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Synthesis of Starburst Oligoanilino[60]fullerene and Poly(Dimethylsiloxane) Triblock Copolymers

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ABSTRACT

A new synthetic approach for the fabrication of core-shell like conducting elastomers was described. The approach utilized the facile intermolecular self-assembly of poly(dimethylsiloxane) (PDMS) in DMSO leading to formation of a core particle, while soluble oligoaniline (A_x) segments dispersed in the solution phase resembling a shell overlayer for building the morphology. This morphology was demonstrated by *bis*[penta(tetraanilino)fullerene] *bis*(aminopropyl)poly(dimethylsiloxane) [PDMS-(F5A₄)₂] triblock co-oligomers synthesized using a functionalized C₆₀ derivative as a linker. Observation of ¹H NMR spectroscopic responses on the PDMS particle formation in DMSO-*d*₆ is consistent with the proposed core-shell geometry with oligoaniline moieties located at the shell overlayer.

Key Words: Fullerene; Tetraaniline; Hexa(dianilino)[60]fullerene; Hexa(tetraanilino)[60]fullerene; Oligoanilino[60]fullerene-poly(dimethylsiloxane) conjugate; Elastic triblock copolymer.

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INTRODUCTION

Processibility of intrinsic conducting polymers remains as a target for improvement, perhaps, by the approach of nanotechnology. In an effort to incorporate prerequisite mechanical properties with the conductivity, preparation of composites comprising of conductive polypyrrole (PPy) on submicron-sized particles of non-conductive polystyrene (PS) latexes containing sulfonic acid groups acting as dopants for the growing PPy were recently demonstrated.^[1] Similar composite formulation of polyaniline (PANi) on vinyl chloride–vinylidene chloride–methyl methacrylate–acrylate copolymer^[2] or butadiene–styrene–vinyl pyridine copolymer derived submicron-sized particles were also made. One approach to enhance the control for homogeneous dispersion of conducting polymer on the surface of supporting substrates was performed by the fabrication of PPy or PANi-coated particles in well-defined core-shell morphology via direct polymerization of aniline with an oxidant, ammonium persulfate on the surface of monodispersed micron-sized PS beads.^[3] The conductivity of a compressed pellet made of these particles was reported to be 3.4×10^{-3} S/cm. Unlike hard spheric PS beads, hydrophobic soft polymers exhibited great tendency to aggregate into a larger particle in aqueous media when they were used as the supporting substrates. The problem can be minimized by application of chemically grafted nonionic poly(ethylene glycol) surfactants at the surface of the soft particle for providing stabilization of the dispersion. The technique gave a convenient means to insert an ultrathin overlayer of conducting polymers, such as PPy, at the interfacial surface area of supporting particles.^[4] Accordingly, by using poly(ethylene glycol)-stabilized polyurethane as the core material, dispersions of core-shell geometry consisting of a conductive PANi shell were reported to form^[5] and such products were marketed under a trade name of ConQuest. However, in a systematic microscopic investigation of a similar approach on PS latexes with a mean parent particle diameter of 129 nm, stable core-shell morphology of PPy–PS particles were confirmed only at a low PPy loading of 4.2% by mass.^[6] At a higher loading level up to 16.6% by mass, stable aggregation of PPy phase-separated nanoparticles in a size of 20–30 nm was observed around larger PS particles instead of the proposed core-shell morphology. Compressed pellet conductivity of these PPy–PS aggregates with a less than 20% PPy loading was found to be 0.01 S/cm, in a lower value than the conductivity of 2.0 S/cm reported for PPy–PS core-shell particles^[7] at a low PPy loading of 5.1% by weight on poly(*N*-vinylpyrrolidone)-stabilized PS latexes. In the case of PANi-coated PS microspheres, a nonuniform morphology of PANi overlayer was observed showing a maximum conductivity of 0.15 S/cm for a sample with PANi loading of 9.5% by weight.^[8] As the supporting particle size was reduced to a nanoscale, 30–50 nm in diameter, aiming for significantly increasing the surface area, using poly(styrene-*co*-styrene sulfonate) latexes as the core substrate, the production of PANi-based conductive nanoparticles with a core-shell morphology was reported to be successful.^[9] Nevertheless, the maximum conductivity of these materials was found to be 0.05 S/cm over a 12.3% of PANi loading, not higher than that of submicron-sized particle samples.

