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A Novel Aryl Amide-Bridged Ladderlike Polymethylsiloxane Synthesized by an Amido H-Bonding Self-Assembled Template

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Abstract: A novel soluble aryl amide-bridged ladderlike polymethylsiloxane (A-LPMS) was synthesized by stepwise coupling polymerization on the basis of amido H-bonding self-assembling template from monomer *N*,*N*′-bis(3-methyldiethoxylsilylpropyl)-[4,4′-oxybis(benzyl amide)]. The monomer was prepared in a high yield by the hydrosilylation reaction of template agent *N*,*N*′-diallyl-[4,4′-oxybis(benzyl amide)] with methyldiethoxysilane in the presence of dicyclopentadienylplatinum dichloride (Cp_2PtCl_2) as catalyst. A variety of techniques including ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, FTIR, XRD, DSC, and, especially, static and dynamic light scattering and viscosimetry were combined to confirm the presence of the ordered ladderlike structure of polymer A-LPMS.

Introduction

In general, ladderlike polysiloxane is divided into two categories: oxygen-bridged polysiloxane (i.e., polysilsesquioxane) and organo-bridged polysiloxane. As early as 1960, Brown et al.[1] first reported the synthesis of a soluble ladderlike polyphenylsilsesquioxane (Ph-T) via “equilibration polymerization”. However, its structure was disputed 11 years later by Frye and Klosowski. They concluded that the Ph-T is not a really ladderlike polymer, but actually “partially opened polycyclic cages”.[2] The reason is that the reactive intermediates (phenylsilanetriols) form some randomly interlaced aggregates rather than the ordered ladderlike ones due to the absence of template assistance.

Different from the oxygen-bridged polysilsesquioxane, organo-bridged polysiloxane usually possesses better compatibility with commercial polymers, improved mechanical properties, and especially versatile structural adjustability. Thus, the synthesis of this new kind of polymer has attracted great interest from polymer chemists all over the world. Unfortunately, it has been over 40 years since Andrianov et al.[3] attempted to synthesize 1,4-phenylene-bridged ladderlike polymethylsiloxane (PLPMS) in 1960. He obtained an insoluble cross-linked gel instead of ladderlike polymer, because the reaction temperature (∼100 °C) used is so high that the template effects of the $\pi-\pi$ stacking of bridged phenylene are entirely destroyed. Thirty years later, Fukuyama et al.[4] again mentioned the preparation of so-called PLPMS of an imaginary ladderlike structure, but no characterization data were given. In recent years, the synthesis of microstructure-controlled polymers based on a self-assembly template of weak interactions (e.g., H-bonding, π-π stacking, van der Waals force) has been investigated.[5] Harata et al.[6] synthesized a polymeric nanotube of cyclodextrins by linking neighboring cyclodextrins prethreaded with poly(ethylene glycol) chain through H-bonding and van der Waals interactions. Stupp et al.[7] prepared two-dimensional polymers through molecular recognition based on homochiral and π-π stacking interactions. Most recently, Joël et al.[8] successfully prepared long-range-ordered lamellar hybrid silica through an amido H-bonding self-assembly.

In the light of these achievements, our group developed a templating scheme to prepare oxygen-bridged ladderlike polysilsesquioxanes.[9] It involves preaminolysis of trichlorosilane with 1,4-phenylenediamine to form a coupled intermediate capable of autoassociation to ladderlike superstructure through H-bonding of amino and silanol groups, followed by hydrolysis and polycondensation process. By this method, a series of ladderlike polysilsesquioxanes $(RSiO_{3/2})_n$ (R = alkyl, aryl, allyl,

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amino, and so on) have been synthesized.[10] In recent years, we also prepared some organobridged ladderlike polysiloxanes including phenylene-bridged polysiloxane and its mesomorphic polymers,[11,12] diphenyl ether-bridged polysiloxane and aryl ester-bridged polysiloxane via $\pi-\pi$ stacking template.[13,14] Although these materials possess various interesting properties, their structure imperfection and irregularity are noticeable due to the weak template effect of phenylenediamine caused by fragile amino H-bonding (N−H···N) and weak $\pi-\pi$ interactions. Most recently, we reported the synthesis of ladderlike polysiloxane based on a hydroquinone H-bonding self-assembling template.[15] However, its regularity is still limited because of the easy destruction of H-bonding via oxidation of hydroquinone. In addition, its ladderlike structure was not fully confirmed, due to lack of light scattering and viscosimetry investigation. Obviously, efficient templates with strong secondary interactions are extremely desirable for preparing highly ordered ladderlike polysiloxanes.

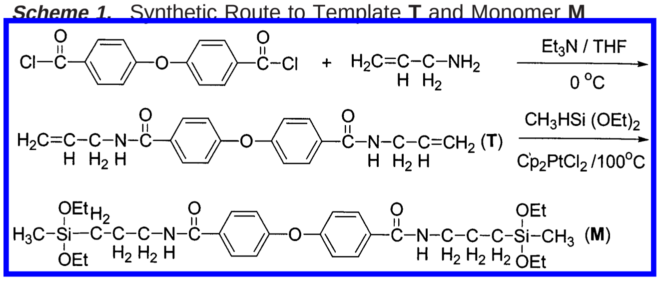
It is well-known that the amido H-bonding (N−H···O═C) existing in natural or synthetic polyamide is much stronger and stabler compared with the $\pi-\pi$ stacking interaction. For example, poly(*p*-phenylene terephthalamide) can form H-bonding-based lyotropic liquid crystal in concentrated sulfuric acid or *N*-methylpyrolidone (NMP), which has been spun into a high-strength fiber (Kevlar) for use in bullet proof vests by Du Pont Co. since the early 1970s. So far, many 1-, 2-, and 3-dimensional supramolecular arrays aggregated through amido H-bonding interaction have been reported.[16] Herein, we report the design and preparation of a new template, *N*,*N*′-diallyl-[4,4′-oxybis(benzyl amide)] (**T**), which possesses much stronger intermolecular amido H-bonding and its use as a powerful template to synthesize highly ordered aryl amide-bridged ladderlike polymethylsiloxane (A-LPMS).

