Final Report

Design and Synthesis of Starburst Conjugate Polymers toward Preparation of Conductive Elastomers

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This report results from a contract tasking National Taiwan University as follows: The contractor will investigate the area of Conducting Elastomers for Gap Treatment with respect to the low-observable maintenance of B-2 and F-22 aircraft. This research will provide an increased understanding of the interplay between the conductivity a

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Polyaniline-based Starburst and Core-shell Conductive Elastomers

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Introduction

Application of conductive polymers requires significant improvement of the materials mechanical and elastic properties in different environment. The simplest approach to combine electronic conductivity with the desirable mechanical strength of polymers in a large-scale preparation is to make a direct blending of conductive polymers with conventional soluble polymers or thermoplastics.[1,2] However, incompatibility of conducting polymers with the hosting polymer matrix, causing irreversible phase-separation or aggregation of microparticles, and the significantly reduced conductivity of final products continue to present as major problems. The tendency of conductive particles to migrate has created inconsistency in electronic performance of these blends. Other preparative methods by design, including *in situ* polymerizations,[3,4] interfacial polymerization,[5] and emulsion polymerization,[6,7] become potentially important approaches in producing technologically valuable blends. We demonstrated previously the utilization of interpenetrating networks (IPN) for the construction of conductive elastomers.[8-11] In that approach, synthesis of conductive polymer composites exhibiting crucial elastic and mechanical properties using *in situ* polymerization of conductive polymer precursors within the supporting polymer matrix was applied. The procedure was performed by first incorporating polymerizable monomers inside the supporting polyurethane elastomer matrix of fullerenol-crosslinked poly(urethane–ether) network followed by a controlled diffusion of oxidative catalysts into the matrix for initiating the polymerization reaction, or vise versa. Specifically, polymerization of aniline monomers at the near-surface region of the polyurethane elastomer thin film in the presence of persulfate oxidant gave conductive polyaniline-interpenetrated fullerenol–polyurethane elastomers (C_{60}-PU-PANi).

Core-shell copolymer structures with the elastic polyurethane core and the polyaniline shell represents an interesting approach for enhancing processability of bulk elastic materials and retaining a low threshold of conductivity.[12] In this report, we describe two synthetic

preparations of core-shell copolymer-based conductive elastomers. One method uses highly charged poly(sulfostyrene)-grafted polybutadiene as a core particle for anchoring the polyaniline shell. The other method utilizes the starburst polyaniline structure derived from the fullerene cage bound on the elastic polysiloxane core submicroparticle. The later synthetic approach becomes possible upon availability of facile starburst hexanilino, hexa(dianilino), hexa(tetraanilino), and hexa(hexadecaanilino)[60]fullerenes syntheses using hexanitro-[60]fullerene (HNF) as a reactive precursor molecule.[13] Hexanitro[60]fullerene was prepared by direct nitration of the C_{60} molecules using gaseous nitrogen dioxide as the nitration agent.[14,15] The tertiary nitro groups of nitrofullerene compounds can be located at allylic or benzylallylic carbon atoms in the structure of HNF. This type of nitro function was found to act as excellent leaving group readily for replacement by a nucleophilic substituent. Utilization of this reactivity towards electron-donor nucleophiles, a synthetic approach was developed for producing oligoanilinated fullerenes as intramolecular donor–acceptor A–$(D)_6$ analogous starburst macromolecules with a well-defined arm number and chain length. Connection of oligoaniline donor–fullerene acceptor A–$(D)_6$ starburst macromolecules onto polysiloxane core particle forms a dendritic core-shell conductive elastomers. Efficient synthesis of starburst oligoanilines is also demonstrated using hexamalonate and pentamalonate [60]fullerene adducts as precursor molecules where C_{60} serves as a molecular core.

In the case of poly(sulfostyrene)-grafted polybutadiene–polyaniline core-shell structural approach, a polyaniline (PANi) shell bound on a submicroparticle of rubber core by charge interaction is demonstrated. During this approach, polymerization of sodium salt of 4-styrenesulfonic acid by a free radical initiator in the hydrophobic phase of oligobutadiene diol (PBD), dispersed in an ethylene glycol solution, was performed. Incorporation of polyaniline based on the charge interaction principle follows those reported by Yang.[16–19] Polymerization of aniline monomers was carried out using ammonium persulfate as the oxidant in aqueous hydrochloric acid solution containing polyanionic rubber copolymer submicroparticles. The resulting rubber-modified polyaniline products form stable and uniform latex in the reaction solution, even with a high polyaniline loading of as high as 58% by weight. For the latex solution with a polyaniline concentration below 37% by weight, thin films with good quality can be fabricated simply by casting and water evaporation. The conductivity of these cast films, after one-week storage in a desiccator, was found to be 0.1 S/cm, which is in a similar magnitude as that of PANi-poly(4-styrenesulfonic acid) complexes reported[20] without incorporating the rubber content. These results indicated promising success in the fabrication of conductive

elastomers with the coexistance of elastic physical properties in the latex phase of the rubber core and requisite electrical properties of the polyaniline shell.
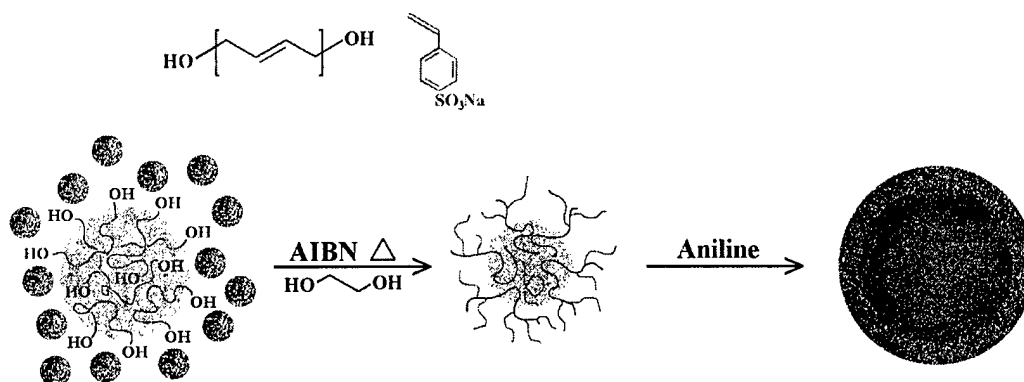
Scheme 1. Schematic preparative representation of poly(sulfostyrene)-grafted polybutadiene–polyaniline core–shell structures.

Experimental

General. Pure C_{60} (99.5%) was purchased from Southern Chemical Group, Georgia and checked by chromatography prior to the use. Sodium salt of 4-styrenesulfonic acid was purified by first dissolving in water followed by precipitating from aqueous sat. NaCl. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Aniline was distilled under vacuum and stored under N_2 for further use. Hydroxy functionalized polybutadiene diol with a number average molecular weight (M_n) of 2,800 was supplied by Aldrich and used as received. Diazabicyclo[5.4.0]undec-7-ene was purchased from Acros Organics, Belgium. Benzene and toluene were dried and distilled over Na.

Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer. UV–vis spectra were recorded on a Hitachi U-3410 UV spectrometer. HPLC analyses and separations were performed on Waters Delta Prep. 4000 HPLC system equipped with a Waters 486 UV detector operated at 340 nm, controlled and processed by Millinum software. A normal-phase silica column was used for the chromatography of malonated adducts of C_{60} using THF–toluene in a ratio of 1:9 as eluent at a flow rate of 0.6 ml per minute. Thermogravimetric analyses (TGA) data were collected on a thermogravimetric analyzer 2950 of TA Instruments with a heating rate of 10 °C per min. Mass spectroscopic studies were performed by the use of either the positive ion fast atom bombardment (FAB$^+$) technique with a direct probe on a JEOL JMS-HX110 high performance mass spectrometer or the negative ion desorption chemical ionization (DCI$^-$)

technique with a direct probe on a JEOL JMS-SX102A mass spectrometer at the NSC instrumentation center of National Tsing-Hwa University, Taiwan. Elemental analyses of fullerene derivatives were carried out at either the Institute of Nuclear Energy Research, Taiwan or the E + R Microanalytical Laboratory, Inc., Corona, New York.

Synthesis of dodecaethyl-hexakis(methano)[60]fullerene dodecacarboxylate 1 and decaethyl-pentakis(methano)[60]fullerene decacarboxylate 2. A modified literature procedure[21-24] was applied in the preparation of **1** and **2** using a mixture of DMA (10 equiv.) and diazabicyclo[5.4.0]undec-7-ene (DBU, 10 equiv.) in the ethyl malonate-addition reaction on C_{60} at ambient temperature for a period of 7 days. The resulting product mixtures were subjected to repeated chromatographic separation (SiO_2, THF–toluene in a ratio of 1:9 as eluent). Three thin layer chromatography (TLC) fractions of the products, C_{60}–[$C(CO_2Et)_2$]$_n$, were isolated and identified by their molecular ion mass as the tetrakismalonate adduct of C_{60} (R_f 0.62, m/z 1353, 13% yield), the pentakismalonate adduct of C_{60} **2** (R_f 0.53, m/z 1511, 27% yield), and the hexakismalonate adduct of C_{60} **1** (R_f 0.44, m/z 1669, 12% yield). The mass spectrum (direct probe, FAB$^+$) of tetrakismalonate adducts of C_{60} m/z (relative intensity, %) 1353 (100, n = 4), 1195 (9.9, n = 3), 1037 (5.7, n = 2), 878 (4.2, n = 1), and 720 (38.8); IR υ_{max} (KBr) 3441 (br), 2983 (C–H), 2938, 2907, 2874, 1747 (s, ester carbonyl), 1465, 1446, 1391, 1369, 1299, 1235 (s), 1180 (shoulder), 1108, 1065, 1023, 861, 815, 737, 708, and 528 cm^{-1}; UV–vis (THF, 1.0×10^{-5} M) λ_{max} (rel. intensity) 294 (0.66) and 469 (0.06) nm. Pentakismalonate adduct of C_{60} **2** m/z (relative intensity, %) 1511 (100, n = 5), 1353 (16.9, n = 4), 1195 (13.7, n = 3), 1037 (11.2, n = 2), 878 (8.1, n = 1), and 720 (44.7); UV–vis (THF, 1.0×10^{-5} M) λ_{max} (rel. intensity) 286 (0.73) and 444 (0.06) nm; IR υ_{max} (KBr) 3454 (br), 2983 (C–H), 2939, 2908, 2875, 1747 (s, ester carbonyl), 1466, 1447, 1392, 1370, 1297, 1233 (s), 1179 (shoulder), 1112, 1098, 1073, 1023, 859, 817, 737, 708, and 525 cm^{-1}. Hexakismalonate adduct of C_{60} **1** m/z (relative intensity, %) 1669 (100, n = 6), 1511 (15.5, n = 5), 1353 (10.9, n = 4), 1195 (8.8, n = 3), 1037 (4.3, n = 2), 879 (4.6, n = 1), and 720 (53.7); IR υ_{max} (KBr) 3455 (br), 2985, 2939 (C–H), 2910, 2875, 1747 (s, ester carbonyl), 1467, 1448, 1393, 1370, 1297, 1241 (s), 1223 (s), 1177 (shoulder), 1096, 1080, 1020, 859, 815, 715, and 527 cm^{-1}; ^{1}H NMR δ 1.17–1.34 (m, 36H), 4.31–4.41 (m, 24H); UV–vis (THF, 1.0×10^{-5} M) λ_{max} (rel. intensity) 278 (0.71) and 337 (0.29) nm.