Here, we demonstrate a new approach of fabricating core-shell nanoparticles by linking oligoanilines (A_x) directly with a low- T_g substrate via the C_{60} cage to effect formation of the corresponding fullerene conjugates.^[10,11] Direct attachment of conjugate oligomer donor (D) arms onto the fullerene cage may allow us to design starburst macromolecules in a AD_n array with the C_{60} cage as an acceptor (A). Utilization of oligoaniline emeraldine base with a well-defined chain length instead of polydisperse PANi



should facilitate an easier control and characterization of resulting conducting oligomer–elastomer nanostructures. Accordingly, we synthesized *bis*[penta(oligoanilino)][60] fullerene-poly(dimethylsiloxane) triblock co-oligomers using hexanitro[60]fullerene (HNF) as a reactive precursor molecule and linker for chemically binding A_x onto elastic poly(dimethylsiloxane) (PDMS).

EXPERIMENTAL

Materials and Methods

C_{60} (99.5%) was purchased from either Bucky USA or Southern Chemical Co. and used as received. Tetrahydrofuran (THF) was dried and freshly distilled over sodium and benzophenone. *Bis*-(aminopropyl)poly(dimethylsiloxane) (BAPDMS) (M_n 1500, 2200, or 27,000) was obtained from Shin-Itsu Co., Japan. All other chemicals and solvents were purchased from Acros Ltd. and used as received. Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. 1H NMR spectra were recorded on a Bruker AC-300 Spectrometer. Gel permeation chromatography (GPC) was performed in THF on a JASCO PU-1580 instrument operating at flow rate of 1.0 mL/min at 40°C, equipped with Jordi gel DVB bed columns (a length of 250 mm and an inner diameter of 10 mm) and a UV detector JASCO UV-1570. All experimental procedures were carried out under an atmosphere pressure of nitrogen.

Synthesis of *bis*[Penta(Anilino)fullerene] *bis*(Aminopropyl)Poly(Dimethylsiloxane)

A solution of HNF (50 mg, 0.05 mmol, 2 equiv.) in dry THF (10 mL) was placed in a dry flask equipped with a stir-bar and a condenser tube. To this solution, a mixture of BAPDMS (M_n 1500, 38 mg, 0.025 mmol) and pyridine (0.01 mL) in THF (5.0 mL) was added dropwise with vigorous stirring. The reaction was allowed to continue at room temperatures for a period of 1.0 h. A second solution mixture containing aniline (0.056 mL, 0.6 mmol, 24 equiv.) and pyridine (0.1 mL) in THF (5.0 mL) was then added to the mixture. The resulting dark brown colored mixture was stirred at 50°C for another 12 h. At the end of the reaction, it was centrifuged and the clear brown supernatant concentrated to give a dark liquid. The products were precipitated from the liquid upon the addition of diethyl ether. The precipitates were collected by centrifugation and washed repeatedly with diethyl ether followed by methanol. The solids were then air dried to afford *bis*[penta(anilino)fullerene]*bis*(aminopropyl)poly(dimethylsiloxane) [PDMS-(F5A)₂] in roughly 80% yield. FT-IR (KBr, cm^{-1}) ν_{max} 3433, 2966, 1632, 1499, 1448, 1414, 1349, 1263, 1097, 1017, 866, 800, 694, and 664. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.0–6.5 (broad peaks), 0.047–0.038 (m).

Synthesis of *bis*[Penta(Dianilino)fullerene] *bis*(Aminopropyl)Poly(Dimethylsiloxane)

To a suspension of NaH (5.0 mg, 0.2 mmol) in THF placed in a centrifuge tube and capped with a septum, was added to a solution of *bis*(aminopropyl)poly(dimethylsiloxane)



