cis*-syndiotactic or *trans*-syndiotactic LP. And if the NLO chromophore molecules, as the guests, can be simultaneously trapped in the pores of SP, this system would be expected to have good comprehensive second harmonic generation/nonlinear optical (SHG/NLO) properties. Generally, the SHG/NLO polymer can be prepared by physical blending, in this case the NLO chromophore molecules are dispersed in the polymers. Because the chromophore molecule is a polar compound, it aggregates easily to form a cluster containing 10~10⁵ molecules, the aggregation would

decrease the allowed content of chromophore and limit efficient poling. Besides, the molecular thermal motion can de-orient the already poled chromophore molecules. So, in order to obtain a good SHG/NLO polymer system we have to prevent the chromophore molecules from undergoing aggregation and also to prevent the poled chromophore molecules from undergoing de-orientation. How can we solve these problems?

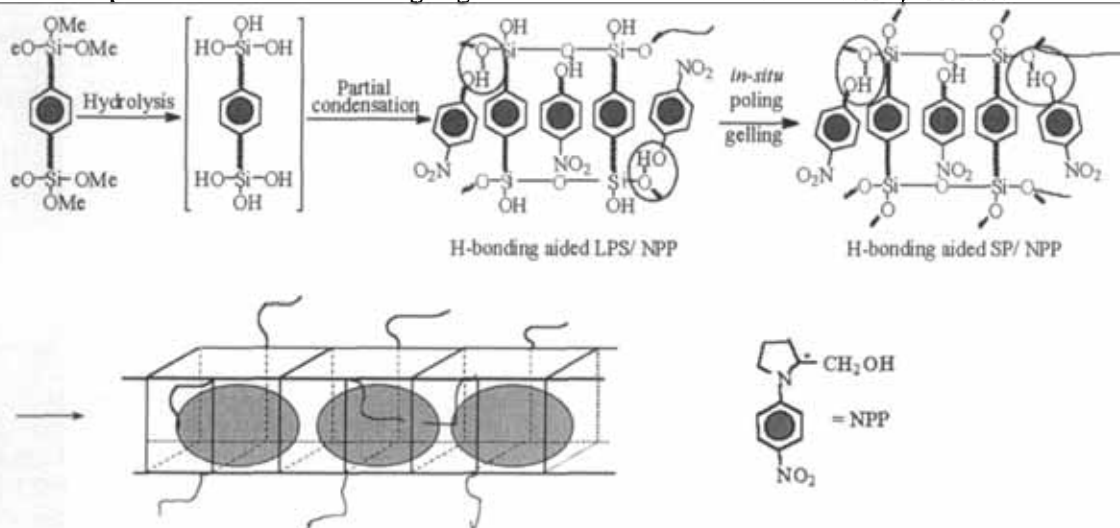


Fig. 7 Schematic process of forming sieve-plate (SP) and its clathrate

Years ago, Shea reported an organo-bridged polysilsesquioxane, in which an aggregate of semiconductor molecules CdS containing ca. 10^5 molecules was trapped^[34]. This clathrate can be used in the semiconductor device with a quantum effect. We presume that if the pore size of the polymer network can match that of the NPP molecule precisely, we can expect to trap NPP molecules in the pores of the polymer network on the molecular level, and the aggregation and the de-orientation might be avoided. By molecular simulation, the length and the width of NPP, a typical SHG/NLO chromophore, are 0.8 nm and 1.2 nm, respectively. A new monomer was tailor-made to match these sizes^[35–39], the distance between the two silicon atoms is 1.2 nm which is equal to that of NPP. Figure 7 shows the proposed preparative process for the clathrate. At first, the designed monomer is hydrolyzed to get a silanol which is then condensed to get the ladder oligomer and the prepolymer. In the meantime, NPP molecules and the ladder oligomers and prepolymers are self-assembled through H-bonding to form a clathrate system in which NPP molecules are arranged in the same or opposite direction. Next, by *in-situ* poling/gelling almost all the NPP molecules become oriented and, in turn, fixed by crosslinking simultaneously.

