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A glance at the relation of stepwise coupling polymerization to supramolecular chemistry

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Abstract

A relationship between supramolecular chemistry and *stepwise coupling polymerization* (SCP) found by our group is briefly described. By SCP reaction a series of new kinds of microstructure-controlled polymers and their corresponding supramolecular inclusions such as: (1) reactive ladder-like polysiloxanes (LPS); (2) liquid crystalline ladder-like polysiloxanes and their metal complexes including fishbone-like LCPs (FBLCPs) and their metal complexes (M-FBLCPs) and rowboat-like LCPs (RBLCPs); (3) tubular polymers (TPs) and their supramolecular inclusions (TPIs) and (4) sieve-plate-like network polymers (SNPs) and their supramolecular clathrates (SNPC) have been successfully prepared. It is reasonably stated that SCP is a supramolecular interaction-aided reaction and moreover, SCP is an effective method to generate new supramolecules. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Stepwise coupling polymerization; Supramolecular interaction

1. Introduction to SCP reaction

The stepwise coupling polymerization (SCP) reaction route is illustrated in Fig. 1, which is given in some reviews on SCP elsewhere [1–4]. A tetrafunctional silicon compound, (A,B,C,D)Si, (a), where A,B,C,D represent four different reactive groups linking to Si-atom, respectively, is chosen as starting monomer. A bridged intermediate (b) is first obtained by the reaction of monomer Si(A,B,C,D) with α,ω-coupling agent (abbreviated as α,ω-C)

X-▭-X

Then, in the second step, a ladder-like oligomer (C) or polymer (C′), (LPS), is formed by the reaction of the intermediate (b) with another (α,ω-C)

Y-▭-Y

If the LPS is of *cis*-isotactic configuration, a tubular polymer, TP (d), can be prepared. Alternatively, if the LPS is of non-*cis*-isotactic such as *cis*-syndiotactic configuration, a sieve-plate network polymer, SNP (e), can be obtained by further coupling with

Z-▭-Z

Moreover, suitable rod-like or sphere-like molecules can be entrapped into the pores of TP or SNP as guest by in situ tube-closure reaction to form the corresponding supramolecular inclusions (TPIs). Obviously, the molecular recognition ability featuring the shape, size and chemical affinity of these different multi-dimensional and structure-ordered polymers can be controlled by choosing the monomers Si(A,B,C,D) with different groups (A,B,C,D) with different groups (A,B,C,D) and appropriate (α,ω-C)s.

2. The new microstructure-controlled polymers prepared by SCP

2.1. Reactive ladder-like polysilsesquioxanes (LPS)

As early as in 1960s, Brown et al. [5,6] first prepared soluble, ladder-like polyphenylsilsesquioxane (abbreviated

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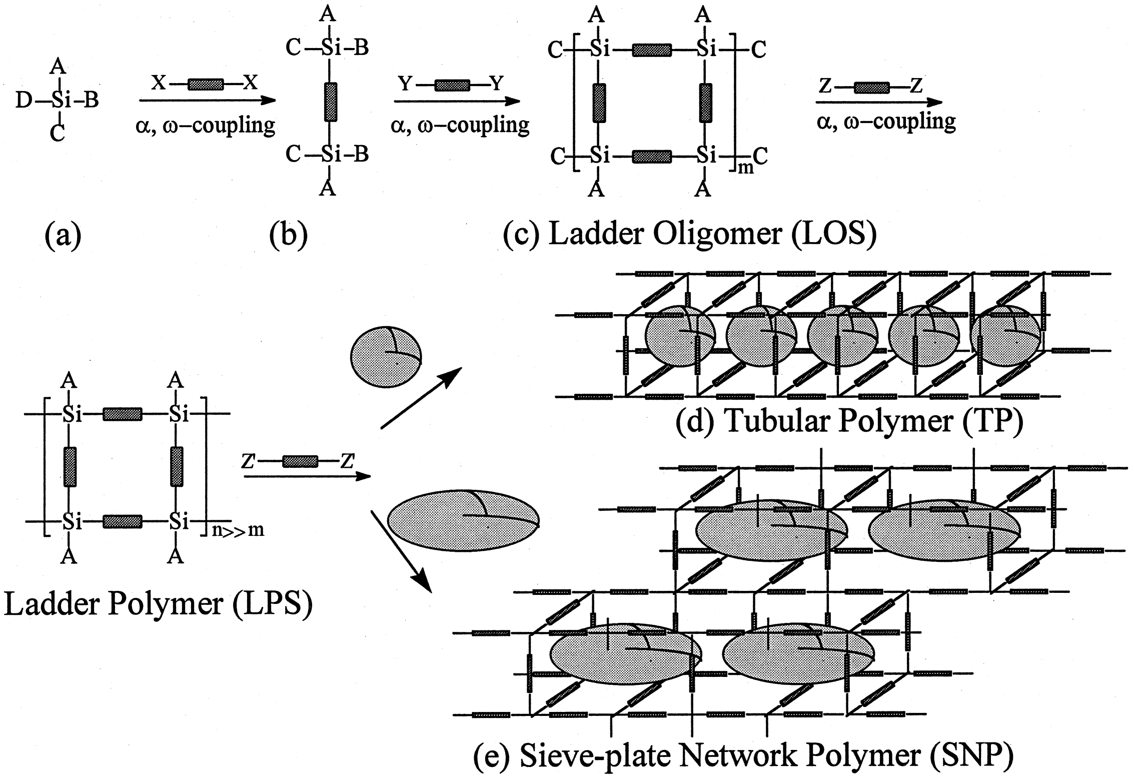