Experimental Section

Materials. All the reagents and solvents were commercially available and of analytical grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone complex. Methyldiethoxysilane and *N*-methylpyrrolidone (NMP) were dried with zeolite overnight and then distilled twice prior to use. The catalyst of hydrosilation reaction, dicyclopentadienyldichloroplatinum (Cp_2PtCl_2), was prepared according to a literature report.[17]

Techniques. Light scattering measurements (SLS and DLS) were performed with a DLS-700 apparatus (Otsuka Electronic Co. Ltd.) equipped with He−Ne laser source (10 mW, $\lambda = 632.8$ nm). Determination of differential refractive index increment (dn/dc) was made with a RM-102 differential refractometer (Otsuka Electronic Co. Ltd.) at a wavelength of 632.8 nm to give a value of $dn/dc = 0.073$. The FTIR measurement was performed with a Perkin-Elmer 80 spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR measurements were carried out on Varian Unity 200 (USA) operating at 200 MHz, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. Chemical shift δ was given in ppm, referenced to an internal standard, tetramethylsilane (TMS, $\delta = 0$ ppm), for ^{1}H or ^{13}C NMR and an external standard, hexamethyldisiloxne (MM, $\delta = 6.9$ ppm), for ^{29}Si NMR. Chromium(III) acetylacetonate was used as a relaxation reagent. The XRD analysis was recorded on a Rigaku D/MAX 2400 diffractometer. DSC experiments were performed on a Mettler Toledo Star-822 differential scanning calorimeter at a heating rate of 20 °C/min. MS measurements were carried out on a BIFLEX III MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometer (Bruker Analytical System, Inc) utilizing a 5-chlorosalicylic acid matrix containing sodium ions. Element analysis was measured with a Heraeus CHN-RAPID DATEL System instrument. It is noteworthy that all experiments should be conducted in a fume hood due to low toxicity of the solvents and reagents used.

Scheme 1. Synthetic Route to Template **T** and Monomer **M**



Synthesis of Template *N*,*N*′-Diallyl-[4,4′-oxybis(benzyl amide)] (T). The synthetic route to template **T** and monomer **M** is shown in Scheme 1. To a 100 mL flask were added 20 mL of THF, 1.7 mL (0.022 mol) of allylamine, and 3.0 mL (0.022 mol) of triethylamine. Then, 3.0 g (0.01 mol) of 4,4′-oxybis(benzoyl chloride) dissolved in 40 mL of THF was added dropwise into the flask over 3 h under stirring at 0 °C. The reaction mixture was stirred at room temperature for an additional 2 h. After removing THF, residual allylamine, and triethylamine by vacuum distillation, a residual yellowish solid was obtained. The solid was washed with water and recrystallized twice in acetone to give a white needlelike crystal of template T in 71% yield. Mp: 153.7 °C. FTIR (KBr, cm^{-1}): 3314 (s, ν N−H), 3069−2969 (ν C−H), 1638 (vs, ν C═O), 1597, 1494 (ν C═C_{arom}), 1245 (ν C−N), 877 (γ C−H). ^{1}H NMR (DMSO-d_6): 9.0 (s, 2H, NH); 7.8, 7.0 (d, d, 4H, 4H, C_6H_4); 5.0−5.2, 5.7−5.9 (m, 6H, CH_2═CH); 3.8 (m, 4H, NHCH_2).

Synthesis of Monomer *N*,*N*′-Bis(3-methyldiethoxylsilylpropyl)-[4,4′-oxybis(benzyl amide)] (M). To a 100 mL Schlenk flask were added 3.0 g (8.9 mmol) of template **T** and 5 mg of catalyst Cp_2PtCl_2. The reaction system was vacuumized and refilled with argon, and this process was repeated three times. Under the argon atmosphere, 50 mL of NMP and 3.1 mL (20 mmol) of methyldiethoxysilane were injected into the system. The reaction mixture was stirred at 100 °C for 12 h. Then after the NMP and residual methyldiethoxysilane were distilled out under reduced pressure, monomer **M** was obtained in 93% yield as a white, waxy solid. Characterization data for **M** are listed in Table 1.