Synthesis of diethyl-methano[60]fullerene dicarboxylate 3. A reported procedure was applied in the preparation of **3**.[21-24]

*General procedure for the synthesis of fullerene dodeca(hexadecaanilino)adduct **4**, deca(hexadecaanilino)adduct **5**, and di(hexadecaanilino)adduct **6**.* A dry flask equipped with a stirring bar and a condenser was charged with the diethyl-bismalonate adduct of C_{60} **3** (180 mg, 0.2 mmol) and a solvent mixture of DMSO (10.0 ml) and THF (2.0 ml) under N_2. It was added diazabicyclo[5.4.0]undec-7-ene (0.6 ml, 4.0 mmol), followed by hexadecaaniline (the emeraldine base form, 660 mg, 0.45 mmol) in DMSO (5.0 ml). The reaction mixture was stirred at 85 °C for 15.0 h. At the end of the reaction, it was quenched with water to effect precipitation of the solids. The solids were washed with acetonitrile and dissolved in DMSO (15 ml). The DMSO solution was added slowly by acetonitrile (300 ml) to result in precipitation of the products, which were isolated by centrifuge. This purification process was repeated twice until no starting hexadecaaniline was detectable on chromatography [TLC, SiO_2, R_f = 0.7–0.75, THF–$CHCl_3$ (1:1)–pyridine (one drop)]. The resulting blue solids were then dried under vacuum at 40 °C to yield di(hexadecaanilino)-methano[60]fullerene dicarbamide **6** (615 mg, 83%). IR υ_{max} (KBr) 3388 (br), 3035, 2933 (C–H), 2860, 1656 (amide), 1600, 1506 (s), 1300, 1172, 1123, 1044, 829, 751, 698, and 508 cm^{-1}; UV–vis (DMSO, 1.5 x 10^{-6} M) λ_{max} 325 (benzenoid absorption) and 595 (quinonoid absorption) nm. ^1H NMR δ 6.67 (m, 17H), 6.90 (m, 86H), 7.11 (m, 25H), and 7.75 (N–H, 8H, disappear in D_2O).

Similar reaction conditions were applied in the preparation of dodeca(hexadecaanilino)-hexakis(methano)[60]fullerene dodecacarbamide **4** and deca(hexadecaanilino)-pentakis(methano)[60]fullerene decacarbamide **5** from the corresponding dodecaethylhexamalonate adduct of C_{60} **1** and decaethylpentamalonate adduct of C_{60} **2**, except 13.0 and 11.0 equivalents of hexadeca-aniline, respectively, were used. A product yield of 70–78% was obtained for both compounds of **4** and **5**. For the compound **4**: IR υ_{max} (KBr) 3387 (br), 3033 (br), 2931 (C–H), 2859, 1659 (amide), 1599, 1505 (s), 1298, 1171, 1128, 826, 750, 697, 636, and 507 cm^{-1}; UV–vis (DMSO, 1.0 x 10^{-6} M): λ_{max} 323 (benzenoid absorption) and 595 (quinonoid absorption) nm; ^1H NMR (number of protons per arm) δ 6.67 (m, 8H), 6.94 (m, 44H), 7.11 (m, 12H), and 7.7–7.9 (N–H, 4H, disappear in D_2O). For the compound **5**: IR υ_{max} (KBr) 3382 (br), 3280 (br), 3036, 2936 (C–H), 2865, 1648 (amide), 1600, 1504 (s), 1300, 1174, 1116, 828, 751, 697, 619, and 509 cm^{-1}; UV–vis (DMSO, 1.0 x 10^{-6} M): λ_{max} 325 and 595 nm; ^1H NMR (number of protons per arm) δ 6.67 (m, 8H), 6.90 (m, 44H), 7.11 (m, 12H), and 7.6–7.8 (N–H, 4H, disappear in D_2O).

*Synthesis of hexanitro[60]fullerene (HNF) **7**.* A modified procedure was applied.[14,15] A two-necked reaction flask A (50 ml) was equipped with a vertical dropping funnel with a

stopcock on one neck and a connecting gas bubbling tube on the other. The gas-bubbling tube was attached by two drying tubes (one with $CaCl_2$ and the other one with P_2O_5) and inserted into a empty flask covered with a septum via a syringe needle. A long cannula tubing was used for connecting this flask and the second two-necked reaction flask B. The flask B was attached with a bubbling tube, which was extended into a trapping flask containing aqueous sodium hydroxide solution (2 N). For the minimization of the back-flow of moisture from alkaline solution, a drying tube ($CaCl_2$) was installed in between the flask B and the trapping flask. A steady, slow inert gas (N_2) flow was allowed starting from the top of dropping funnel, through the reaction flasks A and B in sequence, into the alkaline solution in the trapping flask.

The dropping funnel and the reaction flask A were charged with conc. HNO_3 (50 ml) and copper powder (40 g), respectively. In the reaction flask B was placed a solution of C_{60} (1.0 g) in dry benzene (700 ml) under N_2. The inert gas bubbling through the C_{60} solution in the flask B was adjusted to a flow rate of 5 ml per min. The fullerene solution was deoxygenated for at least 20 min prior to the reaction. Concentrated HNO_3 solution was then allowed to be added dropwise into the flask A cooled under a water bath at 20 °C. Brown fume was produced immediately upon the contact of conc. HNO_3 with Cu. It was carried by the steady flow of N_2 gas and bubbled through the C_{60} solution in the flask B. Within 2.0 h of reaction, the purple solution of C_{60} was changed to orange-red progressively. The mixture was stirred at 30 °C for an additional 17 h to give an orange solution with suspended solids. At the end of reaction, excessive nitrogen dioxide (NO_2) was removed by bubbling of N_2 gas and destroyed in the trapping solution. Benzene was then evaporated from the product solution under a reduced pressure to give bright orange solids. The solids were suspended in anhydrous *n*-hexane, separated from *n*-hexane solution by the centrifuge technique, washed with hexane quickly under N_2, and dried under vacuum at 40 °C to afford solids of hexanitro[60]fullerene **7** (1.35 g). Physical data of **7** bore a close resemblance to that reported previously.[14,15]

Synthesis of hexaanilino[60]fullerene (HAF) 8. A round bottomed flask (dried, 50 ml) equipped with a condenser and a magnetic stirring bar was charged with hexanitro[60]fullerene, $C_{60}(NO_2)_6$, (1, 400 mg, 0.4 mmol) and THF (20 ml) under N_2. Freshly distilled aniline (1.13 g, 12.0 mmol, 30 equiv.) in THF (10 ml) was added to the flask, followed by triethylamine (2.0 g). The reaction mixture was stirred at 50 °C for 6 h. It was then cooled and quenched with a mixture of water, THF and ethylacetate. The organic layer (THF and ethylacetate) was washed three times with brine and once with H_2O. The solution was dried over anhydrous Na_2SO_4 and filtered. Most of solvents were then removed until a viscous dark brown liquid was obtained.

Products were precipitated from the liquid by addition of an excess of hexane. Solid precipitates were centrifuged, washed with hexane until no detection of aniline on TLC, and dried under vacuum to yield hexanilino[60]fullerene 2 (475 mg, 94%). IR υ_{max} (KBr) 3392 (br, N–H), 3052 (C–H), 2978 (C–H), 1600 (s), 1495 (s), 1314, 1252, 1067, 751 (s), 693 (s), and 536 cm^{-1}; UV-vis (THF, 2.5 x 10^{-6} M): λ_{max} 242 and 295 (shoulder) nm. ^{1}H NMR (CDCl$_3$) δ 1.58 and 6.7–7.3. Anal. Calcd for $C_{96}H_{66}N_6O_{15}$ as $C_{60}(NHC_6H_5)_6$–15H$_2$O: C, 74.71; H, 4.28; N, 5.45; O, 15.56. Found: C, 74.34; H, 4.54; N, 5.44; O, 15.68 (by difference). Mass Spectrum (DCI$^-$–MS, direct probe, negative ion, mass of the highest ion peak in the fragmentation group), m/z 721, 813 (n = 1, rel. intensity 100), 904 (n = 2), 995 (n = 3), 1086 (n = 4), 1177 (n = 5), and 1268 (n = 6), consistent with anionic polynitrated C_{60} formula of $C_{60}(NC_6H_5)_n^-$.

Synthesis of hexa(tetraanilino)[60]fullerene (HTAF) **9**. In a dry flask with a magnetic stirring bar, hexanitro[60]fullerene (0.39 g, 0.39 mmol) dissolved in THF (10 ml) was charged under N$_2$. To this solution, tetraaniline (1.03 g, 2.82 mmol, 7.2 equiv.) in dry THF (15 ml) was added, followed by triethylamine (3.0 g). The deep blue-colored reaction mixture was stirred at 50 °C for 6.0 h and quenched by the addition of water and THF. The organic layer was then washed three times with brine and dried over anhydrous Na$_2$SO$_4$. After removal of most of the solvents, the dark blue products were precipitated upon the addition of ether (50 ml). The precipitates were filtered and washed with ether untill no blue coloration in the washings was observed. The solids were then dried in vacuum at 40 °C and purified by preparative TLC [SiO$_2$, R_f = 0.1 using THF–CHCl$_3$ (1:1) as eluent] to yield hexa(tetraanilino)[60]fullerene **9** (0.82 g, 72%). IR υ_{max} (KBr) 3381 (br, N–H), 3031 (C–H), 1596, 1509 (s), 1303, 1245, 1171, 1071, 828, 748, 694, and 501 cm^{-1}; UV-vis (THF, 2.5 x 10^{-6} M): λ_{max} 303 and 548 nm. Anal. Calcd for $C_{204}H_{138}N_{24}O_{12}$ as $C_{60}(NHC_6H_4NC_6H_4NC_6H_4NHC_6H_5)_6$-12H$_2$O: C, 78.62; H, 4.45; N, 10.79; O, 6.17. Found: C, 77.42; H, 4.13; N, 10.90; O, 7.55 (by difference).