DSC measurement (Fig. 8) shows that the pure NPP has a melting peak at 118°C, while the title clathrate film which contains even 50 mol% of NPP does not show any melting peak, the DSC curve is a horizontal line. That indicates that there is no NPP crystalline aggregate. In other words, the NPP molecules are dispersed on the molecular level.

Figure 9 is the IR spectrum of the title film. Spectrum a) represents NPP and spectrum b) belongs to the title film. It is obvious that there is a blue-shift by 7 cm^{-1} between the two samples. That is due to the change in conjugation, because in pure NPP the NO_2 group is co-planar with the benzene ring, but when the NPP molecule is trapped in a confined pore the NO_2 group can no longer be co-planar with the benzene ring. The NO_2 group becomes warped. Thus, the conjugation is decreased. The AFM images show that for pure sieve-plate polymer the distance between the two adjacent polymeric chains is 0.4 nm and the distance for the title clathrate system is increased to 1.4 nm which is similar to the length of NPP. This result indicates that the NPP molecules can prop up the polymer chains when they are trapped in the pores.

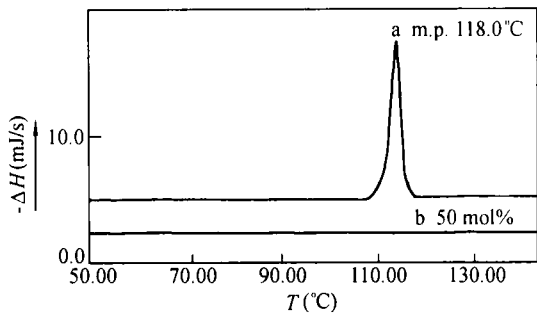


Fig. 8 DSC thermograms of pure NPP and SP/NPP clathrate

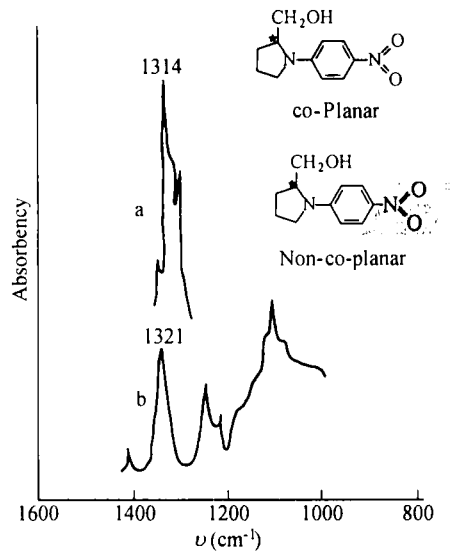


Fig. 9 FTIR spectrum of NPP a) and SP/NPP clathrate b)

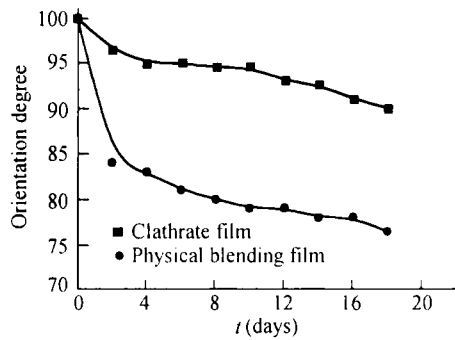


Fig. 10 Comparison of SHG decay property between SP/NPP clathrate (above) and blending (bottom) samples