Synthesis of *N*,*N*′-Dipropyl-[4,4′-oxybis(benzyl amide)]-Bridged Ladderlike Polymethylsiloxane (A-LPMS). Monomer **M** (3.0 g, 5 mmol) was dissolved in 30 mL of NMP. A mixed solution of 0.45 mL (25 mmol) of water and 20 mL of NMP was added dropwise into the monomer solution over 4 h under ice−water bath. The reaction mixture was stirred at room temperature for several hours and was slowly warmed to 40 °C for another 10 h to complete the hydrolysis reaction. Then, a drop of concentrated H_2SO_4 was added into the mixture to catalyze the condensation reaction. The reaction system was stirred at

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Scheme 2. A Proposed Mechanism for the Synthesis of Polymer A-LPMS

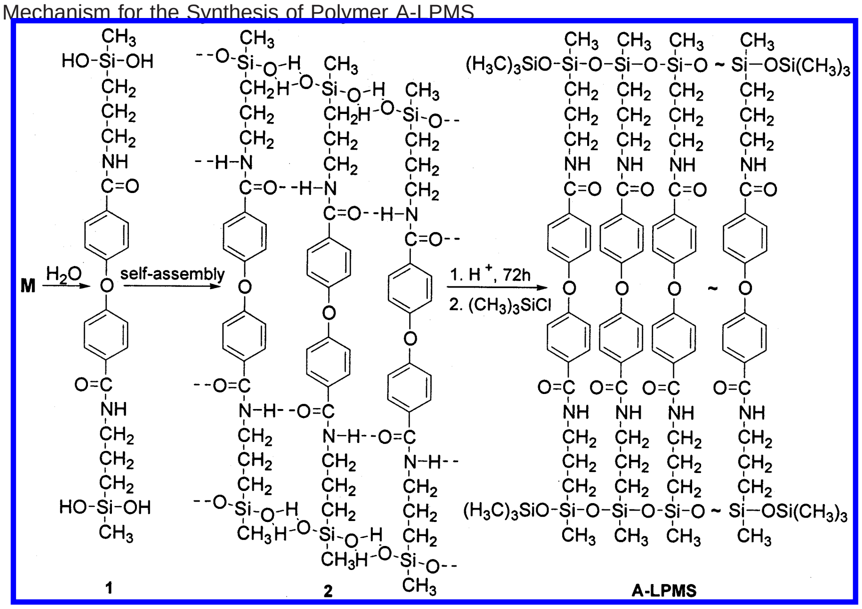

Table 1. Characterization Data of Monomer **M**

characterization items	results
appearance	white waxy solid
solubility	highly soluble in polar solvents: acetone, THF, NMP, etc.
FTIR (cm^{-1}) (KBr)	3315 (s, ν NH); 2972, 2879 (ν CH); 1638 (vs, ν C═O); 1597, 1495 (ν $C═C_{arom}$); 1245 (ν CN); 1170, 1079 (ν SiOEt); 878 (γ CH_{arom}); 799 (ν SiMe)
^1H NMR (δ in ppm)	9.0 (s, 2H, NH); 7.8, 7.0 (d, d, 4H, 4H, C_6H_4); 3.8 (q, 8H, OCH_2); 3.4 (m, 4H, $NHCH_2$); 1.6 (m, 4H, $SiCH_2CH_2$); 1.1 (t, 12H, OCH_2CH_3); 0.7 (t, 4H, $SiCH_2$); 0.1 (S, 6H, $SiCH_3$)
^{13}C NMR (δ in ppm)	165.9 (C═O), 158.4 (Ph), 130.3 (Ph), 129.6 (Ph), 118.3 (Ph), 57.5 (OCH_2), 42.3 ($NHCH_2$), 22.9 (OCH_2CH_3), 18.4 ($SiCH_2CH_2$), 11.0 ($SiCH_2$), −4.8 ($SiCH_3$)
^{29}Si NMR (δ in ppm)	−4.114 $CH_3(OEt)_2SiCH_2CH_2$
XRD	no diffraction peaks
MALDI-TOF MS	calcd for $C_{30}H_{48}N_2O_7Si_2$ (M^+) 604.3, found 627.5 $(M + Na)^+$
elemental analysis	Calcd for $C_{30}H_{48}N_2O_7Si_2$: C, 59.57; H, 8.00; N, 4.63. Found: C, 59.48; H, 7.86; N, 4.72.

40 °C for 72 h under reduced pressure to remove the water released. Occasionally, a small amount of gel would appear during the condensation process, which could be removed by filtering or centrifugation. For end-capping the terminal silanol of the polymer, 40 mg (0.5 mmol) of pyridine and 55 mg (0.5 mmol) of trimethylchlorosilane mixed with 10 mL of NMP were added dropwise into the flask under stirring. The mixture was stirred at room temperature for a further 24 h, followed by the addition of 10 mL of water as precipitating agent. Finally, some solids gradually emerged that were dried in a vacuum oven at 50 °C for 24 h to give the titled polymer A-LPMS as a white solid in 57% yield.

Results and Discussion

Synthesis of Monomer M. Monomer **M** was synthesized via a hydrosilylation reaction of template **T** with methyldiethoxysilane. It is known that an amido group can retard the hydrosilylation reaction because it can slightly poison the catalyst Cp_2PtCl_2 via coordination.[18] Hence, as shown in Scheme 1, the reaction should be conducted at higher temperature (100 °C) to destroy this coordination, and consequently, the monomer **M** was obtained in a high yield of 93%.

It can be found from ^1H NMR data of monomer **M** (Table 1) that the above-mentioned hydrosilylation reaction leads to the almost exclusive formation of β-adduct product. The reason for the absence of α-adduct is possibly the use of highly polar solvent (NMP) and the higher steric hindrance of $CH_3SiH(OEt)_2$ in the formation of α-adduct than β-adduct.[19] In addition, ^{13}C NMR data listed in Table 1 show similar results that there is only the β-adduct resonated at 18.4 ($SiCH_2CH_2$–), 11.0 ($SiCH_2CH_2$–), and −4.8 ppm ($SiCH_3$) without any other byproducts. Moreover, it is shown from the ^{29}Si NMR data (Table 1) that only β-adduct product $CH_3(OEt)_2SiCH_2CH_2$– ($\delta = -4.114$ ppm) is produced. The same conclusions can also be obtained from FTIR spectrum, MALDI-TOF measurement, and element analysis of monomer **M**, as shown in Table 1. There is no diffraction peak for monomer **M** in XRD measurement, suggesting that the monomer is an amorphous solid. In a word, it is demonstrated from FTIR, ^1H NMR, ^{13}C NMR, ^{29}Si NMR, XRD, element analysis, and MALDI-TOF results that the monomer **M** obtained is the expected pure template compound.