Synthesis of hexa(hexadecaanilino)[60]fullerene (HHDAF) **10**. In a dry flask purged with nitrogen, hexanitro[60]fullerenes (0.11g, 0.11 mmol) dissolved in THF (5.0 ml) was charged under N$_2$. To this solution hexadecaaniline (0.96 g, 0.66 mmol, 6.0 equiv.) in dry THF (20 ml) was added followed by triethylamine (3.0 g). To enhance the solubility of the products in solution, N-methyl pyrolidinone (7.0 ml) was also added. The deep violet-colored reaction mixture was stirred at 50 °C for 24 h. At the end of reaction, THF was removed by rotary evaporation. The remaining black-colored solution was poured into water (40 ml) causing precipitation the products. The dark violet-colored precipitates were washed several times with

water (10 ml each) and filtered. The solids were further washed several times with acetonitrile (10 ml each) for removal of unreacted hexadecaaniline until no violet color shown in the washings and dried under vacuum at 40 °C to afford hexa(hexadecaanilino)[60]fullerene **10** (0.98 g) in 94% yield. Chromatographic purification of **10** was performed on TLC [SiO$_2$, R_f = 0.8 for hexadecaaniline and R_f = 0.1 for **10** using THF–CHCl$_3$ (1:1) as eluent or R_f = 0.9 for hexadecaaniline and R_f = 0.2 for **10** using THF–CHCl$_3$ (3:1) as eluent]. IR υ_{max} (KBr) 3407 (br, N–H), 2934 (C–H), 2855, 1658, 1594, 1507 (s), 1303, 1262, 1183, 1143, 1051, 824, 755, 696, and 508 cm^{-1}; UV-vis (THF, 2.5 x 10^{-6} M): λ_{max} 229, 317, and 584 nm. Anal. Calcd for C$_{636}$H$_{552}$N$_{96}$O$_{48}$ as C$_{60}$[(NHC$_6$H$_4$NC$_6$H$_4$NC$_6$H$_4$NH- C$_6$H$_5$)$_4$]$_6$-48H$_2$O: C, 74.13; H, 5.36; N, 13.05; O, 7.46. Found: C, 74.3; H, 5.2; N, 12.4; O, 8.1 (by difference). DCI$^-$–MS of **10** m/z 721 (C$_{60}$, 85.1), 548 (n = 6), 637 (n = 7), 728 (n = 8), 820 (n = 9), 912 (n = 10), 1003 (n = 11), 1093 (n = 12), 1185 (n = 13), 1276 (n = 14), 1367 (n = 15), and 1459 (n = 16) for hexadecaaniline ions, H(C$_6$H$_4$NH)$_n^-$; also m/z 561 (n = 6), 653 (n = 7), 744 (n = 8), 835 (n = 9), 927 (n = 10), 1018 (n = 11), 1110 (n = 12), 1200 (n = 13), 1292 (n = 14), 1383 (n = 15), and 1475 (n = 16) for HN(C$_6$H$_4$NH)$_n$H$^-$ ions.

Synthesis polysulfostyrene grafted poly(1,4-butadiene). Preparation of polysulfostyrene grafted poly(1,4-butadiene) copolymers was carried out at 80 °C under N$_2$ in a three-necked flask (250 ml) equipped with a mechanical stirrer. The quantity of reactant and solvent components were summarized in Table 1. A latex-like suspension of poly(1,4-butadiene) diol (2.0 g) in polystyrene sulfonic acid (2.0 g)-containing dioxane–H$_2$O or ethylene glycol (10–15 ml) solution was formed rapidly upon vigorous stirring. The AIBN initiator (100 mg) was added at ambient temperature. The reaction solution was then deoxygenated by bubbling with a stream of N$_2$ gas for a period of 10 min. The polymerization reaction began as the temperature was raised to 80 °C. After a polymerization period of 8.0 h, the reaction mixture was cooled down to room temperature. Precipitation of the products became effective upon addition of acetone. Removal of residual reactants, organic solvents, and polysulfostyrene homopolymer (PSS) was achieved by dispersing the copolymer products in water (10 ml), followed by slow addition of acetone until the precipitation of copolymer solids. This purification procedure was repeated at least twice. The resulting polysulfostyrene-grafted poly(1,4-butadiene) copolymer solids (PSSB1 to PSSB4) were further purified three times by solvent extraction with hexane for removing the remaining residual free polybutadiene starting materials.

Synthesis polyaniline-polysulfostyrene grafted poly(1,4-butadiene) core-shell particles.

Polymerization of aniline in the presence of polysulfostyrene-grafted poly(1,4-butadiene) copolymer latex in H_2O was typically carried out at room temperature by using a 1:1.25 mole ratio of aniline to ammonium persulfate oxidant in dilute HCl solution (0.1 N) for a period of 4 h (detailed conditions are shown in Table 2). The resulting PANi-containing polysulfostyrene-grafted poly(1,4-butadiene) latex was purified by slow addition of acetone until effective precipitation of the products. Removal of residual reactants was achieved by dispersing the copolymer products in water (25 ml), followed by slow addition of acetone to effect precipitation of copolymer solids. This purification procedure was repeated at least twice. Final products of polyaniline-polysulfostyrene grafted poly(1,4-butadiene) core-shell particles can be kept in aqueous solution. The yield of polyaniline as a percentage by weight of the product was summarized in Table 2.

Results and Discussion

Monomalonization and polymalonization of the fullerene molecule were demonstrated by the reaction of bromomalonate ester or a mixture of malonate ester and CBr_4 with C_{60} in the presence of diazabicyclo[5.4.0]undec-7-ene (DBU).[21] The yield of the reaction can be improved by the use of reversible-template activation with 9,10-dimethylanthracene (DMA).[22] Polymalonization at all-equatorial sites of C_{60} leading to a hexakis-adduct with a symmetrical octahedral functionalization pattern was achieved at a yield of 20–30% in the presence of DMA.[23] However, complication of these reactions arises from the coexistence of incomplete malonation products, as isomeric tetrakis-adducts and the pentakis-adduct,[24] even after a prolong reaction period. It is rather tedious to isolate and separate these mixtures from each other in a pure form. By following the reported procedure using a mixture of DMA (10 equiv.) and DBU (10 equiv.) in the ethyl malonate-addition reaction on C_{60} at ambient temperature for a period of 7 days, the resulting product mixtures were subjected to repeated chromatographic separation (SiO_2, THF–toluene in a ratio of 1:9 as eluent). Three thin layer chromatography (TLC) fractions of products were isolated and identified, according to their molecular mass ion (direct probe, FAB^+–MS), as tetrakismalonate adducts of C_{60} (R_f 0.62, m/z 1353, 13% yield), the pentakismalonate adduct of C_{60} **2** (R_f 0.53, m/z 1511, 27% yield), and the hexakismalonate adduct of C_{60} **1** (R_f 0.44, m/z 1669, 12% yield). The yield of the hexaadduct **1** can be improved by repeating the same reaction procedure using **2** as a starting material. Incorporation of 9,10-dimethylanthracene on the C_{60} cage was evident as we were able to isolate a mixture of hexakismalonate and dimethylanthracene–pentakismalonate adducts of C_{60} prior to the

chromatographic purification. The ^{1}H NMR spectrum of the later compound showed a clear up-field chemical shift of methyl protons to δ 2.12 (6H, singlet) from δ 3.1, corresponding to that of DMA, along with the shift of aromatic proton peaks to δ 7.27 (4H, doublet) and 7.34 (4H, doublet). These chemical shifts of the protons agree well with those of the [2 + 4] dimethylanthracenic cyclization-adduct of C_{60}. The dimethylanthracenic cap can be removed from the fullerene cage simply by the silica column filtration leading to the isolation of **2**.

Synthesis of starburst dodeca(hexadecaanilino) and deca(hexadecaanilino)[60]fullerene

High molecular weighted polyaniline (PANi)[25,26] exhibits several intrinsic chromogenic structures upon the treatment of either chemical oxidation or reduction, producing various composition forms including blue protonated pemigraniline, violet pemigraniline base, blue emeraldine base, green protonated emeraldine, and colorless leucoemeraldine. Among these different forms, the protonated emeraldine base is the conductive material. Accordingly, switch of the optical absorption and conductivity of polyaniline, upon structural interchange between its benzenoid and quinonoid-forms along the polymer chain, can be achieved simply by the reversible electrochemical redox and chemical protonation–deprotonation treatments. It was proposed that electronic properties of polyaniline can be simulated using oligoaniline models, such as octaaniline in an intermediate emeraldine base oxidation state of B_5Q_2 (B denotes a benzenoid group and Q denotes a quinonoid group in the backbone of oligoaniline.).[27,28] That prompted many studies of oligoanilines aiming to qualitatively reproduce the electronic conductivity of PANi in its low molecular weight version of oligomers.[29] Generation of an appreciable conductivity with oligoanilines becomes possible when a proper oxidation state is made and coupled with the protonation using a Brönsted acid.[30,31] The use of oligoaniline donor (D) as the component of star arms in connection with the fullerenic acceptor (A) core should lead to the corresponding electro- and photo-active $A-(D)_n$ macromolecules, resembling partly the electronic characteristics of PANi.

Starburst fullerene dodeca(hexadecaanilino)adduct **4** and deca(hexadecaanilino)adduct **5** were synthesized utilizing dodecaethyl-hexakis(methano)[60]fullerene dodecacarboxylate **1** and decaethyl-pentakis(methano)[60]fullerene decacarboxylate **2**, respectively, as starting precursor molecules, as shown in Scheme 1. Reaction of the heptaad compound **1** with hexadecaaniline (12.5 equiv.) in its emeraldine base (E.B.) form was carried out in DMSO in the presence of DBU (excess) at 90 °C for a period of 15 h. Similar conditions were applied in the reaction of hexadecaaniline with fullerene pentakisadduct **2** for preparation of the corresponding

macromolecule **5**.

1 (n = 6), **2** (n = 5)
3 (n = 1)

4 (n = 6), **5** (n = 5)
6 (n = 1)
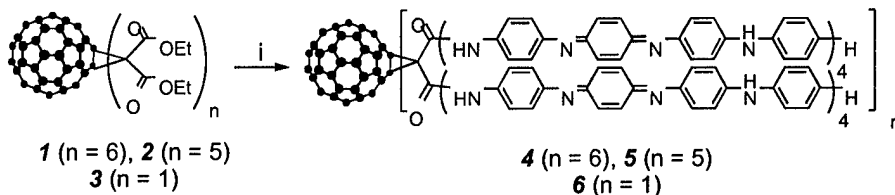
Scheme 1. *Reagents and conditions:* i, hexadecaaniline (EB, 12.5 equiv.), DBU, DMSO, 90 °C, 15 h.

Hexadecaaniline used in this study was prepared by the reaction of tetraaniline in its leucoemeraldine reduced form with $(NH_4)_2S_2O_8$ (1.5 equiv.) in aqueous HCl solution (0.1 N) at ambient temperature for 2.0 h.[31] Tetraaniline leucoemeraldine can be generated by the reduction of tetraaniline emeraldine using hydrazine (NH_2NH_2) as a reducing agent. Purification of the starting compound, tetraaniline emeraldine, was made by column chromatography (SiO$_2$, R_f 0.85) with a mixture of pet ether–CHCl$_3$ (2:3) containing triethylamine (3%) as eluent. In the workup procedure of the hexadecaaniline preparation, the product mixture was neutralized with NH$_4$OH for removal of the acidic protons that led to the isolated hexadecaaniline in its blue emeraldine base form. Soluble impurities remaining in the product was subsequently removed by soxhlet extraction with diethyl ether. A small-scale chromatographic purification of hexadecaaniline on TLC (SiO$_2$) was possible at R_f 0.6–0.75 using THF–CHCl$_3$ (1:1) or THF–EtOAc (1:2) as eluent. The molecular ion mass group at *m/z* 1450–1458 depending on the number of quinonoid units in the structure of hexadecaaniline was detected in the negative ion desorption chemical ionization mass spectrum (DCI⁻–MS).[13,32] At the end of the amidation reaction for the synthesis of **4** and **5**, all solid materials precipitated upon the addition of water were collected and subsequently washed with acetonitrile for removal of DBU and the unreacted hexadecaaniline. The process was continued until colorless in further washings was observed. Separation and purification of the macromolecules **4** and **5** from a trace amount of hexadecaaniline remaining in the product solid can be done by dissolving them in DMSO, followed by reprecipitation upon addition of acetonitrile to the solution. A sample of **4** or **5** free of hexadecaaniline was confirmed by TLC chromatography (SiO$_2$, THF–DMSO) and obtained in a high yield of 85–95%. Nucleophilic substitution reactivity of the terminal amino functional group of each hexadecaaniline molecule is apparently higher than that of the in-chain amino groups in replacing the ester ethoxy group. It is partially owing to the extended resonance of non-reactive quinonoid units, which contribute up to a 50% content in the structure