Table 2. Comparison of two kinds of poled NLO films

Item	SP/NPP film	Blend film
Appearance	1) Transparent, hard & uniform; 2) No phase separation when C = 50 mol% of NPP	1) Translucent & rotten film 2) Phase separation when C = 25 mol% of NPP
NLO- d_{33}	$\geq 2 \times 10^{-8}$ e.s.u.	$\leq 1 \times 10^{-9}$ e.s.u.
Temporal stability	Decay slowly by 5 % after 10 days (at R.T.)	Decay fast by 20 % after 10 days (at R.T.)
DSC	Without melting peak of NPP	A melting peak of NPP at 118°C
FTIR	A blue-shift of ν_{NO_2} of NPP at 1321 cm^{-1}	ν_{NO_2} of NPP at 1314 cm^{-1}
AFM	Periodically parallel & bright lines with spacing of 1.4 nm	Many black spots of NPP aggregates
Solubility	Acetone-inextractable	Acetone-extractable to give a yellow solution
Remarks	Mainly dispersed at molecular level	Mainly dispersed with molecular aggregates

Next, Fig. 10 demonstrates the difference in decay situation of the two samples. The bottom curve is for a general physically blended sample. The upper curve is for the title clathrate film. The former decays much faster than the latter. All results are summarized in Table 2, which indicates that the title film can contain even as much as 50 mol% of NPP without phase separation. But for the general physically blended film when the content

reaches 25 mol% phase separation occurs. Compared with the physically blended film, the NLO property of the title film is increased by 10 times and the decay property for the title film is improved too. Thus, we can draw the conclusion that the improved NLO property of the title film arises from the fact that the NPP molecules are dispersed on molecular level therein.

TUBULAR POLYMER (TP)

The first organic TP, polycyclodextrin nanotube, was prepared by the Japanese chemists Harada and Kamachi in 1993^[40]. This is a great contribution to the field of polymer science and material science.

There is another kind of TP, which is constructed from *cis*-isotactic LP by (1+1) or (2+2) mode as shown in Fig. 11 and Fig. 12.