Synthesis of the Titled Polymer A-LPMS. A proposed mechanism for the formation of the polymer A-LPMS is shown in Scheme 2. It should be emphasized that keeping the H-bonding template in play throughout the whole synthetic process is absolutely essential to the highly ordered, ladderlike structure of polymer A-LPMS. So in the hydrolysis step, water should be added very slowly at low temperature to gradually hydrolyze the monomer **M**, resulting in the formation of intermediate **1**, whose silanols groups (≡Si−OH) can form the stable square-planar H-bonding proved by Kakudo.[20] Then, via strong H-bonding interactions of C═O···H−N and Si−OH themselves, a speculative extended H-bonding self-assembled ladderlike supramolecular structure **2** is formed, which was condensed with concentrated H_2SO_4 as catalyst to form lad-

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Table 2. Light Scattering Data of the Polymer A-LPMS

no.	M_w	R_g	A_2	R_h	R_g/R_h	$[\eta]$
1	2.0×10^4	18.1	2.8×10^{-4}	10.4	1.74	3.50
2	6.5×10^4	29.2	1.3×10^{-4}	16.7	1.75	14.1
3	9.4×10^4	41.0	1.3×10^{-4}	24.5	1.68	23.9
4	2.1×10^5	53.3	5.6×10^{-5}	33.1	1.60	50.1
5	1.2×10^6	67.0	2.1×10^{-6}	49.7	1.35	67.0

derlike oligomer and further condensed to ladderlike polymer A-LPMS. To prevent the polymer from cross-linking, trimethylsilylation of terminal silanols was performed using trimethylchlorosilane as end-capper and pyridine as HCl absorbent. The main factors affecting the regularity of the ladderlike structure of polymer A-LPMS are discussed below.

Effect of Temperature on the Synthesis of Polymer A-LPMS. It was found that the regularity of polysiloxane is strongly affected by the reaction temperature. If the hydrolysis reaction was carried out at high temperature (>60 °C) or water was added too rapidly, some insoluble gel immediately emerged. The reason is that the H-bonding is broken at high temperature, resulting in destruction of the ladderlike superstructure **2** and formation of randomly interlaced derivatives. The latter are rapidly condensed into an insoluble three-dimensional network of gels. For the same reason, although the ordered ladderlike superstructure **2** has been formed, insoluble gels would be generated if the final polycondensation reaction was conducted at high temperature. Therefore, it is necessary to strictly control the reaction temperature (usually not more than 50 °C) to guarantee the H-bonding template effect throughout the whole synthetic process.

Effect of Catalyst on the Synthesis of the Polymer A-LPMS. As we all know, the condensation reaction of silanols can be promoted in the presence of acid or base as catalyst. As mentioned above, the H-bonding of aryl amide groups is stable under acidic conditions. Moreover, acidic catalyst usually has stronger condensing ability than the basic one for the silanols having electrodonating groups. Hence, to prevent the amido group from decomposition and the H-bonding from breaking by alkali catalyst, the sulfuric acid is chosen as the condensation catalyst. The preferred proton concentration is found to be 10^{-2}–10^{-3} mol L^{-1}. In addition, since the polycondensation reaction is a balance process between monomer and polymer, the water of condensation reaction byproduct must be removed timely from the reaction system in order to obtain a high molecular weight polymer. Therefore, the reaction mixture must be continuously stirred and evaporated under reduced pressure.

Effect of Medium Polarity on the Synthesis of Polymer A-LPMS. To maintain a strong H-bonding template effect in polymerization, nonpolar or low-polar solvent should be preferred. However, these solvents normally have a very poor solvating power for the high polar reaction intermediates (**1** and **2**) and the final polymer A-LPMS. So a suitable solvent needs to have a balance between the polarity and solvating power. Since H-bonding-based poly(*p*-phenylene terephthalamide) can keep strong lyotropic liquid crystallinity in NMP or concentrated sulfuric acid, the polar aprotic NMP was chosen as the reaction solvent.

Characterization of Polymer A-LPMS. Investigation of solution properties of the polymer A-LPMS was conducted by light scattering (LLS and DLS) and viscosimetry methods. The details of light scattering instrumentation were described elsewhere.[21] All samples for determination were carefully treated by precipitation of polymer from NMP solution with distilled water and further purified by reprecipitation from dimethyl sulfoxide (DMSO) solution with methanol for the purpose of narrowing the molecular weight distribution. Dusts and other impurities were removed by pressure filtration [sintered glass filter S_2 for viscometric measurement and 0.2-μm microfilter (Millipore) for light scattering measurement]. The M_w of the polymer A-LPMS is measured by SLS instead of the usual GPC method, because the polymer A-LPMS is a relatively stiff wormlike macromolecule of a double-chained skeleton; nevertheless, the standard compound (polystyrene) usually used for calibrating a GPC instrument is a flexible linear polymer that takes a coil-like conformation in THF. The results of the light scattering experiment are summarized in Table 2.