(BAPDMS, M_n 1500, 38 mg, 0.025 mmol) in THF (5 mL). The mixture was shaken for 1.0 h at ambient temperatures. The suspension was centrifuged to separate and remove unreacted NaH. The clear supernatant was added to a solution of HNF (50 mg, 0.05 mmol, 2.0 equiv.) in THF (10 mL) at -10°C . The brown colored reaction mixture was stirred for 1.0 h while allowed to warm slowly to room temperature. A solution mixture of *N*-phenyl-1,4-phenylenediamine (67 mg, 0.6 mmol, 24 equiv.) in THF (5.0 mL) and pyridine (0.1 mL) was then added. The resulting dark brown solution was stirred at 50°C for an additional 12 h. At the end of the reaction, the mixture was centrifuged and the clear solution concentrated. The products were obtained by precipitation upon addition of acetonitrile. Precipitates were collected by centrifugation and washed with acetonitrile, followed by water and methanol. The resulting dark brown solids were air-dried to afford *bis*[penta(dianilino fullerene)] *bis*(aminopropyl)poly(dimethylsiloxane) [PDMS-(F5A₂)₂] in an estimated yield of 79%. Spectroscopic data of PDMS-(F5A₂)₂: FT-IR (KBr, cm^{-1}) ν_{max} 3394, 2965, 1599, 1553, 1514, 1498, 1314, 1263, 1093, 1018, 802, 749, 696, and 497. ¹H NMR (300 MHz, THF-*d*₈) δ (ppm) 7.5–6.5 (broad peak), 0.11 (s), and ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) 7.4–6.5 (broad peak), -0.06 (broad peak). The sample was stored in methanol prior to use.

Synthesis of *bis*[Penta(Tetraanilino fullerene)] *bis*(Aminopropyl)Poly(Dimethylsiloxane)

In a dry centrifuge tube capped with a septum was placed NaH (5.0 mg, 0.2 mmol) and kept under nitrogen. To this was added a solution of *bis*(aminopropyl)poly(dimethylsiloxane) (BAPDMS, M_n 1500, 38 mg, 0.025 mmol) in dry THF (5.0 mL). The mixture was shaken for an hour at room temperature and then centrifuged. Clear supernatant was separated and placed into a reaction flask. While cooling down to -10°C , it was added dropwise with a solution of HNF (50 mg, 0.05 mmol, 2.0 equiv.) in THF (10 mL) with vigorous stirring. Reaction mixture was further stirred for a period of 1.0 h and warmed up to room temperature. To this brown colored solution mixture was added tetraaniline (A₄) (100 mg, 0.27 mmol, 11 equiv.) in THF (10 mL) and triethylamine (0.2 mL). The resulting dark purple mixture was stirred at 50°C for 12 h. At the end of the reaction, a small quantity of suspended solids formed were separated and removed by centrifugation. The clear deep purple solution obtained was concentrated to a thick liquid carefully without possible precipitation of solids on the wall of the flask. The products were then recovered by the addition of diethyl ether to effect its precipitation. Precipitates were collected by centrifugation and re-dissolved in a minimum amount of THF, followed by re-precipitation with diethyl ether with ultrasonication. This process was repeated until no blue coloration was observed in ether supernatant. The resulting blackish purple solids were washed with water followed by methanol to give *bis*[penta(tetraanilino fullerene)] *bis*(aminopropyl)poly(dimethylsiloxane) [PDMS-(F5A₄)₂] in an approximate yield of 75%. Spectroscopic data of PDMS-(F5A₄)₂: FT-IR (KBr, cm^{-1}) ν_{max} 3396, 2966, 1599, 1509, 1305, 1262, 1175, 1094, 1019, 803, 750, 696, and 667. ¹H NMR (300 MHz, THF-*d*₈) δ (ppm) 8.0–6.3 (broad peaks), 0.10 (m). The sample was stored in methanol prior to use.