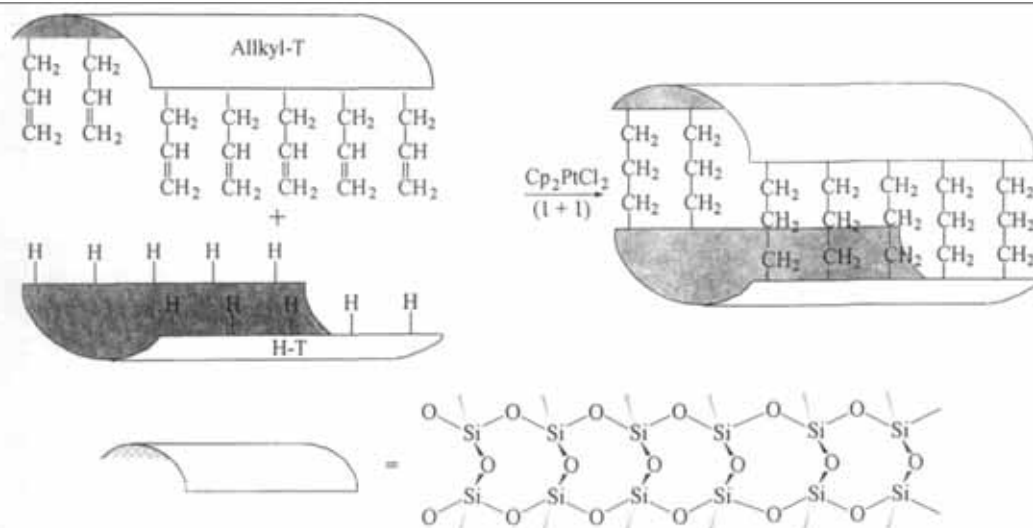


Fig. 11 Schematic representation of the forming process of 1+1 mode TP

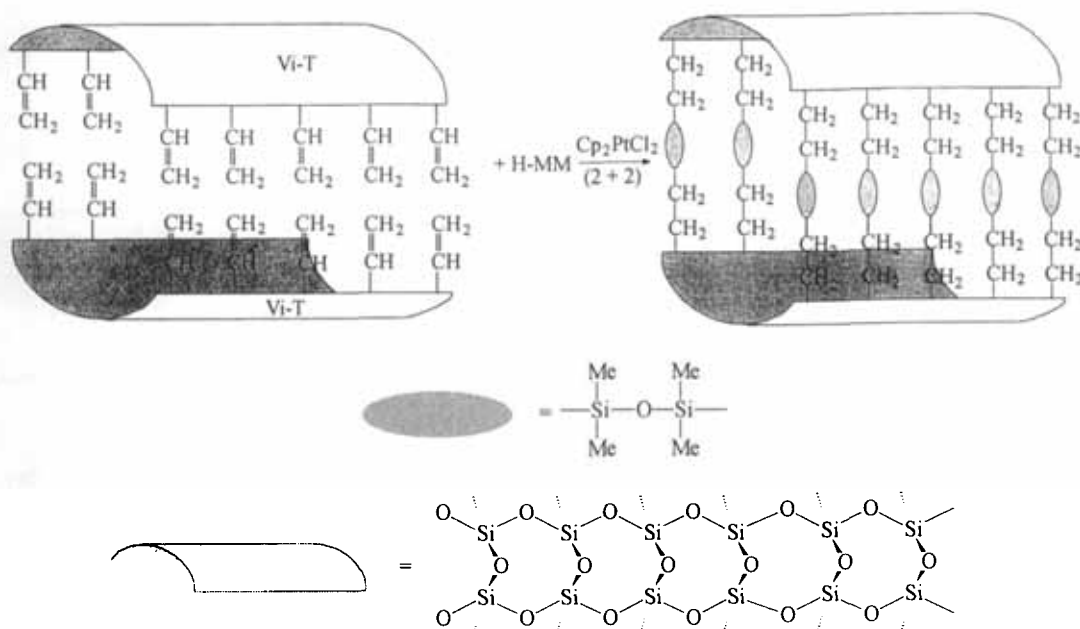


Fig. 12 Schematic representation of the formation process of 2+2 mode TP

Why can the LP form TP? The first reason is that the reactive LP prepared by SCP has a *cis*-isotactic configuration and the second reason is that there are molecular interactions such as hydrogen-bonding, donor-acceptor, π - π interaction and so on, between two kinds of reactive LPs or between the reactive LPs and the couplers. These are conducive to the formation of a tubular structure. The third reason is that the silicon compounds have a strong ring-forming tendency.

We prepared a (2+2) mode tube from Vi-T and H-MM^[41-47] and also a (1+1) mode TP from A-T and H-T^[48]. Moreover, we prepared a series of TPs with different pore sizes and different chemical affinities by changing the small mass coupler or bridge of the LP^[49-52] as shown in Table 3. We also trapped LC molecules and organic fluorescent probes into the inside of the TP to form a supermolecular inclusion system. For example, TP₅ was prepared with two ladder polyallylsilsesquioxanes (A-T) and two coupler phenyl ether-bridged tetramethyldisilanes in (2+2) mode; a liquid crystal BBOA of 2.5 nm length and 0.75 nm diameter was *in-situ* trapped in the tubular polymer. Figure 13 depicts the tube-forming and *in-situ* trapping process. Under a polarizing microscope the blend of BBOA and TP₅ exhibited birefringence caused by the crystalline BBOA phase while for the clathrate of BBOA and TP₅ with the same BBOA content, 7 wt%, no birefringence was observed. This means in the latter situation that BBOA molecules trapped in the TP₅ are molecularly dispersed without any aggregation and crystallization.