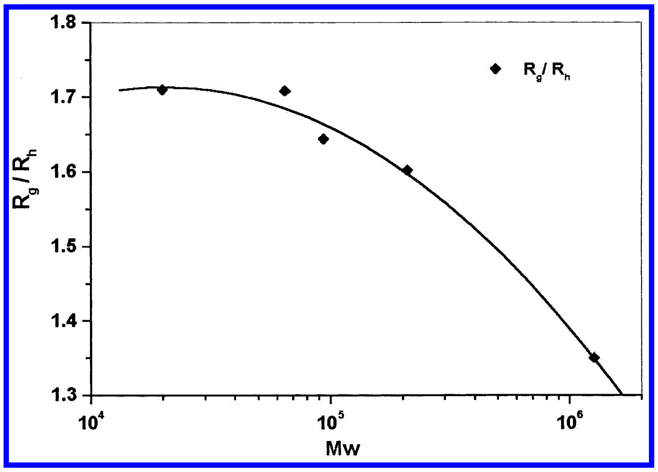

Figure 1. The relationship between R_g/R_h and M_w of the polymer A-LPMS.

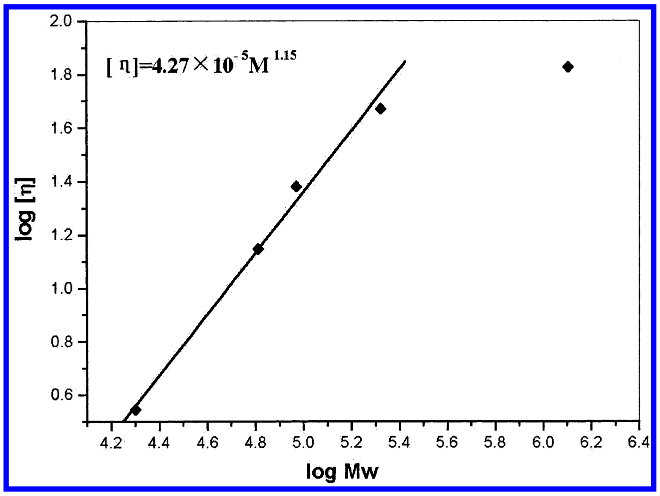

Figure 2. Molecular weight dependence of intrinsic viscosity $[\eta]$ of the polymer A-LPMS.

More meaningfully, the molecular shape of A-LPMS in solution can be described by a combination of the light scattering and viscosimetry measurement. As shown in Table 2, both the radius of gyration (R_g) and the hydrodynamic radius (R_h) increase with increasing M_w, but the second virial coefficient A_2 decreases with increasing M_w. The R_g/R_h ratio is plotted

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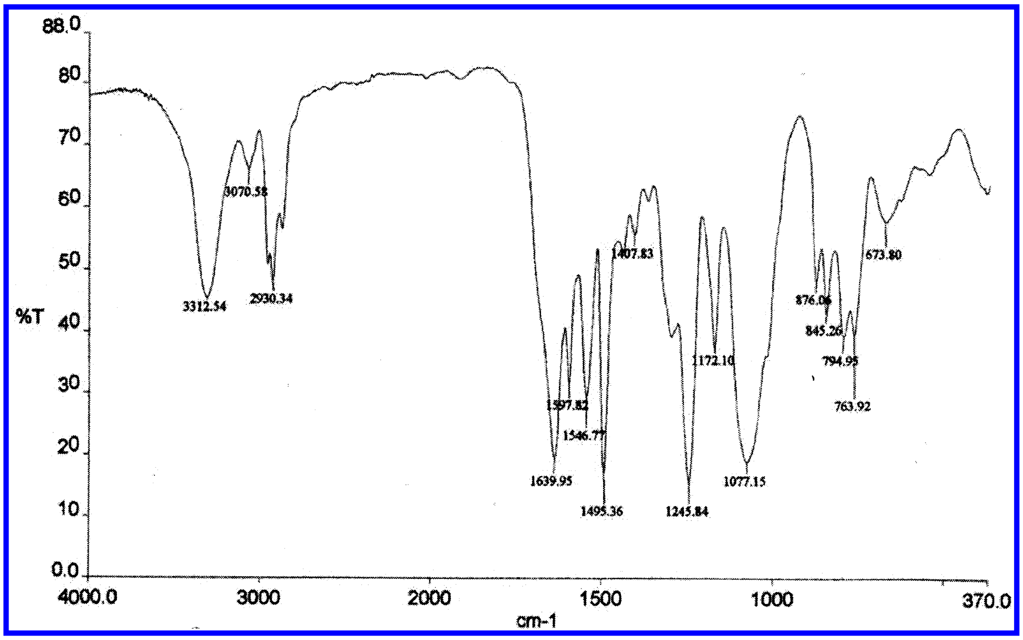

Figure 3. FTIR spectrum of the polymer A-LPMS.

against M_w in Figure 1. It has been proved that, for a given polymer/solvent system, the R_g/R_h ratio mainly depends on the chain architecture, conformation, and polydispersity.[22] For example, R_g/R_h values of 0.78, 1.24, and >2 stand for a hard sphere,[23] a Gaussian coil,[24] and a rigid rodlike polymer,[25] respectively. The comparatively large values of $R_g/R_h = 1.6-1.8$ indicate that the polymer A-LPMS has a rather extended conformation in NMP solution with rare branches. Namely, the chain of polymer A-LPMS is not like a flexible coil but like a semirigid soft ladder. Bohidar et al.[26] also found analogous results in investigation on gelatin−glutaraldehyde supramolecular structures, where the relatively high value of $R_g/R_h = 1.5-1.6$ indicates that the supramolecule mostly possesses "double-strand" ladderlike structure, rather than a branched random architecture. It was found that the R_g/R_h value becomes smaller as M_w increases, showing that the A-LPMS molecule has a tendency of contract with an increase of M_w. This is consistent with the conclusion drawn by Josef[27] as well as Fang[28] that the rigidity of the ladderlike polysiloxane decreases as M_w increases.