RESULTS AND DISCUSSION

Tetraaniline and hexadecaaniline represents a low molecular weight version of PANi. It consists of 4 and 16 repeating aniline units, respectively. In general, as the molecular weight of phenylamine-containing organo polymers increases, nucleophilicity of their primary amino end-group decreases. It was found not to be the case when oligoanilines were allowed to react with HNF. In fact, all versions of oligoaniline exhibit good reactivity in replacing fullerene nitro group under mild conditions. High reactivity of HNF toward primary amines overcomes the decrease in nucleophilicity due to the increase of molecular weight. We propose that replacement reaction occurred by 1,3-substitution of allylic nitro groups by amines. Multiple attachment of oligoanilines onto one C_{60} cage forms the corresponding starburst conjugate molecules. Examples were given by hexa(tetraanilino)[60]fullerene ($F6A_4$) and hexa(hexadecaanilino)[60]fullerene ($F6A_{16}$) prepared by the reaction HNF with A_4 and hexadecaaniline, respectively. When one equivalent of the amine reagent is used in the reaction with HNF, a major product of monoorganoamino(pentanitro)[60]fullerene may be obtained with expected minor products of diorganoamino(tetranitro)[60]fullerene and, possibly, triorganoamino(trinitro)[60]fullerene. The yield of these minor products decreases when the amino reagent used changes from a small molecule to a larger oligomer or polymer in size. Difficulty for reactive polymer chain-ends to bind each other should slow down formation of the bisoligomeric adduct of the HNF derivative. Therefore, a reasonable control on the synthesis of triblock copolymer structures can be achieved with the production of pentablock copolymer in only a minimum quantity, if a slightly excess of HNF and a low polymer reagent concentration are applied to decrease the reaction kinetics. Pentablock copolymers were the byproducts of two or more reactive amino polymers attacking on one HNF molecule.

Our approach for incorporation of elastic segments in bonding with conductive segments includes the use of *bis*(3-aminopropyl)poly(dimethylsiloxane) (BAPDMS) and A_x as the linking elastomer and the conductive component, respectively. Structure of conductive elastomer comprises of two starburst oligoanilino[60]fullerene molecules linked with *bis*(3-aminopropyl)poly(dimethylsiloxane) (BAPDMS) segment forming a structure of $(F5A_x)$ -PDMS- $(F5A_x)$. Our synthetic method for the conductive elastomer preparation was derived from the facile synthesis of hexa(oligoaniline)[60]fullerenes using HNF as an intermediate reagent.^[12] Hexanitro[60]fullerene consisting of six electron withdrawing $-NO_2$ leaving groups exhibits high reactivity due to the extended allylic conjugation of nitro groups on the fullerene cage. Replacement of these nitro groups by nucleophiles can lead to attachment of multiple structural components on C_{60} . The primary amino end group of A_x possesses sufficient nucleophilicity and could replace nitro groups of HNF easily, leading to the formation of starburst conjugate macromolecules.^[13] Similarly, the incorporation of elastic component can be made using BAPDMS for linking itself to the fullerene core, via aminopropyl end-groups, followed by substitution of remaining nitro groups with A_x for linking conductive components.

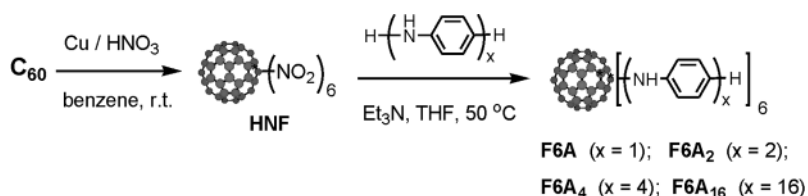
Synthesis of A_x begins with the oxidative coupling reaction of phenylamine dimer. The first A_x as A_4 was prepared by a modified procedure based on the reported method.^[14] Thus, *N*-phenyl-1,4-phenylenediamine was dimerized using ferric chloride hexahydrate as an oxidant in aqueous hydrochloric acid at 0°C followed by dedoping of the product with ammonium hydroxide. Isolation and purification of the A_4 emeraldine