Fig. 1. Stepwise coupling polymerization.

as Ph-T) instead of the usual insoluble random network polymers by ''equilibration polymerization'' using the trifunctional monomer (phenyltrichlorosilane). But, this method cannot be used to synthesize reactive LPS such as ladder-like polyhydrosilsesquioxane (H-T) or polyvinyl (or allyl) silsesquioxane (Vi-T or A-T) due to the harsh reaction conditions used (at 250°C in the presence of KOH). We designed the so-called ''SCP'' to prepare a series of LPS including polymethylsilsesquioxane (Me-T) [7,8], Ph-T [9], especially, reactive H-T [10,11], allyl-T or Vi-T [12], polyestersilsesquioxane (E-T) [13], polyalkylsilsesquioxane [14] and ladder polyphenylene-bridged siloxanes [15].

A proposed route for the supramolecular H-bonding-assisted synthesis of LPS is shown in Fig. 2. By preaminolysis of trichlorosilane with (α,ω-C), *p*-phenylenediamine (PDA), which is one kind of SCP, the bridged intermediate (1) was first obtained, which is then hydrolyzed to form intermediate (2). Its OH-groups can form planar hydrogen-bonds suggested by Kakudo and Watase [16], Kakudo et al. [17] and Kasai and Kakudo [18]. Because of the existence of tetrahedral configuration of the Si-atom and through the H-bonding interaction the compound (2) can be self-assembled to generate the *cis*-isotactic oligomeric bridge aggregate (3) and oligomer (4). Next, the bridge of (4) is hydrolyzed and further condensed to form intermediate (5) and finally the title polymer (6) with regular ladder-like skeleton.

2.2. Mesomorphic ladder-like polysiloxanes: fishbone-like and rowboat-like LCPs (FBLCPs and RBLCPs)

The first side-chain liquid crystalline polysiloxane (SCLCP) was prepared by Finkelmann and Rehage in 1980 [19]. To explore mesomorphic ladder-like polymers, two new kinds of LCPs, so-called ''fishbone-like'' (FB) [20–25] and ''rowboat-like'' (RB) LCPs [26,27] have been synthesized by linking the mesogenic groups onto the ladder-like main chain in manner of terminally (end-on) or laterally (side-on) fixing.

The FBLCPs and their metal complexes possess much higher clearing points and wider mesophase ranges by ca. 200°C compared to the corresponding SCLCP with a single main chain. Also, the RBLCP-based second harmonic generation non-linear optical (SHG/NLO) film exhibits low decay SHG property. This is attributed to the ordered supermolecular assembly stabilized by the semi-rigid ladder-like main chain.

The major applied exploration of LPS-based LCPs is related to the photo-active alignment layers (command surface) and pretilt angle-adjustable alignment films with stable and high pretilt angle (~ 11°) [28–32].