Similar results can be found in the viscosity investigation. The viscosity of the titled polymer A-LPMS was determined with Ubbelohde viscometers using NMP as solvent (concentration: 2−7 g L^{-1}). The flow time of pure solvent was maintained at least 100 s and thus the kinetic correction could be negligible. The intrinsic viscosity of A-LPMS was determined by Heller's method.[29] Figure 2 demonstrates the molecular weight dependence of intrinsic viscosity, $[\eta]$. The obtained Mark−Houwink equation is $[\eta] = 4.27 \times 10^{-5}\ M^{1.15}$. It is well-known that the conformation index (α) in the Mark−Houwink equation mainly depends on the chain conformation in solution. For example, under θ-conditions, $\alpha = 0.5$; for an extremely rigid rodlike polymer, $\alpha = 2.0$; and for a flexible polymer, $\alpha = 0.5-0.9$. Clearly, the higher value $\alpha = 1.15$ for the polymer A-LPMS is an indication of the stiffness of the main chain. That is consistent with the results of above-mentioned light scattering investigation. In a word, based on the investigation of solution properties of the polymer A-LPMS, one can conclude that the A-LPMS is a linear, semirigid polymer rather than a flexible, branched macromolecule.

It can be seen from the FTIR spectrum of polymer A-LPMS (Figure 3) that instead of two absorption peaks at 1107 and 1079 cm^{-1} assigned to the Si−OEt group of monomer **M**, a very strong and broad adsorption at 1077.15 cm^{-1}, corresponding to vibration of the Si−O−Si linkage, was observed, which indicates that the monomer **M** has been completely hydrolyzed and condensed to a high polymer containing Si−O−Si bonds. In addition, no vibration peak of silanol (3400−3600 cm^{-1}) is observed, thus indicating that the silylation end-capping reaction is completely finished. It is noteworthy that the strong peaks at 3312.54 and 1639.95 cm^{-1}assigned to an amido group confirm the existence of strong interactions between the amido groups located at the ladder rungs of the polymer A-LPMS.

As shown in the ^1H NMR spectra of polymer A-LPMS (Figure 4), the resonance peaks corresponding to Si−OEt groups have disappeared, suggesting that the monomer **M** has been completely hydrolyzed. The widened humplike peaks of aromatic hydrogen and other groups, arising from the high viscosity of A-LPMS in deuterated DMSO, implies that the monomer has been condensed to a relatively high molecular weight polymer. Unfortunately, the coupling constants are not observed, due to the limits of the NMR instrument used.

Three important structural messages can be deduced from Figure 5. First, there are only two distinct kinds of silicon atom

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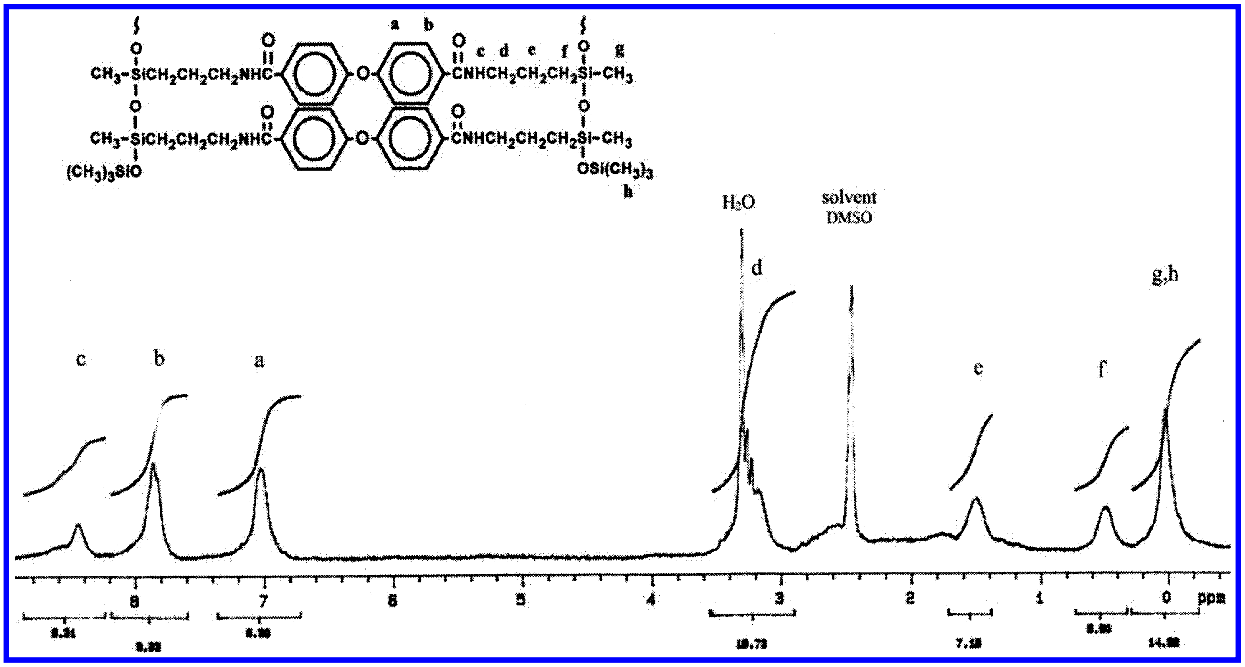

Figure 4. ^{1}H NMR spectrum of the polymer A-LPMS.