base product was carried out by thin-layer chromatography (TLC) at $R_f=0.5$ (SiO_2 , ethylacetate : hexane/1 : 1) or $R_f=0.7$ (SiO_2 , THF : CHCl_3 /1 : 1) under a different solvent polarity. Tetramerization of A_4 in its leucoemeraldine oxidation state with ammonium persulfate in aqueous hydrochloric acid at ambient temperature followed by neutralization with ammonium hydroxide afforded hexadecaaniline in an emeraldine base form. Under these reaction conditions, the oligomerization were limited to the products with a maximum repeating aniline unit of 16. No significant quantity of higher oligomers was detected on GPC. However, the products were found to be complex containing all repeating units of A_4 , such as octaaniline, dodecaaniline, and hexadecaaniline, with the latter as the major product. Hexadecaaniline was purified using the TLC method with $R_f=0.6-0.75$ (SiO_2 , THF : CHCl_3 /1 : 1). Whereas the intermediate HNF was prepared by multiple nitrogen dioxide radical additions on C_{60} . Exclusive hexanitro addition on each C_{60} cage can be accomplished even though tetranitro[60]fullerene [$C_{60}(\text{NO}_2)_4$] was found to be the dominant product within a short reaction period. Conversion of tetranitro[60]-fullerene to hexanitro[60]fullerene [$C_{60}(\text{NO}_2)_6$] followed a slow thermal kinetics. When A_x were subjected to contact with HNF, only one equivalent of these A_x per nitro group of HNF was necessary to achieve completion of the substitution reaction in the presence of triethylamine in THF at 50°C , as shown in Sch. 1.

In this article, we describe the synthesis of new starburst triblock copolymers for the study of molecular self-assembly. They were obtained by the reaction of HNF with BAPDMS in low to medium molecular weights (M_n 1500, 2200, or 27,000) and its further reaction with aniline or short-chain oligoanilines, such as dianiline or A_4 . Selection of PDMS was made due to its high thermal stability and large difference in solubility from A_x in order to enhance phase-separation between these two components. Characterization of these triblock oligomers is relatively easy since a low molecular weight of PDMS segment and well-defined units of A_x facilitate the spectroscopic analyses. A similar synthetic approach can be further exploited in the preparation of conducting elastomers with A_x in a higher chain-length and PDMS with a high molecular weight leading to the desired products with appreciable conductivity and elasticity. In a model study, the reaction of low molecular weight BAPDMS (M_n 1500) with HNF was carried out by slow addition of BAPDMS into a reaction mixture containing triethylamine or pyridine and an excess of HNF in THF under vigorous stirring at ambient temperature. Excessive HNF presence in the mixture allows effective capture of amino end-groups of BAPDMS by HNF to give quantitative yield of PDMS-[F5(NO_2)]₂. The spectroscopic data of this particular sample was used as the reference for the subsequent reaction.

In the consecutive one-pot preparation of PDMS-(F5 A_x)₂, the kinetic rate of BAPDMS in substitution of fullerenic nitro groups can be increased by the use of

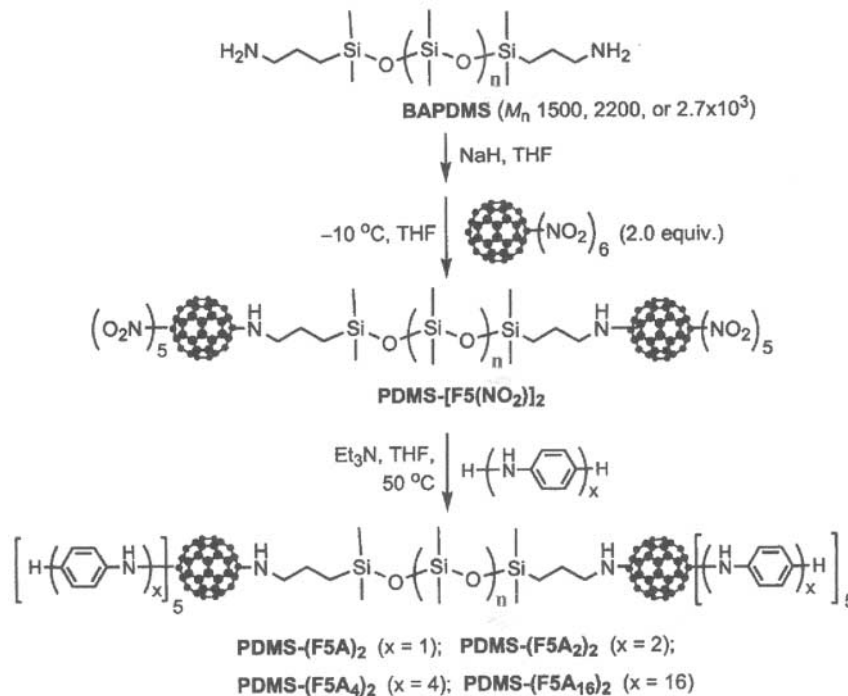


Scheme 1. Synthesis of hexa(oligoanilino)[60]fullerenes using HNF as a precursor molecule.