of the emeraldine base form of hexadecaaniline, along the oligomer chain. That results in deactivation of nucleophilicity of the in-chain amino groups. This preferentially higher chemical reactivity of the terminal amino group in either tetraaniline or hexadecaaniline was also demonstrated recently in nucleophilic substitution reactions with the nitro groups of hexanitro[60]fullerenes. Therefore, conversion of ethyl malonate ester moieties of 1–3 to the corresponding hexadecaanilinate amide 4–6 occurred exclusively at the terminal primary amino group.
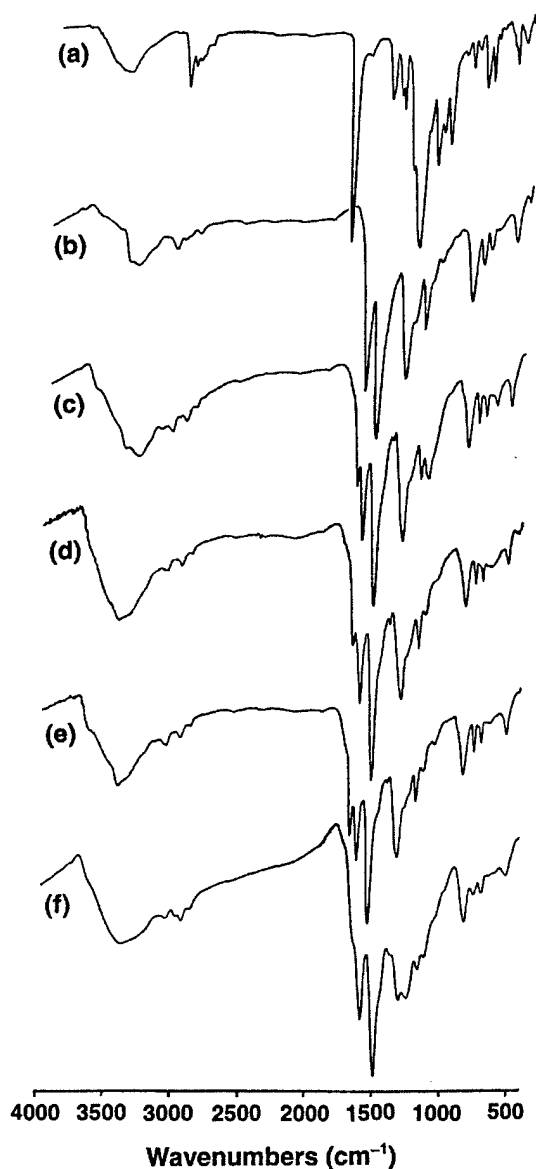
Fig. 1. Infrared spectra of (a) decaethyl-pentakis(methano)[60]fullerene decacarboxy-late 2, (b) hexadecaaniline (the emeraldine base form), (c) deca(hexadecaanilino)-pentakis-(methano)[60]fullerene decacarbamide 5 (E.B.), (d) dodeca(hexadecaanilino)-hexakis-(methano)[60]fullerene dodecacarbamide 4 (E.B.), and (e) di(hexadecaanilino)-methano[60]fullerene dicarbamide 6 (E.B.).

Completion of the amidation was followed by full disappearance of the ester carbonyl absorption band at 1747 cm^{-1} (Fig. 1a) and the ethylene proton peak centered at δ 4.37 and 1.35 in the infrared and ^{1}H NMR spectra, respectively, of the product. It was replaced by the optical absorption band of the amide functional groups at 1650 cm^{-1} (Figs. 1c, 1d, and 1e) and the peaks centered at δ 6.92, respectively, corresponding to the chemical shift of aromatic protons of oligoaniline. The ^{1}H NMR data of 4–6 clearly confirmed full replacement of all ethoxy functional groups in 1–3 by hexadecaanilines. No evidence of residual byproducts, containing partially-amidated dodecaester 1 or decaester 2, in the purified 4 and 5, respectively. As an example, multiple arm-addends on C$_{60}$ lead to a product showing domination of the bands corresponding to the characteristic optical absorption of hexadecaaniline (Fig. 1b) in the spectrum of 4 (Fig. 1d) and 5 (Fig. 1c).

In the case of diethyl-methano[60]fullerene dicarboxylate 3, conversion of its ethyl ester functional groups to pentadecaanilinophenylamides was carried out under similar reaction conditions, except only 2.1 equiv. of hexadecaaniline was applied in a solvent mixture of DMSO–THF (5:1). The resulting product was precipitated by the addition of water and purified by repeated washings with acetonitrile and chromatography (TLC, SiO$_2$), giving di(hexadecaanilino)methano[60]fullerene dicarbamide (E.B.) 6 as dark blue solids in 83% yield. Both the infrared and ^{1}H NMR spectrum of 6 displayed full disappearance of the ester carbonyl absorption band and the NMR ethylene proton peaks, respectively, in close resemblance to those of 4 and 5. It indicated clearly a new band at 1656 cm^{-1} corresponding to the optical absorption of the amide functional groups, as shown in Fig. 1e. The overall spectrum profile is in close resemblance to that of hexadecaaniline emeraldine. The thermogravimetric (TGA) measurement of di(hexadecaaniline)adduct 6 gave a steady weight loss upon heating at a rate of 10 °C per min from 25 to 800 °C. Since the fullerene cage is stable in solid state under N$_2$ up to 800 °C, the residual weight of solids remaining at this temperature range may be indicative of a carbon formation consisting of a high ratio of fullerene-related materials. Accordingly, the detected of residual solid 33% in weight at 800 °C in the TGA experiment should correspond to a carbonaceous material containing roughly 60% of fullerene-related cages.

Facile reaction of hexanitro[60]fullerene with hexadecaaniline

Recently, we reported the synthesis and characterization of hexanitro[60]fullerene (7, HNF), C$_{60}$(NO$_2$)$_6$, containing a well-defined number of addends using the radical addition of nitrogen dioxide as a nitration method.[15] Reactivity of fullerenic nitro groups in the structure of 7 is high

even with weak nucleophiles,[14] such as H_2O, in a neutral solution at elevated temperatures. As the nucleophilicity of reactant increases, faster reaction kinetics is expected. A large increase in reactivity of primary organo-amines toward the replacement of fullerenic nitro groups overcomes the rate-retarding effect induced by the increasing structural complexity of the reactant. This improved precursor approach allows the attachment of multiple oligoanilines onto a C_{60} cage in a moderate to fast rate. Contrary, synthesis of oligoanilinated fullerenes was difficult using a direct addition reaction of C_{60} with oligoanilines even though fullerenes were reported to be reactive with some simple amines.[33,34]

The reaction of C_{60} in either toluene or benzene with gaseous $\cdot NO_2$ at ambient temperatures for a period of 3–4 h gave orange-red products of polynitrofullerenes in a high yield of more than 90%. Generation of nitrogen dioxide radicals was made by either the reaction of sodium nitrite with conc. HNO_3 or the reduction of HNO_3 with copper powder. The degree of nitration was found to follow a stepwise manner with addition of two nitro groups at each step. The rate of nitration can be accelerated to completion by increase of the reaction temperature from 25 to 40 °C. It was accompanied with increase in a comparable yield of hexanitro[60]fullerene (39%) and tetranitro[60]fullerene (47%). Consecutive addition of nitro groups onto TNF was detectable within a reaction period of 16 h as HNF becoming a major product and showing nearly a single peak in its chromatographic profile at the end of reaction. It was concluded that tetranitration of C_{60} was a relatively rapid process that prohibited clean isolation of dinitro[60]fullerene.

Most of fullerenic nitro functional groups of polynitrofullerenes can be located at a tertiary benzyl carbon adjacent to extended olefins. This particular hyper-conjugated structure makes nitro groups acting as potent leaving groups. Nucleophilic replacement of these nitro leaving groups by multi-functional heteroatom-containing alkoxy, thiol, and amino analogous nucleophiles may represent a facile synthetic method for the preparation of new polyfunctionalized fullerene derivatives and polymers. Hydrolytic side-reactions became negligible when primary organoamine compounds were used as nucleophiles under anhydrous conditions. Thus, amphiphilic aniline and polar oligoanilines readily attack 7 forming the corresponding starburst anilinated and oligoanilinated C_{60} molecules, respectively, without showing much complication of hydroxylated byproducts. Complete substitution of all nitro groups in 7 by oligoanilines yielded the corresponding hexa(oligoanilino)[60]fullerenes.

In this study, the acid-doped tetraaniline was prepared by a reported method from N-phenyl-1,4-phenylene diamine (dianiline) using ferric chloride hexahydrate (1.0 equiv.) as an

oxidant in aqueous HCl solution (0.1 N) at ambient temperatures for 2.0 h.[31]   Positive ion fast atom bombardment (FAB$^+$) mass spectrum (direct probe) of the neutralized products of tetraaniline, pre-treated by NH_4OH, showed several fragmented mass groups corresponding to oligoaniline ions of $C_6H_5NHC_6H_4NH^+$, $C_6H_5NH(C_6H_4NH)_3H^+$, $C_6H_5NH(C_6H_4NH)_5^+$, and $C_6H_5NH(C_6H_4NH)_7^+$ at m/z (relative intensity) 183 (21%), 366 (24%), 547 (6.0%), and 729 (1.3%), respectively.   The data are indicative of the existence of aniline hexamer and octamer as minor products resulted from the oxidative coupling reaction of aniline dimer with ferric chloride in addition to the major product of aniline tetramer.   After further separation of the neutralized products on the thin layer chromatographic plates (TLC, SiO_2), tetraaniline 6 in its emeraldine oxidation state was isolated at $R_f = 0.5$ using EtOAc–hexane (1:1) or $R_f = 0.7$ using THF–CHCl$_3$ (1:1) as eluent.