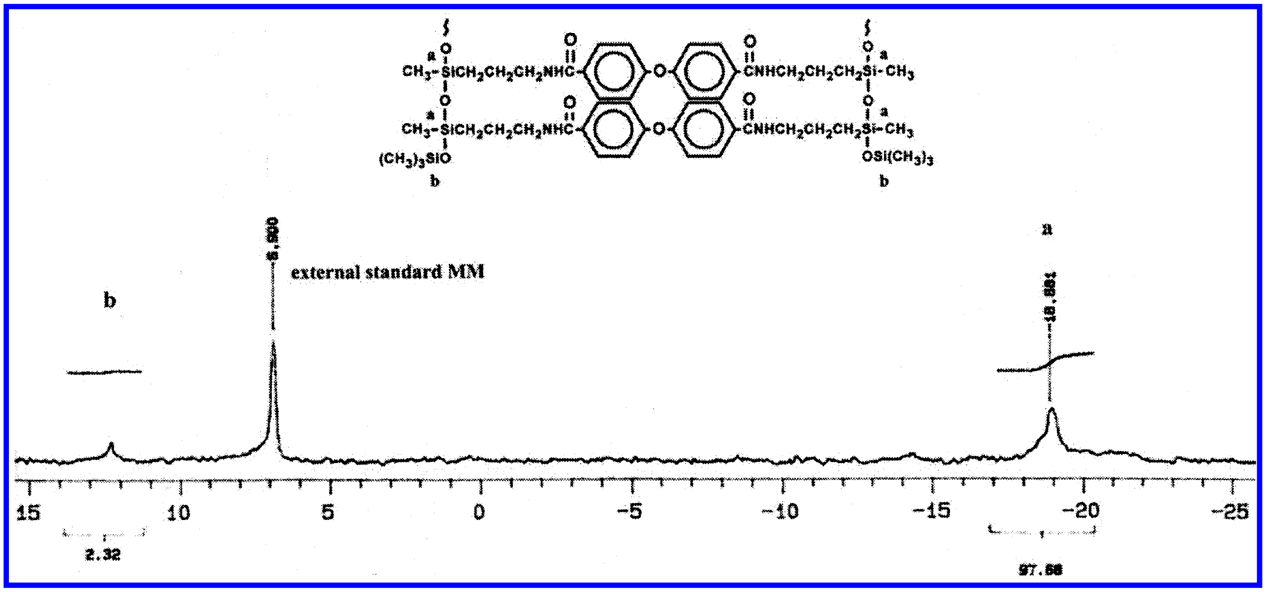

Figure 5. ^{29}Si NMR spectrum of the polymer A-LPMS.

in the polymer A-LPMS (the peak at $\delta = 6.900$ ppm stands for the resonance of the external standard hexamethyldisiloxne). One kind of Si-atom at $\delta = -18.881$ ppm represents the internal silicon atom in the backbone, $CH_3(CH_2)SiO_{2/2}$, and the other one at $\delta = 12.4$ ppm represents the terminal silicon atom $(CH_3)_3SiO_{1/2}$ of the trimethylsiloxyl end-capping group. This result indicates that the polymer A-LPMS consists of two types of structural units, $CH_3(CH_2)SiO_{2/2}$ and $(CH_3)_3SiO_{1/2}$, without noticeable branched moieties. That is consistent with the expected ladderlike structure of A-LPMS. Second, according to the ratio value ($R = 42.1$) of integrated areas of two peaks, the number-averaged molecular weight (M_n) of A-LPMS can be approximately estimated[30] to be 4.2×10^4, which is close to the value ($M_n = 5.1 \times 10^4$) calculated from weight-averaged molecular weight (M_w) by Judith's method[31] (here, $M_w = 6.5 \times 10^4$ measured by static light scattering), indicating that the polymer A-LPMS is a mainly linear rather than branched macromolecule. Third, it is known that the higher the regularity of polymer, the narrower the resonance peak is. Obviously, the narrow half-peak width (less than 1 ppm) at $\delta = -18.881$ ppm of the main-chain unit ($CH_3(CH_2)SiO_{2/2}$) of A-LPMS indicates that A-LPMS has high structural regularity, excluding the presence of the branched structures.

There are two distinct peaks in the XRD spectrum of polymer A-LPMS shown in Figure 6. Referring to Brown,[1] Andrianov,[3] and Shi,[32] the first peak ($d_1 = 2.40$ nm) representing the intramolecular chain-to-chain distance (i.e., the width of ladderlike main chain) of the polymer A-LPMS is narrow and sharp, implying that the polymer has a relatively regular ladderlike skeleton. The value of d_1 (2.40 nm) is approximately