bisanionic BAPDMS. In this case, sodium hydride was used to generate *bisanionic* BAPDMS which further reacted with HNF (2.0 equiv.) at -10°C to afford *bis*(penta[nitro][60]fullerene) *bis*(3-aminopropyl)poly(dimethylsiloxane) {PDMS-[F5(NO₂)₂]₂} as shown in Sch. 2. The use of dilute solution and the specific addition sequence minimizes the formation of poly(dimethylsiloxanated)[60]fullerene byproducts consisting of multiple additions of BAPDMS on one C₆₀ cage. The reaction mixture was periodically examined for the presence of unreacted HNF via the TLC method. The absence of primary amino group in the reaction mixture at the end of reaction was confirmed by a negative response upon treating a part of the reaction mixture taken from the solution with 4-bromobenzaldehyde over molecular sieves at 40°C for a period of 8 h.

Detailed comparison of FT-IR and ¹H NMR spectra of the product materials obtained with and without the treatment of intermediates with 4-bromobenzaldehyde showed a similar pattern of the spectrum profile. For the positive imine formation, its characteristic infrared absorption bands corresponding to $\text{C}=\text{N}$ stretching and the aromatic proton signals in ¹H NMR spectrum can be detected readily. For example, the model reaction between BAPDMS and 4-bromobenzaldehyde carried out under similar reaction conditions did furnish the products containing expected imine moieties showing phenyl proton peaks as double doublet at δ 7.58 and 7.54, iminated methylene proton ($\text{—CH}_2\text{—N}=\text{C—}$) peak as a triplet at δ 3.65, methylene protons as multiplet centered at δ 1.7 and a triplet at δ 0.6, and silyl methyl proton (Si—CH_3) peaks as multiplet at δ 0.07. The spectrum



Scheme 2. Synthesis of *bis*[penta(oligoanilino)fullerene] *bis*(2-aminopropyl)-poly(dimethylsiloxane) as PDMS-(F5A_x)₂.



corresponds well with all assignments of proton peaks arising from imine moieties. Due to the fact that no proton peaks in the spectrum can be assigned for the structure of the parent BAPDMS in the consecutive reaction intermediate, a complete reaction is proposed. Since only two equivalents of HNF was applied in the reaction with BAPDMS, any undesired multiple amine crosslinking on one HNF molecule should result in an excess of HNF remaining in the solution that can be detected on TLC. We also practiced the slow addition of *bis*anionic BAPDMS into the HNF solution to minimize the crosslinking reactions. The absence of HNF in the intermediate reaction stage lead us to conclude that the majority of the product formed is the expected intermediate *bis*(pentanitrofullerene) *bis*(aminopropyl)poly(dimethylsiloxane) PDMS-[F5(NO₂)]₂.

This intermediate was allowed to react further, without isolation, with A₄ in the presence of pyridine base at 50°C, as shown in Sch. 2. The resulting deep blue supernatant obtained upon centrifugation of the reaction product mixture was concentrated on a rotavapor with special care being taken so as to not let the material dry on the walls of the flask. Blackish blue products were then precipitated upon the addition of diethyl ether. The crude material was further purified by repeatedly redissolution in THF followed by reprecipitation from diethyl ether with the application of ultrasonication to remove any excess residual A₄, other starting materials, and byproducts. The purified products of PDMS-(F5A_x)₂ obtained were kept wetted with solvent or only partially air dried since the vacuum dried samples led to tight aggregation and packing making it difficult to redissolve the material in solvents.