2.3. Tubular polymers and their supramolecular inclusions

The first synthetic organic TPs, polycyclodextrins, were reported by Harada et al. in 1993 [33]. The pore sizes of

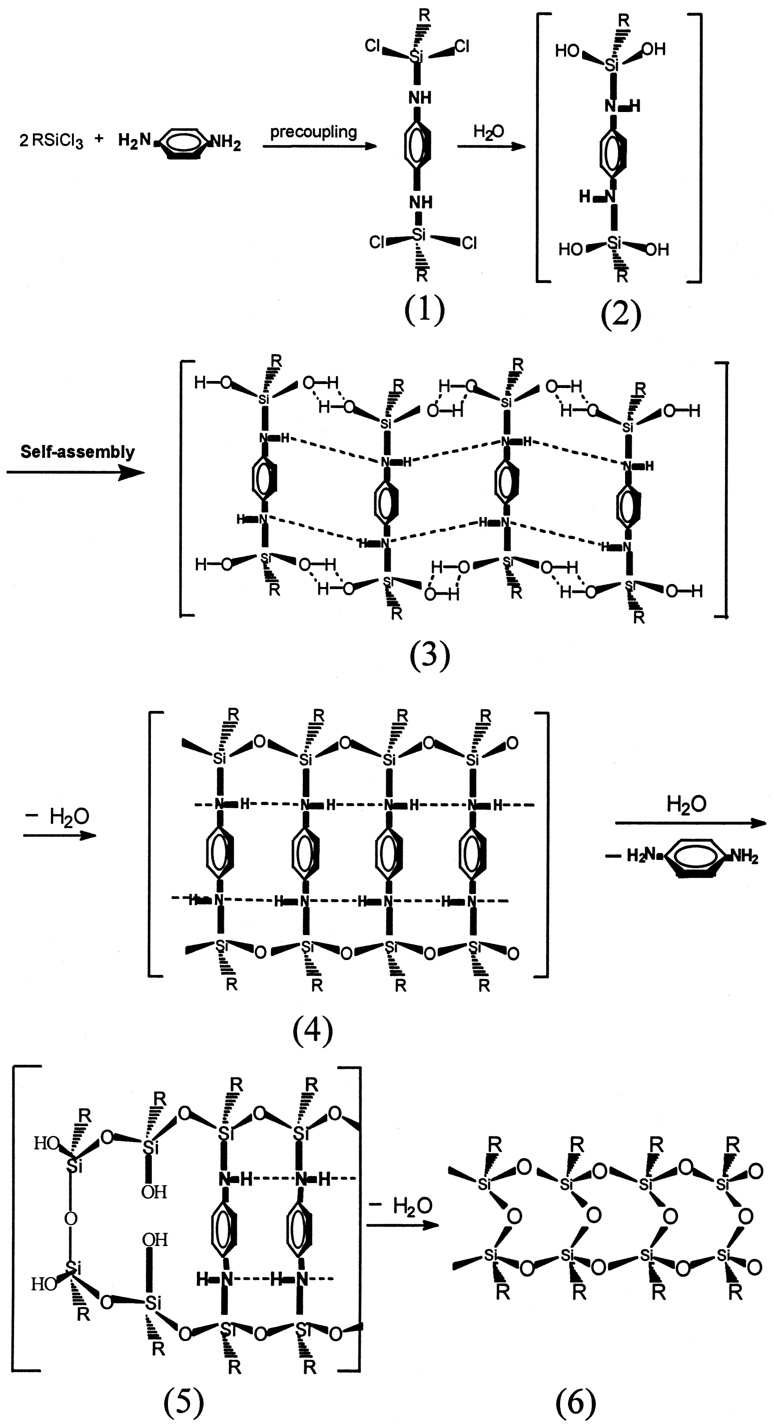

Fig. 2. A proposed mechanism on the LPS formation.

the TPs are dependent on those of the natural products, α, β or γ-cyclodextrins. To synthesize microstructure-controllable TP the reactive *cis*-isotactic LPSs are the ideal candidate building blocks. The TPs can be prepared by $(1+1)$ or $(2+2)$ ways. The former represents that the cross-section of the TP formed consists of a structural unit of one kind of reactive *cis*-isotactic ladder-like macromolecule such as Vi-T or allyl-T, and of a structural unit of another kind of reactive, *cis*-isotactic ladder-like macromolecule such as H-T. The second way represents that the cross-section of the TP formed consists of two structural units of one kind of reactive, *cis*-isotactic ladder-like macromolecule such as Vi-T, allyl-T or H-T and two structural units of another kind of reactive α,ω-coupling