The acid-doped hexadecaaniline was prepared by the reaction of tetraaniline in its leucoemeraldine oxidation state with $(NH_4)_2S_2O_8$ (1.5 equiv.) in aqueous HCl solution (0.1 N) at ambient temperatures for 2.0 h.   Tetraaniline leucoemeraldine was made by the reduction of tetraaniline emeraldine with hydrazine (NH_2NH_2).   After neutralization with NH_4OH and chromatographic isolation of the products on TLC (SiO_2), hexadecaaniline was obtained at $R_f = 0.6$–0.75 using THF–CHCl$_3$ (1:1) as eluent.   Negative ion desorption chemical ionization mass spectrum of hexadecaaniline displayed a series of ion fragmentation groups with the mass of the highest ion peak in the group at m/z 366 (n = 4), 457 (n = 5), 548 (n = 6), 639 (n = 7), 730 (n = 8), 821 (n = 9), 911 (n = 10), 1002 (n = 11), 1092 (n = 12), 1183 (n = 13), 1274 (n = 14), and 1454 (n = 16), corresponding to (aniline)$_n$ ions.   The mass of ions less than that of aniline decamer matches well with the molecular weight of the corresponding oligoaniline in the leucoemeraldine state.   Slight increase of 1–2 quinonoid aniline units (Q, $=C_6H_4=$) per oligoaniline chain was detected in the higher mass ions.   Preservation of the quinonoid aniline structure during fragmentation became more obvious in the matrix-assisted laser desorption ionization (MALDI) mass spectrum of 7.   It showed a similar series of ion fragmentation groups in the higher mass region than m/z 700 with the mass of the highest ion peak in each fragmented group at m/z 726 [H(C$_6$H$_4$NH)$_8$H – 4H], 816 [H(C$_6$H$_4$NH)$_9$H – 5H], 907 [H(C$_6$H$_4$NH)$_{10}$H – 5H], 998 [H(C$_6$H$_4$-NH)$_{11}$H – 5H], 1087 [H(C$_6$H$_4$NH)$_{12}$H – 7H], 1179 [H(C$_6$H$_4$NH)$_{13}$H – 6H], 1269 [H(C$_6$H$_4$-NH)$_{14}$H – 7H], 1359 [H(C$_6$H$_4$NH)$_{15}$H – 8H], 1450 [H(C$_6$H$_4$NH)$_{16}$H – 8H], 1540 [H(C$_6$H$_4$-NH)$_{17}$H – 9H], and 1630 [H(C$_6$H$_4$NH)$_{18}$H – 10H].

Unlike other aliphatic nitro compounds, the fullerenic carbon-nitro bonding is rather weak and vulnerable to nucleophilic replacement and rearrangement in solution at ambient

temperatures. Its stability increases sharply in the solid state at 0 °C. This type of nitro groups can be replaced over an extended period of time by water molecules forming partially hydroxylated nitrofullerene derivatives. Upon the treatment of $C_{60}(NO_2)_6$ in THF with an excess of freshly distilled aniline in the presence of triethylamine at 50 °C for 6.0 h under N_2, hexaanilino[60]fullerene (HAF, **8**) was obtained as a major product (brown solids) in 94% yield. Separation of the compound **8** from the reaction medium was achieved by precipitation and repeated washings with hexane that was accompanied with removal of unreacted aniline, Et_3N, and other byproducts. Further purification of **8** was performed on the thin-layer chromatographic plates (TLC, SiO_2) at $R_f = 0.76$ using a mixture of THF–$CHCl_3$ (1:1) as eluent.

In the case of aniline tetramer and hexadecamer, their nucleophilic substitution reactions with $C_{60}(NO_2)_6$ were found to be much more efficient than a similar reaction with aniline and dianiline. Only one equivalent quantity of tetraaniline or hexadecaaniline per nitro group of HNF was necessary to achieve completion of the reaction in the presence of triethylamine in THF at 50 °C for 6 h or longer. In this reaction, a co-solvent of N-methyl pyrolidinone (NMP) was used for enhancing the solubility of hexadecaaniline in THF prior to the reaction with **7**. Utilization of the co-solvent was also advantageous for preventing precipitation of the partially hexadecaanilinated fullerene intermediates during the reaction. A longer reaction period of 24 h was applied for the reaction with **7** than that for tetraaniline (6.0 h). At the end of reaction, NMP was removed easily from the products upon the addition of water that also caused precipitation of hexadecaanilinated fullerenes from the medium. The solid products were subsequently washed with either ether or acetonitrile for removal of remaining unreacted tetraaniline or hexadecaaniline, respectively. Hexa(tetraanilino)-[60]fullerene (HTAF, **9**) and hexa(hexadecaanilino)[60]fullerene (HHDAF, **10**) were obtained as dark blue to violet solids in 72 and 94% yield, respectively. Appreciable solubility of **10** in NMP and a mixture of NMP–THF made its chromatographic purification possible on TLC [SiO_2, $R_f = 0.9$ for **7** and $R_f = 0.2$ for **10** using THF–$CHCl_3$ (3:1) as eluent]. All products of **8**, **9**, and **10** displayed a sharp single chromatographic peak in their HPLC profile using a reverse-phase MCH–5 column and acetonitrile as eluent. A relatively high purity in terms of the composition of these starburst molecules was confirmed. The retention time of **9** (3.9 min) and **10** (4.0 min) was found to be lower in value than that of **8** (4.5 min), indicating a slightly higher polarity for **9** and **10**.

Synthesis of poly(dimethylsiloxane)-starburst fullereno(oligoaniline) core-shell conductive submicro to nano elastic particles

Improvement of materials impact strength on conductive polymers requires incorporation of elastic polymers for dispersing the external impact force. Incompatibility of conventional linear rubbery structures with the semi-rigid conductive conjugate polymers induces severe phase-separation of these two components in the blend or solution mixing. The lack of electron-transport path between phase-separated conductive macroparticles often significantly reduces the bulk conductivity.
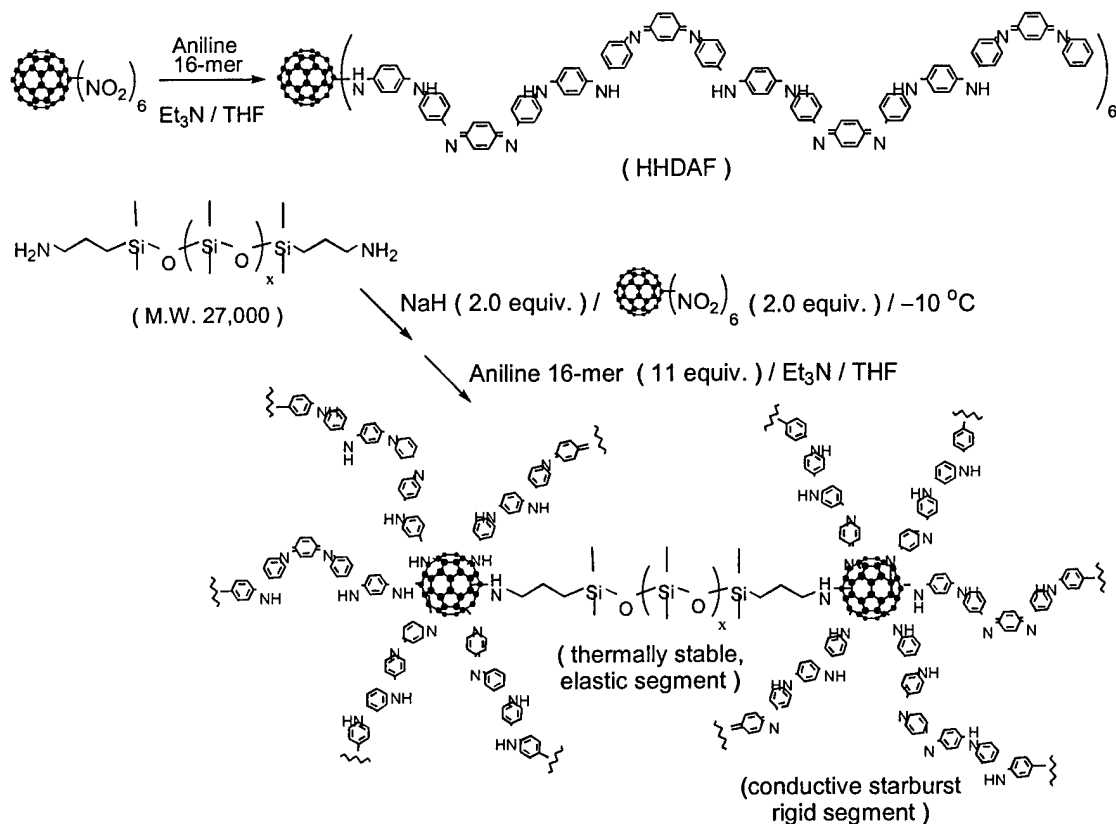
Scheme 2.

One method to enhance the compatibility is to graft conductive polymer segments directly on the elastic polymer chain. The covalent bonding between two incompatible components should fully eliminate their separation tendency. Polyaniline containing an amino end-group makes it suitable for the nucleophilic grafting reaction on elastomeric polymers. Chemical reactivity of polyaniline decreases as its molecular weight increases. The use of aniline oligomer as a conductive component should largely improve the nucleophilic reactivity of its amino end-group and the synthetic yield.

Hexadecaaniline was found to exhibit appreciable high reactivity in replacing fullerenic nitro group under mild conditions. Utilization of hexanitro[60]fullerene (HNF) as a molecular core on the synthesis of starburst conjugate macromolecules, such as hexa(hexadeca-

anilino)[60]fullerene (HHDAF), represents an interesting approach in preparation of conductive composites. Hexanitro[60]fullerene consists of 6 highly electron-withdrawing leaving groups which can be utilized for connecting multiple structural segments with variation of physical and mechanical properties. Our approach for incorporation of elastic segments in bonding with conductive segments includes the application of bis(aminopropyl)- poly(dimethylsiloxane) (BAPDMS) and hexadecaaniline (A_{16}) as the linking elastomer and starburst conductor, respectively.

Reaction of bis(aminopropyl)poly(dimethylsiloxane) with hexanitro[60]fullerene was carried out in a dilute THF solution in the presence of pyridine by slow addition of the BAPDMS solution (0.5 equiv.) onto the HNF solution with vigorous stirring. The use of a dilute solution and the addition sequence minimizes formation of the adduct of poly(dimethyl-siloxanated)fullerenes with multiple addition of BAPDMS on one C_{60} cage. A mild temperature of 40 °C is sufficient for completion of the reaction. In this reaction, the kinetic rate of BAPDMS in substitution of fullerenic nitro group can be largely increased by the application of bisanionic BAPDMS, as shown in Scheme 2. Bisanionic BAPDMS was generated by the treatment of BAPDMS with 2.0 equivalent of sodium hydride. The rapid reaction allowed the substitution proceeding to be performed at a lower temperature of −10 °C. The resulting bis(pentanitro[60]fullereno) bis(aminopropyl)poly(dimethylsiloxane) intermediate was allowed to react further with hexadecaaniline (11 equiv.) in the presence of triethylamine or pyridine at 40 °C without subjecting to prior isolation of the intermediate. At the end of the reaction, a small quantity of insoluble solid byproducts was removed by centrifuge. Excess of hexadeca-aniline remaining in the solution was extracted upon the removal of THF and, subsequently, the addition of acetone that caused precipitation of the products, bis[penta(hexadecaanilinofullereno)] bis(aminopropyl)poly(dimethylsiloxane) [PDMS-(F5A_{16})$_2$], in an overall yield of 60–75%.