IR spectra of oligoanilinated fullerene elastomers PDMS-(F5A_x)₂ are shown in Fig. 1. Characteristic IR bands for PDMS moieties at 2967, 1414, 1262, 1095, 1024, 801, and 702 cm⁻¹ and for A₄ moieties at 3392, 1601, 1510, 1305, 816, 747, 694, and 509 cm⁻¹ are shown in Figs. 1(a) and 1(g), respectively. The change in band intensities between the PDMS and oligoaniline bands was noticeable as the molecular weight and the number of aniline units varies. For example, change in relative band intensities with the decrease of A₄ absorption related to that of PDMS bands for the PDMS-(F5A₄)₂ samples can be

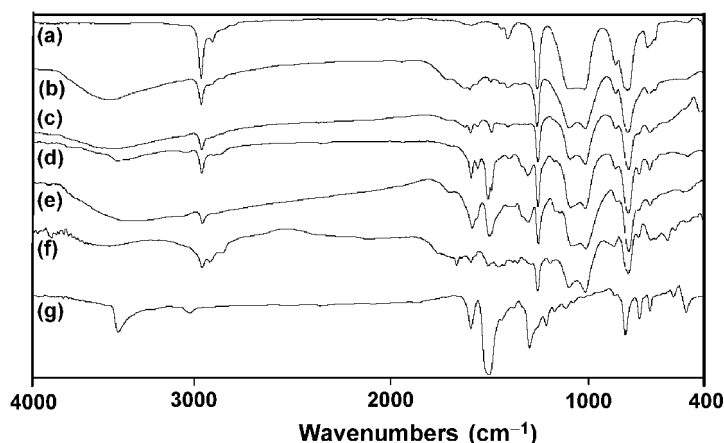


Figure 1. Infrared spectra of PDMS-(F5A_x)₂ products, (a) BAPDMS, (b) PDMS-(F5A)₂ (PDMS M_n 1500), (c) PDMS-(F5A)₂ (PDMS M_n 2200), (d) PDMS-(F5A)₂ (PDMS M_n 1500), (e) PDMS-(F5A)₂ (PDMS M_n 1500), (f) PDMS-(F5A₄)₂ (PDMS M_n 27,000), and (g) tetraaniline.



clearly observed as the molecular weight of PDMS increases from M_n 1500 [Fig. 1(e)] to M_n 27,000 [Fig. 1(f)] in reducing the weight proportion of A_4 . Similar observation was made on elastomer samples PDMS-(F5A)₂ synthesized by the use of aniline and PDMS (M_n 1500) [Fig. 1(b)] and PDMS (M_n 2200) [Fig. 1(c)] as the elastic components. A small decrease in relative band intensities of the aniline absorptions at 1500–1600 cm^{-1} with respect to those of PDMS moieties was still detectable as the molecular weight of PDMS increases slightly. If the molecular weight of PDMS holds constant as M_n 1500, a steady increase of the relative absorption intensity of A_x moieties was clearly shown in samples containing aniline as PDMS-(F5A)₂ [Fig. 1(b)], dianiline as PDMS-(F5A₂)₂ [Fig. 1(c)], and A_4 as PDMS-(F5A₄)₂ [Fig. 1(e)] with a steady increase of the aniline repeating units in the elastomer structure.

Figure 2 shows the GPC plot of the PDMS-(F5A₄)₂ sample obtained from tetraaniline and BAPDMS (27,000) using the detection wavelength of 350 nm which maximize the absorption of fullereno- A_x components. The use of GPC to determine the molecular weight of these materials can be limited if the aggregation persists. However, a clear shift of the A_x absorptive materials from a low molecular weight of A_4 (Fig. 2, thin line) to a much higher molecular weight analogous (Fig. 2, bold line) was evident, indicating the corresponding tetraanilino fullerene-grafting on PDMS. Absence of any peak at a lower elution volume in the GPC diagram than that of the PDMS-(F5A₄)₂ band led us to exclude the possibility of high molecular weight crosslinked products.