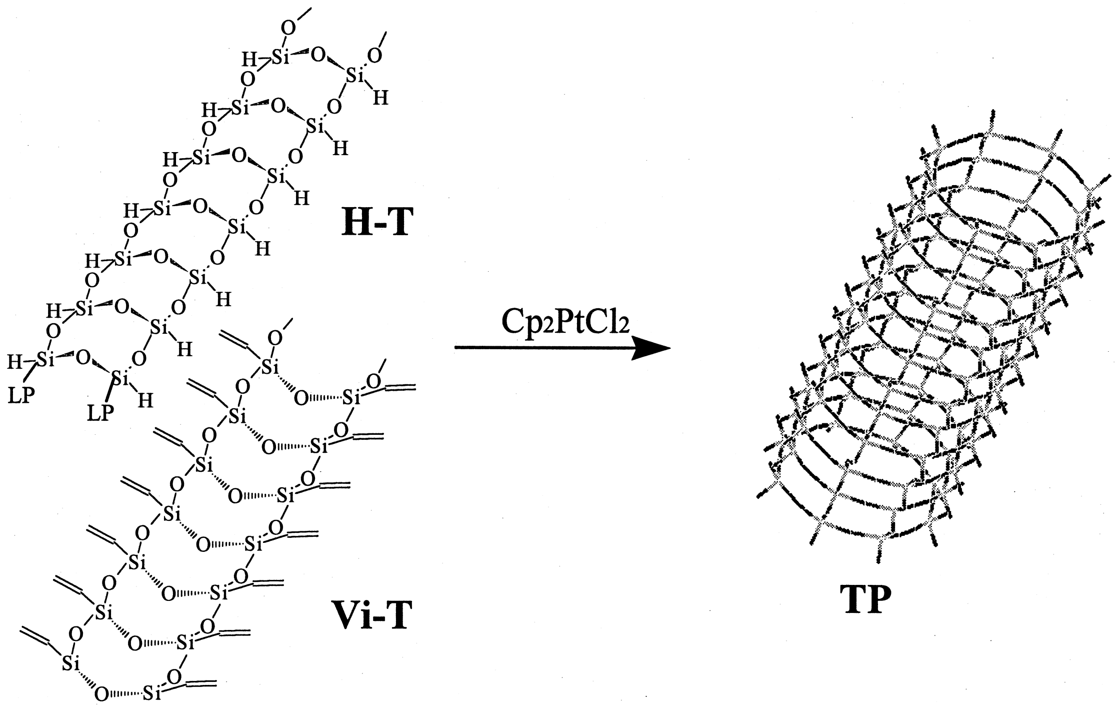

Fig. 3. A proposed ''zipping'' model for TP formation.

agents such as 1,1,3,3-tetramethyldisiloxane (H-MM) or 1,1,3,3-tetramethyldivinyl-disiloxane (V-MM). To make the tube-formation reaction complete, the Pt complex-catalyzed hydrosilylation is used. For example, A (TP) is prepared by the reaction of ladder-like (Vi-T) with H-MM using dicyclopentadienyl-dichloroplatinium (Cp_2PtCl_2) catalyst in tetrahydrofuran (THF) [34,35], which is characterized by infrared spectroscopy (IR), ^{1}H NMR, ^{13}C NMR ^{29}Si NMR, differential scanning calorimetry (DSC), X-ray diffraction method, gel permeation chromatography (GPC), vapour pressure osmometry (VPO), atomic force microscopy (AFM) and corroborated by molecular simulation. These results prove that the product obtained contains a nano-scale tubular structure with the outside diameter $\Phi_o = 1$ nm and inside diameter $\Phi_i = 0.7$ nm.