Infrared spectra of PDMS-(F5A_{16})$_2$ products were shown in Fig. 2. The characteristic IR bands of PDMS moieties at 2967, 1263, 1094, 1022, and 800 cm^{-1} corresponding the optical absorption of C–H stretching, Si–O, and Si–O–Si functional groups are clearly displayed in Fig. 2a. Contrarily, the strong characteristic IR bands of oligoaniline moieties focuses in the range of 1600–1300 cm^{-1} with specific peaks at 1598, 1506, 1300, 1156, 820, 749, and 695 cm^{-1}, as shown in Fig. 2f. A systematic shifting evolution of major infrared absorption bands from the range of 1300–800 cm^{-1} to 1600–1300 cm^{-1} can be followed as the main composition of elastomer-oligoaniline composites, bis(oligoanilinofullerenated)poly(dimethylsiloxane), shifting from poly(dimethylsiloxane)-dominated composite of PDMS-(F5A)$_2$ (Fig. 2b) to hexadeca-
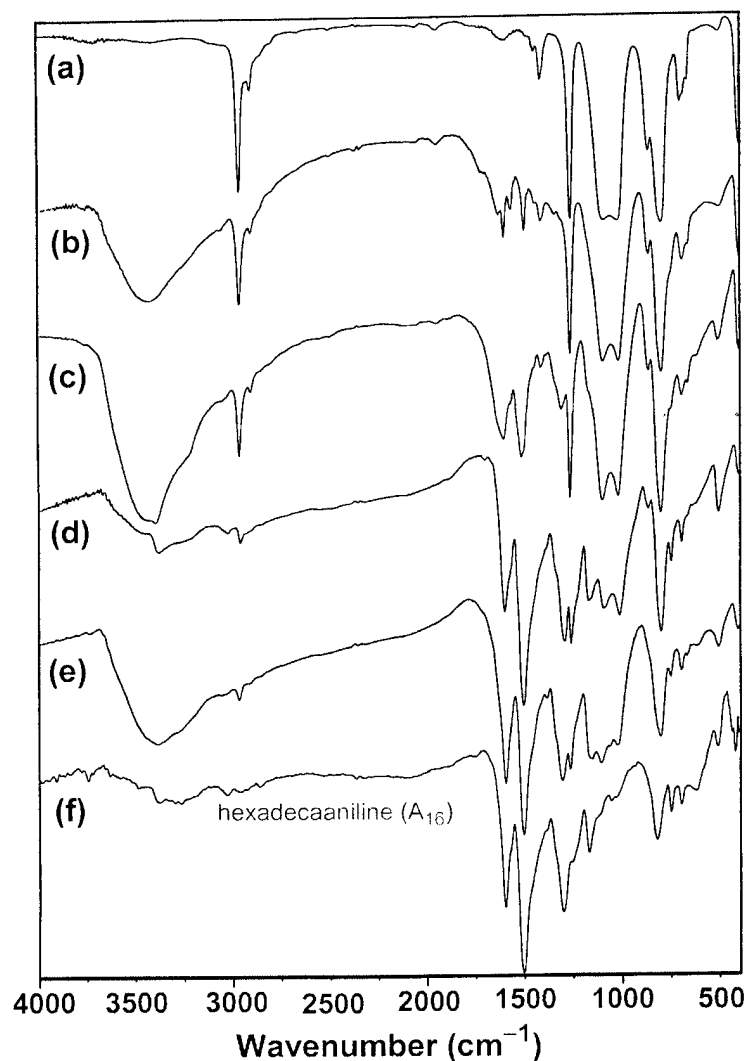
aniline-dominated composite of PDMS-(F5A$_{16}$)$_2$ (Fig. 2e).

Fig. 2. Infrared spectra of PDMS-(F5A$_{16}$)$_2$ products prepared under various reagents of (a) bis(aminopropyl)poly(dimethylsiloxane) (BAPDMS), (b) PDMS-(F5A)$_2$ using PDMS (M_n 1,500) and aniline, (c) PDMS-(F5A$_{16}$)$_2$ using PDMS (M_n 27,000) and hexadecaaniline, (d) PDMS-(F5A$_{16}$)$_2$ using PDMS (M_n 2,200) and hexadecaaniline, (e) PDMS-(F5A$_{16}$)$_2$ using PDMS (M_n 1,500) and hexadecaaniline, and (f) hexadecaaniline (A$_{16}$).

The elastomer PDMS-(F5A)$_2$ was synthesized by the use of PDMS (M_n 1,500) and aniline as the structural components. It consists of one PDMS main chain and two pentaanilinated C$_{60}$ cage as end-groups and shows predominately the IR bands of PDMS moieties. As the percentage of oligoaniline composition increases in PDMS-(F5A$_{16}$)$_2$ samples, a gradual decrease in intensity of the major infrared bands at the absorption range of 1300–800 cm^{-1} (Fig. 2c, 2d, and 2e) was detected that was accompanied with a progressive increase in intensity of the oligoaniline infrared bands at the absorption range of 1600–1300 cm^{-1}. The conductive

elastomer composite samples of PDMS-$(F5A_{16})_2$ were prepared by the reaction of BAPDMS in a medium molecular weight of M_n 27,000 to a low molecular weight of M_n 2,200 and 1,500, respectively, with hexadecaniline as the structural components. These data substantiated successful incorporation of elastic polysiloxane segments on the structures of semi-rigid starburst oligoanilines with variable rubbery properties.
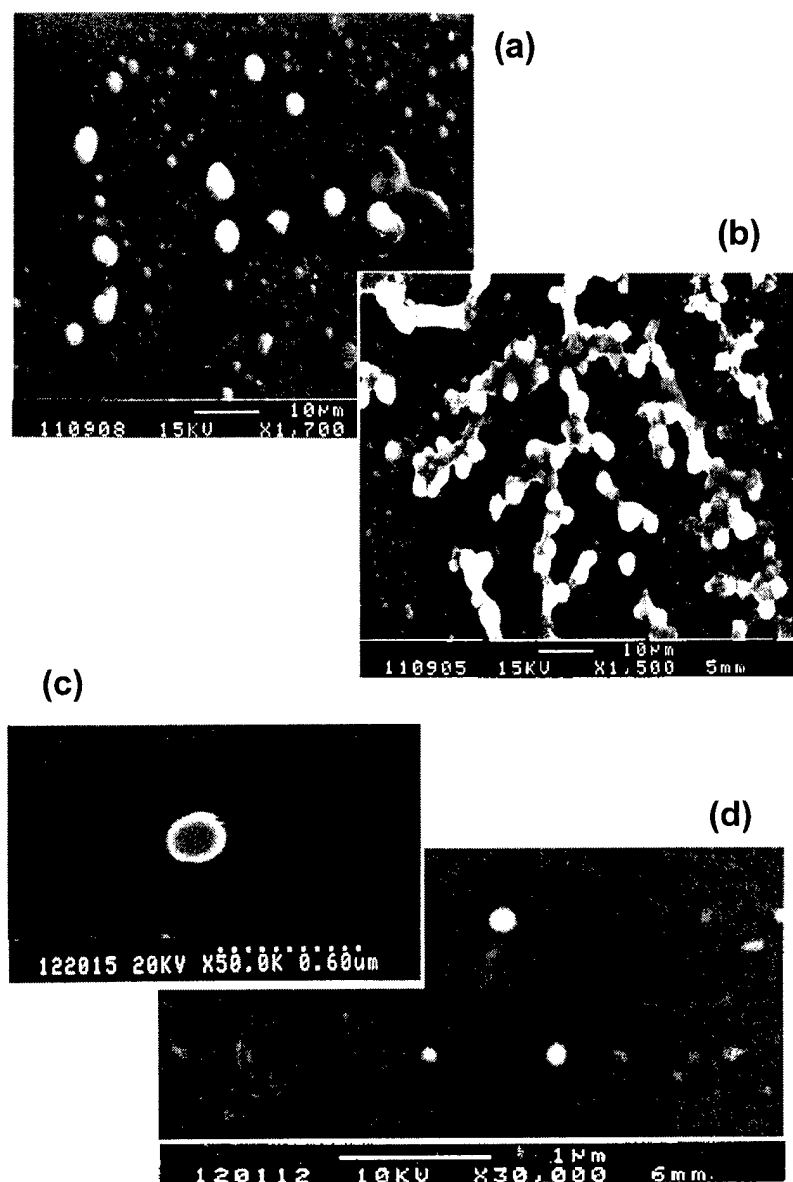

Fig. 3. Microscopic morphology of the particle samples casted directly from a DMSO solution of (a) and (b) PDMS-$(F5A_{16})_2$ with the molecular weight of PDMS moieties of M_n 27,000 showing a particle size of 2.0–5.0 μm in diameter, whereas (c) and (d) are prepared from the same PDMS-$(F5A_{16})_2$ sample by aggregation from a highly diluted THF solution (1.0 x 10^{-5} M), showing a particle size in a diameter of 240 nm in (c) and roughly 120–250 nm in (d).

High incompatibility between hexadecaniline and polydimethylsiloxane moieties makes intermolecular self-assembly of hydrophobic polydimethylsiloxane possible. Aggregation of PDMS moieties into spherical particles can be achieved by slow addition of a THF solution of PDMS-(F5A$_{16}$)$_2$ onto DMSO. Low solubility of the PDMS moiety in DMSO forces itself to coagulate into a small particle. However, the high solubility of hexadecaniline in DMSO allows it to extend into the DMSO solution, resulting in formation of a core-shell particle with polydimethylsiloxane in the core and hexadecaniline residing at the outer shell layer. Interestingly, spherical core-shell particles with a size of 2.0–5.0 μm in diameter (Fig. 3a and 3b) were readily detectable in microscopic investigation of the particle morphology of these PDMS-(F5A$_{16}$)$_2$ (PDMS M_n 27,000) samples casted directly from the DMSO solution. In principle, the aggregated particle size should exhibit dependence on the molecular weight of PDMS moieties and the method of particle preparation. Therefore, a smaller particle size is obtainable by using polydimethylsiloxane in a lower molecular weight than M_n 27,000. We demonstrated that, by using the same PDMS-(F5A$_{16}$)$_2$ (PDMS M_n 27,000) samples in a highly diluted THF solution (1.0 x 10^{-5} M), core-shell particles with a size of 240 nm in diameter (Fig. 3c) and roughly 120–250 nm in diameter (Fig. 3d) were obtained. Based on the mean dynamic volume of these core-shell particles in comparison with that of each polydimethylsiloxane and hexadecaniline moiety, the outer surface of the particle should be well packed with penta(hexadecanilino)C$_{60}$ derivatives.

Synthesis of polybutadiene-polyaniline core-shell conductive elastic submicroparticles.

Incorporation of polyaniline macromolecules on the surface area of polybutadiene (PBD) elastomer submicroparticles was achieved by the static charge interaction as first demonstrated by Yang.[16-18] For attracting the positively charged aniline monomers and polyaniline products at the surface of the particle forming a shell structure effectively covering the elastomer core, a great number of negatively charged sulfostyrene salts grafted on a polybutadiene particle are required. Anionic sulfostyrene grafting reaction was initiated by AIBN-derived free radicals in the hydrophobic phase of polybutadiene. Thermal decomposition of AIBN in the polybutadiene submicroparticle at 80 °C, under deoxygenated condition, generates cyanoisopropyl radicals. The radical center can be transfer onto the polybutadiene main chain ready for the grafting of styrene sulfonic acid at the interfacial area between the surface of hydrophobic particles and the aqueous phase. The level of polysulfostyrene (PSS) grafting is correlated to the concentration of radical center generated at the interfacial region. Presumably, the short life-time of the

internal radical center at the polybutadiene submicroparticle may lead to rapid radical coupling, in the absence of polymerizable monomers, resembling the crosslinking reaction of polybutadiene chains. Effective crosslinking should enhance the elastic properties of the resulting sulfostyrene-grafted core-shell particles.