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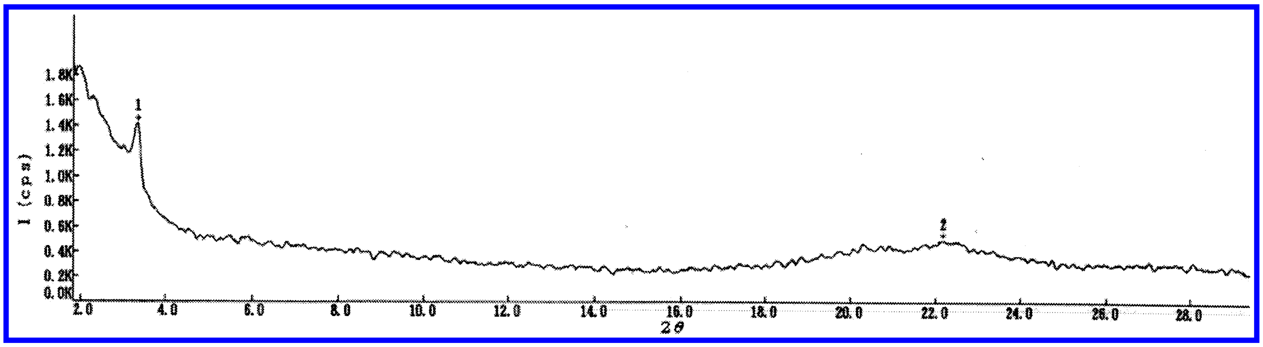

Figure 6. XRD pattern of the polymer A-LPMS.

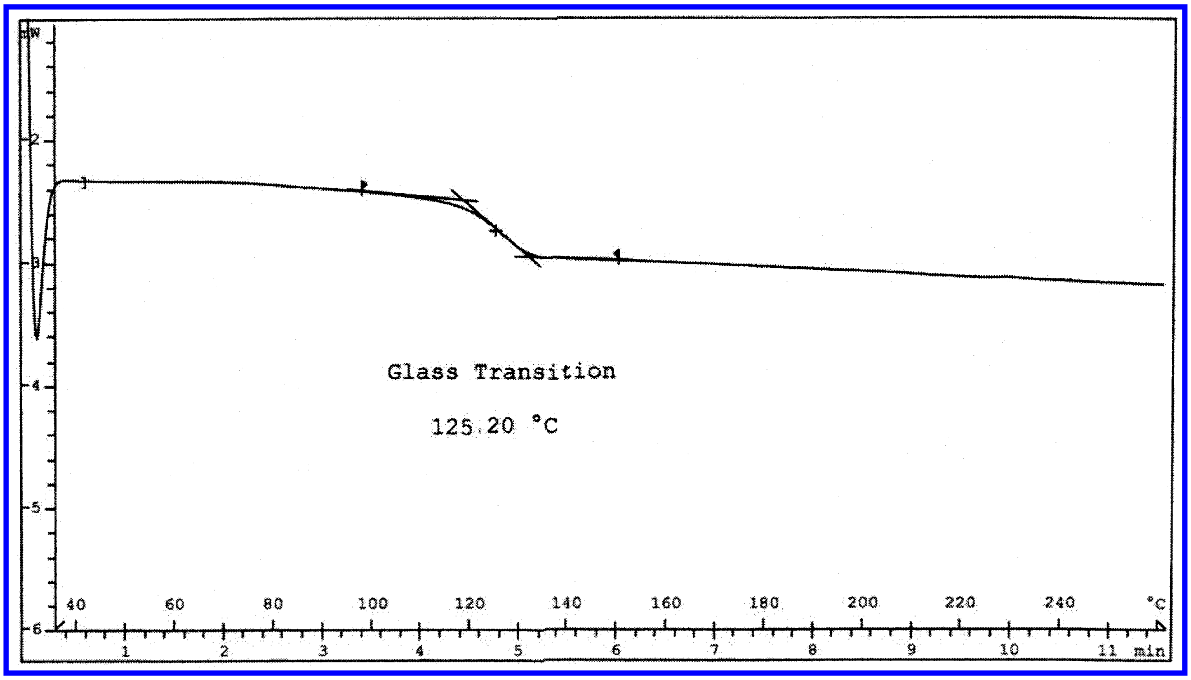

Figure 7. DSC curve of the polymer A-LPMS.

equal to the calculated intramolecular chain-to-chain distance based on a molecular dynamic simulation (2.27 nm, simulated by Alchemy 2000) of polymer A-LPMS. The second diffusing peak ($d_2 = 0.48$ nm) possibly stands for the thickness of the macromolecular chain or the intermolecular spacing between the polymer molecules.

To study the flexibility of the macromolecular chain of A-LPMS, one can compare the glass transition temperature, T_g, between the single-chained and ladderlike polysiloxanes. It is well-known that the common single-chain poly(dimethylsiloxane) is very flexible, with $T_g < -50$ °C. However, the T_g of A-LPMS is as high as 125.20 °C (Figure 7). That reveals that the polymer A-LPMS has a relative stiff backbone. A possible explanation for this discrepancy is that polymer A-LPMS has a unique double-chain structure and a rigid ladder rung of strong H-bonding interactions which remarkably restricts the internal rotation of the Si−O−Si bond and the segment mobility of polymer.

Conclusion

A novel soluble, high molecular weight organo-bridged ladderlike polymethylsiloxane, A-LPMS, has been synthesized for the first time through the use of an aryl amido H-bonding-based self-assembly template. The polymer was characterized by a combination of FTIR, ^{1}H NMR, ^{29}Si NMR, XRD, DSC, and, especially, light scattering and viscometry methods. The results show that the polymer is a semirigid, highly ordered, ladderlike macromolecule. Such an H-bonding-assisted synthetic method can be utilized to prepare a variety of highly ordered organo-bridged ladderlike polysiloxanes.

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