A supramolecular tubular polysiloxane inclusion, TPI, has been also prepared by in situ tube-closure and entrapping rod-like Schiff-base liquid crystal molecule, *p*-

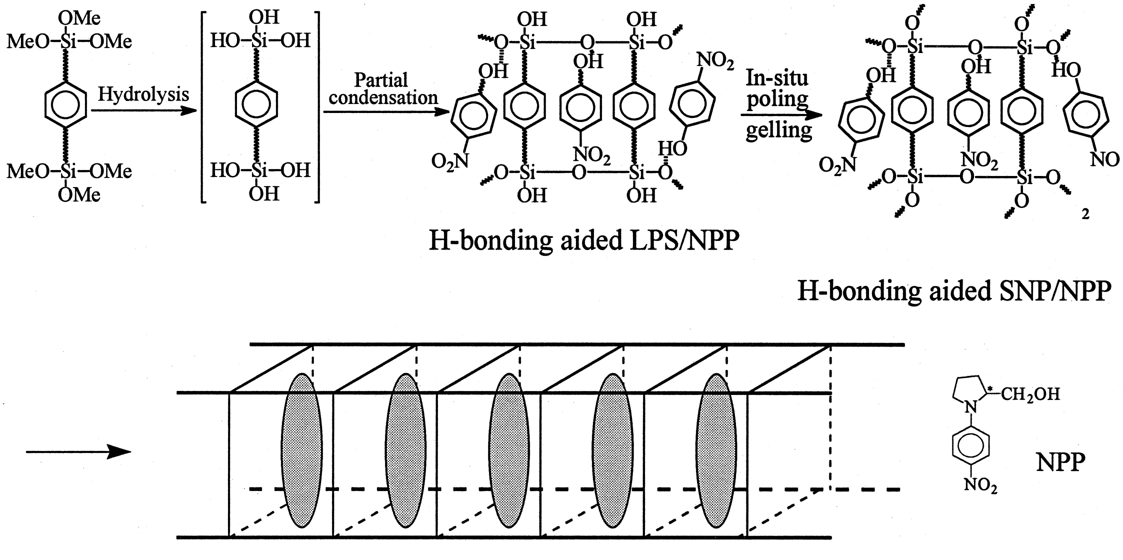

Fig. 4. Proposed mechanism for preparation of the SNP/NPP supramolecular clathrate film.

butoxybenzylidene-p'-dodecoxyaniline (BBDA) within the pore of TP [36,37]. Investigation by polarized light microscopy (PLM), DSC, IR, AFM and molecular simulation gives a preliminary support to the existence of the title supramolecular inclusion.

A proposed $(1+1)$ way of a zipping mechanism for the construction of TP from Vi-T and H-T is shown in Fig. 3.

2.4. Sieve-plate-like network polymers and their supramolecular clathrates (SNPC)

This work is related to preparation of SHG/NLO polymer. In general physical bending the chromophoric molecules are dispersed within the pores of crosslinking polymer at molecular aggregate (ca. 10^{2-5} molecules). So, the SHG/NLO property is rather low such as fast decay of the signal, inferior NLO activity and poor mechanical behavior. A novel SHG/NLO, self-assembling crosslinking film with high SHG coefficient ($d_{33} = 2 \times 10^{-7}$ esu by IR diehroism) was prepared by molecular design and ''in situ poling and sol–gel process'' [38–40]. In the presence of a NLO chromophore (S)-($-$)-1-(4)-nitrophenyl-2-pyrrolidinemethanol (NPP), a designed organo-bridged monomer, bis-(1,4-allyloxybenzene)trimethoxysilane was synthesized and hydrolyzed to form a ladder polysiloxane, to which NPP molecules were self-assembled by H-bonding. Then the ladder polymer was further condensed to produce a SHG/NLO film constructed with a sieve-plate silicone gel and NPPs entrapped. The content of NPP is a high as 50 mol% in comparison with 25 mol% of general blending. A proposed mechanism for the formation of this low-decay SHG/NLO supramolecular clathrate film is shown in Fig. 4 where the self-assembly of NPP by H-bonding is clearly illustrated.

3. Preliminary conclusion

The SCP is a supramolecular interaction-assisted reaction. The supramolecular interactions include the hydrogen-bonding, transition-metal ion-ligand coordination van der Waals force... and so on, which play an important role to control the microstructures including the stereochemical configuration and the shape, size of the pore of the polymers. Moreover, the SCP reaction can be employed to prepare supramolecular systems such as ladder-like liquid crystalline polymers and their metal complexes, and numerous inclusions of well-defined structure polymer and functional molecules entrapped in it.

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