Experimently, ethylene glycol was found to be the most suitable solvent with a high solubility for both of the salt of sulfostyrene monomer and PBD among several reaction conditions studied, as shown in Table 1. Its good compatibility facilitates the formation of the stable and uniform suspension solution of polybutadiene particles in the polar phase of ethylene glycol. In other words, the use of non-polar solvent, such as hexane, tends to swell and enlarge the PBD particle size that reduced the accessible interface for reaction. PBD utilized in this synthesis consists of a relatively low molecular weight and hydroxyl-functional end-groups, which allowed linear PBD itself to aggregate and form a stable suspension solution in polar solvent in a particle size of roughly 3 to 4 μm as measured by optical microscopy. Presumably, a large distribution of hydroxy groups at the outer shell of the elastic particle is expected owing to its hydrophilicity. Addition of AIBN initiator in a small quantity of hexane to the latex-like suspension solution disperses the initiator into the hydrophobic phase of the suspension. The use of sulfostyrene salts as monomers increases the distribution of polystyrene moieties in the polar solvent phase. However, the higher solubility of styrene sulfonic acid in ethylene glycol affords better homogenicity of the graft polymer products. At the end of polymerization, only water-soluble copolymers were isolated and purified by slow precipitation from acetone dilution for the removal of possible poly(styrene sulfonic acid) homopolymer impurities. Unreacted free polybutadiene, if any, was removed by repeated hexane washes of the product particles. The yield of PSS grafted PBD copolymer was found to be 65–75% with the PSS content in the range of 60–80% by wt. depending on different conditions applied. In principle, a higher PSS content gives a thicker conductive polyaniline attachment at the core-shell structure while a higher PBD content leads to better elasticity of the products. After purification, the sample of PSSB4 can be dispersed in H_2O forming a stable homogeneous solution, indicating the grafting nature of PSS on PBD. The weight ratio between PSS and PBD was determined by elemental analyses of the sulfur and sodium content of the products. Apparently, the core-shell structure with an outer hydrophilic shell prohibits the full detection of protons in the structure of hydrophobic core by the ^1H NMR spectroscopic measurements in D_2O. By utilization of ethylene glycol as an internal standard for calibration and quantification of sulfostyrene moieties in PSSB4, for example, an estimated PSS vs PBD ratio of 45:55 by wt. was obtained. This ratio

correlates to a much lower quantity of PSS in the composition of PSSB4 in comparison with that of 80:20 found by elemental analysis. We interpret the difference by effective dispersion of a substantial amount of grafted polysulfostyrene segments in the polybutadiene phase as a gradient core-shell composition.

Table 1. Polymerization reaction conditions, yield, and the ratio of PSS–PBD graft copolymers.

Samples	SS / PBD / AIBN	Solvent	Temp.	Yield	Product (wt%) PSS : PBD[a]
PSSB1	2 g / 2 g / 100 mg	Dioxane:H$_2$O (80:20, 10 ml) Hexane (1.0 ml)	80 °C	52 %	88 : 12
PSSB2	2 g / 2 g / 100 mg	Ethylene Glycol (20 ml) Hexane (5.0 ml)	80 °C	74 %	65 : 35
PSSB3	2 g / 2 g / 100 mg	Ethylene Glycol (15 ml)	80 °C	70 %	57 : 43
PSSB4	2 g / 2 g / 100 mg	Ethylene Glycol (11 ml)	80 °C	65 %	80 : 20[b]

[a] Determined by elemental analyses.   [b] Treated with solvent extraction.

Polymerization of aniline in the presence of core-shell PSS–PBD latex was typically carried out at room temperature by using a 1:1.25 mole ratio of aniline to ammonium persulfate oxidant in aqueous HCl solution (0.1 N) for a period of 4 h, as shown in Table 2. The resulting Pani-containing PSS–PBD solids were isolated from the latex by precipitation upon slow addition of acetone. Repeated purification was performed by dispersion of core-shell PBD–PSS–PANi particles in water followed by slow addition of acetone to effect reprecipitation of the products. These core-shell particles can be kept in aqueous solution for the long-term storage without phase separation. In a separated experiment, we found that a small amount of PBD oligomer can be dispersed in the PSS-containing aqueous solution without actually a covalent bonding with PSS. PSS molecules may serve as surfactants. However, the dispersion is not stable during the polymerization of aniline. Formation of polysulfostyrene–polyaniline complexes causes disintegration of the latex particles from the surfactants and destabilizes the PBD dispersion that resulted in precipitation of PBD solids form the aqueous solution. Therefore, observation of stable homogeneous aqueous solution of PBD–PSS–PANi particles, such as PSSB4-Pani samples containing an appreciable amount of PBD core and a similar number of sulfostyrene and butadiene repeating units, revealed coalesce of PBD and PSS

components and the graft-bonding of PSS moieties on the PBD main chain.

Table 2. Polymerization reaction conditions and yield of polyaniline on PSS–PBD graft copolymers.

Samples	PSSB4 / HCl (0.1 N)	Aniline	$(NH_4)_2S_2O_8$	PANi (wt%)[a]
PSSB4–PANi1	1.0 g / 50 ml	44 mg	135 mg	16.0 %
PSSB4–PANi2	1.0 g / 50 ml	87 mg	272 mg	28.0 %
PSSB4–PANi3	1.0 g / 50 ml	135 mg	412 mg	37.0 %
PSSB4–PANi4	1.0 g / 50 ml	181 mg	558 mg	44.0 %
PSSB4–PANi5	1.0 g / 50 ml	225 mg	681 mg	50.0 %
PSSB4–PANi6	1.0 g / 50 ml	268 mg	822 mg	54.0 %
PSSB4–PANi7	1.0 g / 50 ml	317 mg	970 mg	58.0 %

[a] The weight percentage content of PANi in final products was determined by elemental analyses.
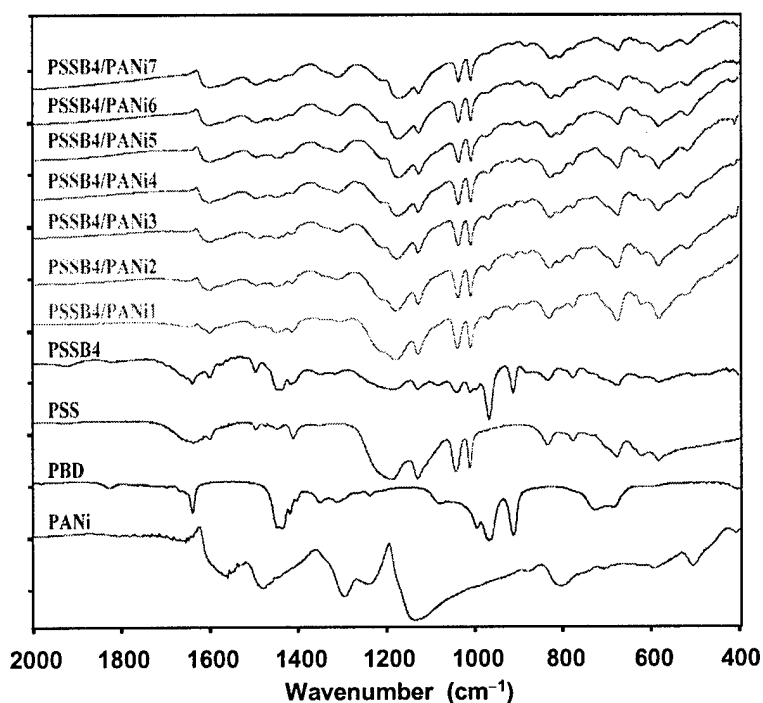

Fig. 4. Infrared spectra of polyaniline (PANi), polybutadiene diol (PBD), polysulfostyrene (PSS), PBD–PSS grafted copolymer (PSSB4), and conductive core-shell elastic microparticles (PSSB4-PANi-n, n = 1 to 7 as shown in Table 2).

The infrared spectrum of core-shell PSS–PBD structures, such as PSSB4 in Fig. 4, showed characteristic features of both PBD and PSS moieties with optical absorption of main polybutadiene bands at 967 and 912 cm^{-1} and PSS bands at 1010–1200 cm^{-1}. Higher

absorption intensity of PBD bands than that of PSS bands revealed a relaxed phase of PBD moieties with a coagulated phase of charged PSS moieties in the solid core-shell structure. As the complexation of polysulfostyrene anions with protonated polyaniline cations becomes effective at the outer shell region covering the hydrophobic particle core, it causes the shift of PBD moieties into a condensed phase displaying a much declined optical absorption of all PBD bands, as shown in infrared spectra of all PSSB4-PANi samples. In other words, the band intensity at 1010, 1042, 1129, and 1189 cm^{-1}, corresponding to optical absorption of the $-SO_3$ stretching, increases significantly and dominates in all spectra of PSSB4-PANi samples.
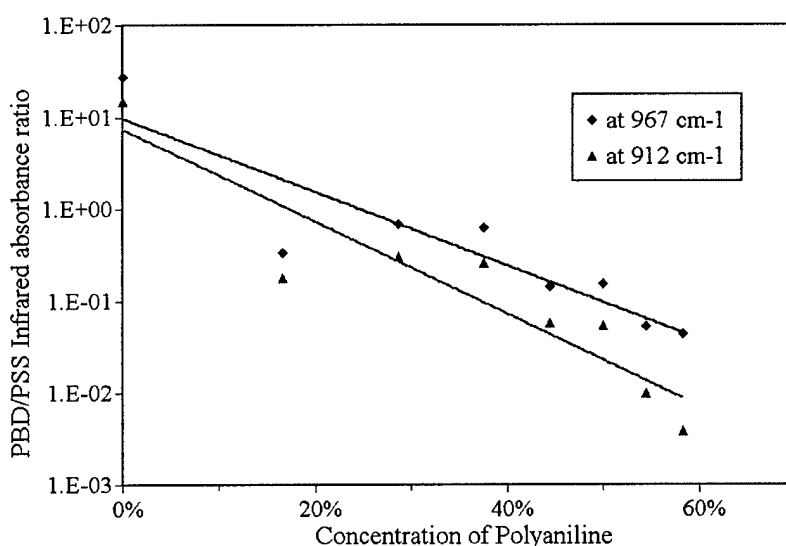

Fig. 5. Polyaniline concentration-dependent I_{912}/I_{1046} and I_{967}/I_{1046} ratios of infrared bands corresponding to absorption of PBD moieties. It decreases with the increase of PANi content from 0 to 60% by wt.

This unique characteristic of core-shell structures has also been observed in PANi-coated polystyrene latex.[35] The absorbance intensity of PBD bands at 967 and 912 cm^{-1} can be correlated with that of the PSS band at 1046 cm^{-1}, which remained relatively constant upon variation of the polyaniline content in PANi1 to PANi7. As shown in Fig. 5, both I_{912}/I_{1046} and I_{967}/I_{1046} ratio decrease with the increase of PANi content from 0 to 60% by wt. This further provides a support on an increasing degree of phase separation of PBD moieties upon the increase of charge density and the thickness of the external shell.