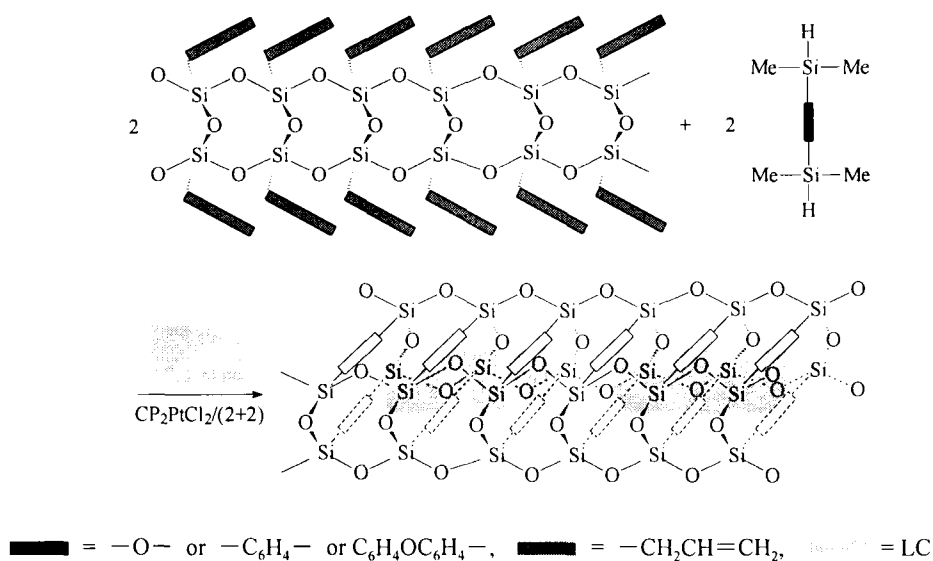


Fig. 13 Schematic representation of *in-situ* trapping of LC in a tube-polymer

Figure 14 shows the DSC curves of a) TP₅, b) the clathrate TP₅/BBOA and c) the blend of BBOA and TP₅. Similarly, only sample c) exhibits a melting point while sample b) shows an almost horizontal line. This result also indicates that LC molecule BBOA does not form a crystal when trapped in the clathrate.

X-ray diffraction (XRD) patterns of a) the starting material, reactive ladder polymer, A-T and b) the TP₅ are shown in Fig. 15. It is obvious that compared with A-T the diffraction peak of TP₅ is shifted to small angles, indicating that TP₅ has a higher regularity than its precursor A-T.

The atomic force microscopy (AFM) images of a) A-T, b) TP₅ and c) TP₅/BBOA show that the tube diameters for the three samples are 0.85, 1.27 and 1.28 nm, respectively. This result is consistent with the data calculated by molecular simulation.

Figure 16 shows the cross section of TP₅ based on molecular simulation. The inside shape is not circular but approximately rectangular. If an organo-bridged reactive LP is used the TP therefrom would have a circular pore.

Table 3 summarizes the characterization data of five TPs prepared so far.

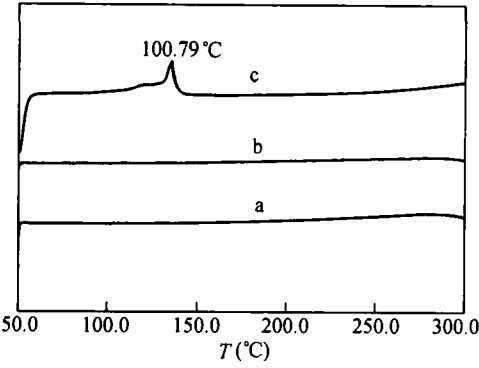


Fig. 14 DSC curves of a) TP, b) TP₃/LC and c) the blend of LC (BBOA) and TP₃

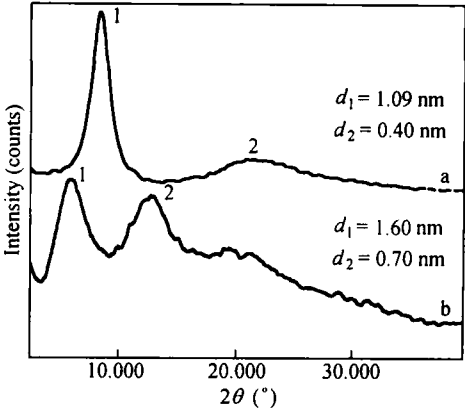


Fig. 15 Comparison on X-ray diffraction patterns of a) ladder polymer (Allyl-T) and b) tube-polymer (TP)