High incompatibility between the polar A_4 and nonpolar PDMS moieties makes intermolecular self assembly of PDMS possible in polar solvents. Low solubility of PDMS moiety in DMSO forces itself to coagulate into particles. In other words, the high solubility of A_4 in DMSO allows it to stretch into the DMSO solution resulting in core-shell like particles with PDMS concentrated in the core with an overlayer of A_4 on the surface. This morphology hypothesis was examined by the ¹H NMR spectroscopic studies using a sample of PDMS-(F5A₄)₂ (PDMS M_n 1500) recorded in DMSO-*d*₆. For the comparison, ¹H NMR spectrum of PDMS-(F5A₄)₂ sample was also recorded in THF-*d*₈ [Fig. 3(a)]. Since both components of PDMS and A_4 are soluble in THF, relatively good

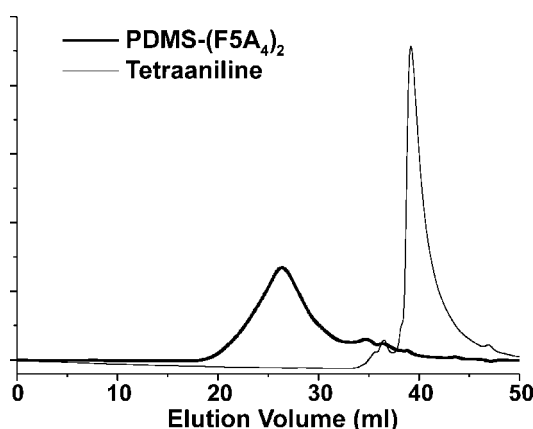


Figure 2. Gel permeation chromatography plot of PDMS-(F5A₄)₂ (bold line, PDMS M_n 27,000) and A_4 (thin line) using THF as eluent, with a flow rate of 1.0 mL/min, at 40°C.



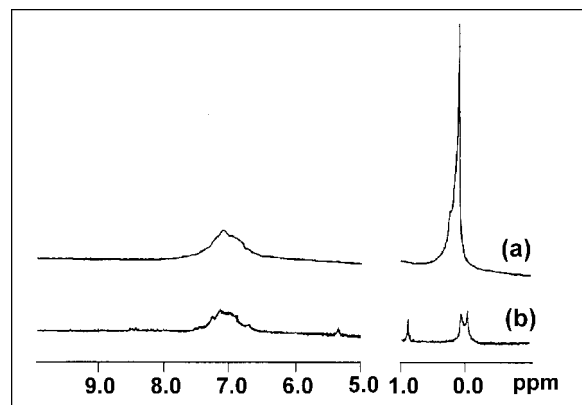


Figure 3. ^1H NMR spectrum of PDMS-(F5A₄)₂ with M_n 27,000 of PDMS moiety in (a) THF- d_8 and (b) DMSO- d_6 .

resolution of proton peaks of these two components was observed at δ 0.1 and 7.0, respectively. As the solvent was changed to DMSO- d_6 , the peak intensity of the silyl methyl protons at δ 0.0 diminishes as shown in Fig. 3(b) from that recorded in Fig. 3(a), while the aromatic proton peak intensity and shape remained nearly the same as those of Fig. 3(a). These spectroscopic changes allow us to interpret them as the results due to the occurrence of intermolecular self-assembly of PDMS moieties. The polar DMSO solvent causes the insoluble PDMS segments to coagulate and form particles making PDMS being less exposed to the solvent whereas the less polar solvent THF can solvate the PDMS moiety allowing it to stretch into the solution. The coagulation effect significantly restricts silyl methyl protons mobility in solution and reduces the peak resolution accordingly. In contrast to this, the steady proton peak resolution of A₄ indicated clearly its major segment portion in DMSO solution. That excluded their presence inside the PDMS coagulated particles as well. Since both A₄ and PDMS components are chemically bonded to each other, the only reasonable interpretation for the NMR data is made by the core-shell morphology of PDMS-(F5A₄)₂ particles in DMSO.

CONCLUSION

Utilization of hexanitro[60]fullerene, [C₆₀(NO₂)₆] as a linker for binding one elastic PDMS segment with A_x segments relied on its high reactivity toward primary amine group. Efficient one-pot synthesis of PDMS-(F5A₄)₂ was demonstrated using *bisanionic bis*(aminopropyl)poly(dimethylsiloxane) in the reaction with HNF, followed by A_x. Large solubility difference between PDMS and A_x moieties in DMSO led to intermolecular self-assembly of PDMS into elastic submicron particles with an overlayer of chemically bound A_x. The core-shell morphology of the particles in DMSO- d_6 was examined by the ^1H NMR spectroscopic studies. The results agree well with our structural hypothesis of triblock co-oligomer behavior in self-assembly.



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