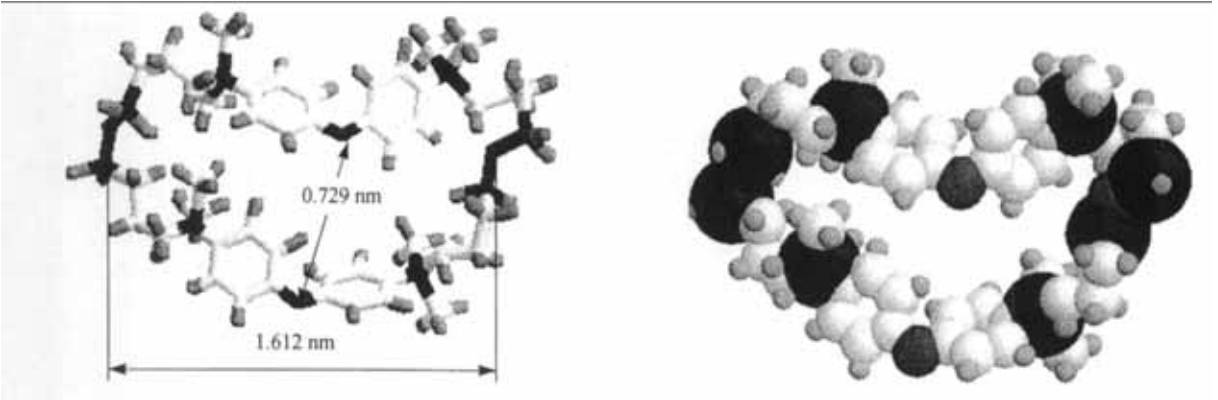


Fig. 16 Molecular simulation of tube-polymer (TP₃)

Table 3. Characterization data of five kinds of TPs

TP	Mode	Order of polarity	Width and length		Methods
			AFM	Molecular simulation (cross section)	
1) ALLYL-T + H-T	I + I	5	0.26±0.02 nm	0.44 × 0.70 nm	Solubility, FTIR, ¹ H-NMR, DSC, GPC, XRD, AFM, molecular simulation
2) 2Vi-T + 2HMM	II + II	1	0.72±0.02 nm	0.57 × 0.94 nm	Solubility, FTIR, ¹ H-NMR, POM, GPC, VPO, DSC, XRD, QELS, AFM, simulation
3) 2Allyl-T + 2HMM	II + II	2	0.96±0.02 nm	0.50 × 1.17 nm	Solubility, FTIR, ¹ H-NMR, POM, GPC, VPO, DSC, XRD, AFM, simulation
4) 2Allyl-T + 2M ₄	II + II	4	1.02±0.02 nm	0.43 × 1.45 nm	
5) 2Allyl-T + 2M ₅	II + II	3	1.27±0.02 nm	0.73 × 1.61 nm	

M₄ = HSi(CH₃)₂C₆H₄(CH₃)₂SiH, M₅ = HSi(CH₃)₂C₆H₄OC₆H₄(CH₃)₂SiH

As mentioned above the existence of nano-tubular cavities has been preliminary confirmed by a combination of characterization techniques including IR, NMR, X-ray diffraction, vapor pressure osmometry (VPO), atomic force microscopy (AFM), fluorescence spectral analysis, DSC, difference in solubility and molecular simulation. All these studies were performed to elucidate the structure of the nanotubular cavities and

also to provide guidance for the selection of proper guest molecules in constructing a TP-based functional supramolecular clathrate. However, due to the small size of the cavities, up to now it is still difficult to obtain a direct observation of individual TP molecules, and hence, the guest molecules to be selected are greatly restricted. At present, work on the preparation and characterization of TPs of larger size is in progress.

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