Absorbance frequency of IR bands at 1010, 1042, 1129, and 1189 cm^{-1}, corresponding to the stretching absorption of SO_3 groups, was found to shift progressively at a different degree as the quantity of polyaniline incorporated on the core-shell particles increased from 16 to 58 % by wt. Complexation of polystyrene sulfonic anion with protonated polyaniline cation may induce

the shift. It is much visible at the absorbance frequency of 1189 cm^{-1}. Accordingly, the corresponding shift of the UV-vis absorption band of quinonoid moieties on samples PSSB4–PANi4 to PSSB4–PANi7 with higher polyaniline content was also detected as a casted film on the glass slide. The cationic quinonoid absorption band centered at 750 nm was correlated to the presence of polarons and bipolarons.[36] Therefore, the shift from 758 nm of PSSB4–PANi1 to a longer wavelength of 780 nm of PSSB4–PANi7, as shown in Fig. 7, may suggest a continuous conducting phase in all of these core-shell elastic structures that is enhanced by an increased quantity of PANi. Interestingly, the highly polyanilnated core-shell microparticles of PSSB4–PANi7 exhibit a consistently higher optical absorption intensity at long wavelengths extending beyond 2000 nm, indicating an highly extended charge conjugation along the polymer chain. That should significantly improve the electronic properties of the casted film.
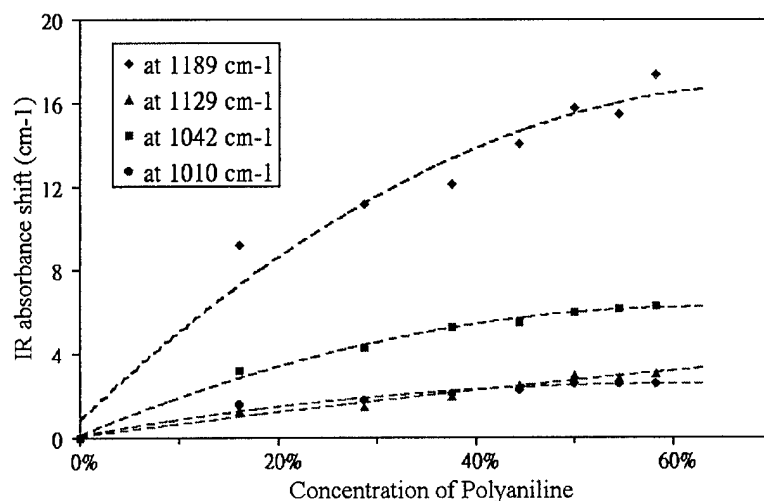

Fig. 6. The infrared absorbance shift of SO^{-3} bands in wavenumber with the increase of polyaniline content of the core-shell particles.

For electrical conductivity measurements, thin films of the PSSB4–PANi7 sample were prepared by casting from its aqueous solution, followed by evaporation of the water medium at ambient temperature. Pressure-contact four-point-probe method[37] was employed for the measurement of the conductivity. Without external doping, conductivity of PSSB4–PANi1 and PSSB4–PANi2 was found to be 1.0 S/cm at ambient temperature. Further removal of residual moisture on the film in a desiccator for a period of one week, the conductivity was found to decrease by one order of magnitude as 0.1 S/cm, which, in fact, is in a similar magnitude as that of PSS–PANi complexes without rubber modification.
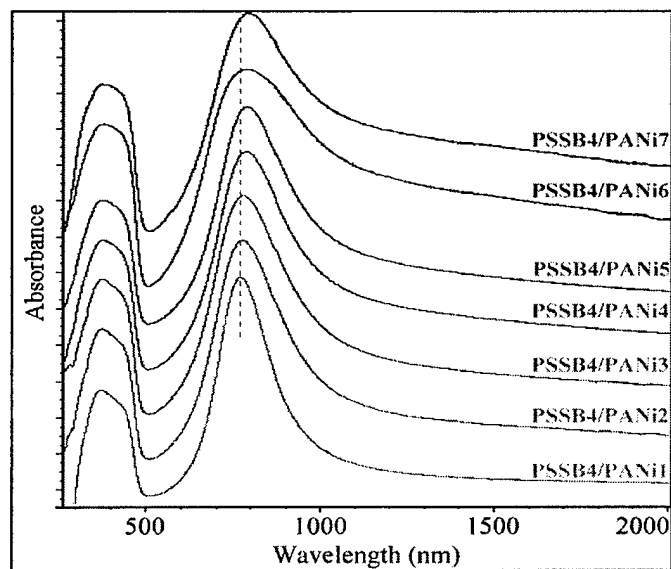
Fig. 7. UV-vis-near-IR spectra of elastic core-shell microparticles, PSSB4–PANin (n = 1 to 7), as a casted film on the glass slide, indicating an extended optical absorption at long wavelenghts.
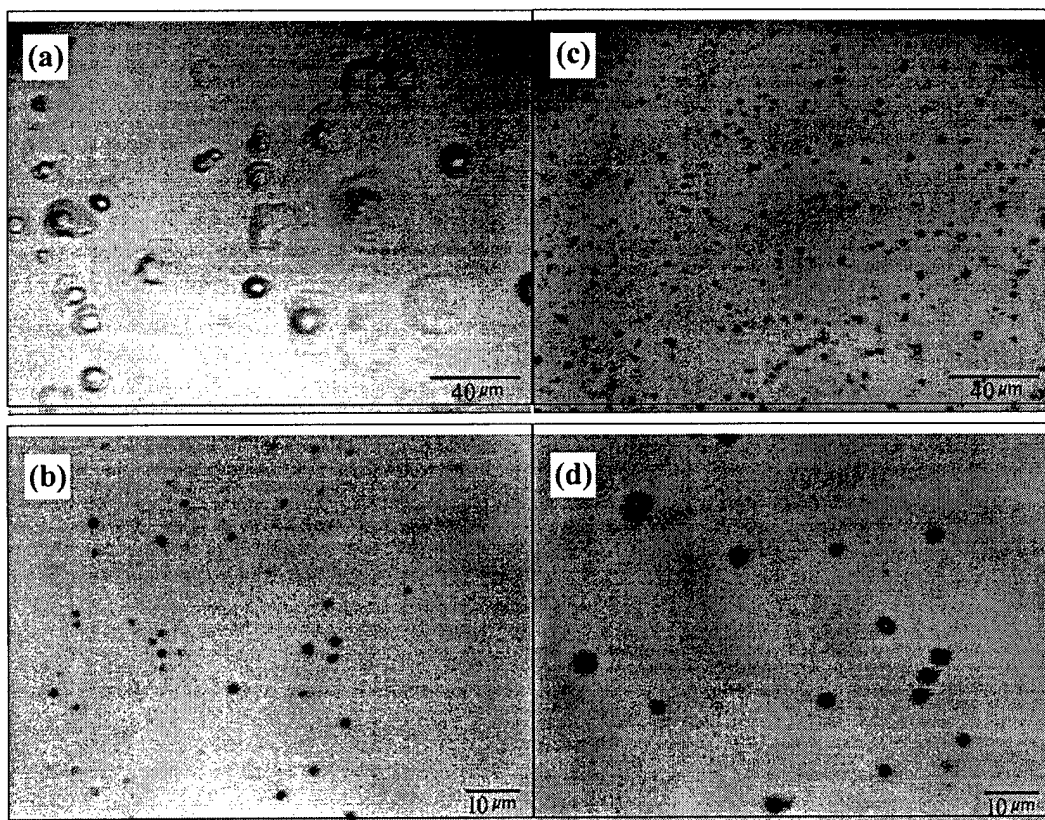

Fig. 8. Microscopic morphology of the casted particle samples of (a) PSSB4–PANi1, (b) PSSB4–PANi1, (c) PSSB4–PANi7, and (d) PSSB4–PANi7 from an aqueous dilute solution at different concentrations.

Examination of the core-shell particle structure was performed by casting PSSB4–PANin

(n = 1 to 7) samples on a glass slide from a dilute aqueous solution in the optical microscopy measurement. Figs. 8a and 8b showed the morphology of the casted sample PSSB4–PANi1 from two different concentrations. A concentration-dependency of the particle size from 3.0 to 16 μm was observed. Dynamically, PSS–PBD particles were able to aggregate when the inter-particle distance is close enough, especially, at temperatures far above the glass transition temperature, T_g, of polybutadiene. With a low loading of polyaniline on the core-shell structure of PSSB4–PANi1, possibility of soft flexible segments of polybutadiene to aggregate between particles enhances at a higher concentration, forming particles with a larger diameter of 16 μm. Contrarily, at a low concentration of 10 μM, a smaller particle size of 3.0 μm in diameter can be obtained. However, the distribution of the particle size is not homogeneous.
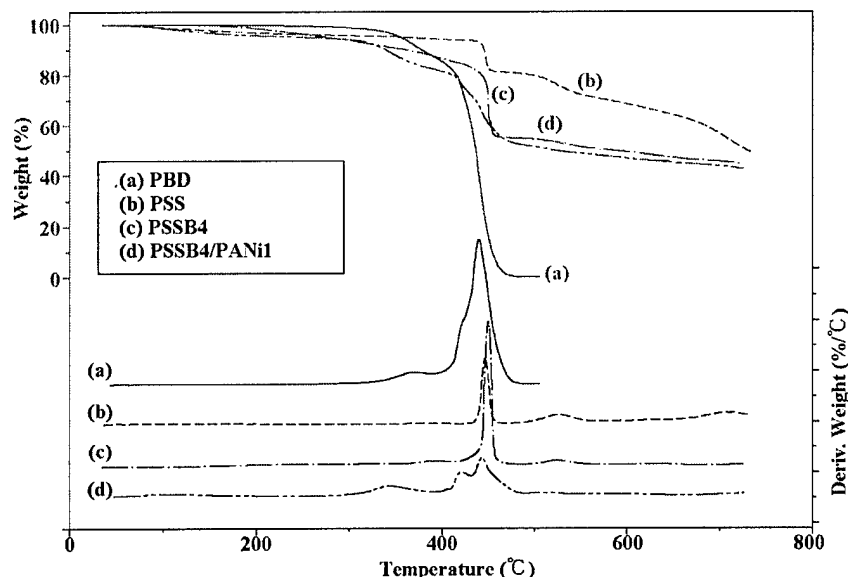

Fig. 9. Thermogravimetric analysis (TGA) of poly(butadiene diol) (PBD), polysulfostyrene (PSS), the PBD-PSS grafted copolymer PSSB4, and PSSB4-PANi1 at a heating rate of 10 °C/min under N_2. PSS-containing samples have been dried at 100 °C under vacuum over night prior to the measurement.

As the loading of polyaniline increases in the core-shell particles at the outer shell, the probability for aggregation of polybutadiene soft segments between particles is significantly reduced. That improves the stability of the elastic conductive core-shell particles by fully blocking the PBD core from dynamic merging. Incorporation of more cationically charged polyaniline may also enhance the intra-particle phase separation of anionic polysulfostyrene and polybutadiene moieties. Accordingly, a relatively constant particle size of 4.0 μm in diameter independent of the solution concentration was observed in the case of PSSB4–PANi7 samples, as shown in Figs. 8c and 8d.

Thermal stability of these elastic core-shell conducting particles was examined by thermogravimetric analysis (TGA). As shown in Fig. 9a, the major weight loss with full thermal degradation of PBD was observed to occur at 440 °C. A similar thermal degradation also appeared in polybutadiene-containing samples of PSS (Fig. 9b) and PSSB4 (Fig. 9c) with a much less percentage of weight loss. Interestingly, the difference of weight loss between PSS, prepared by the same procedure described above in the absence of PBD, and PSSB4 at 460 °C is roughly 20% by wt, which agrees well with the weight percentage of polybutadiene moieties in the composition of PSSB4 as determined by elemental analysis. It was followed by the elimination of SO_2 at 525 °C at the similar temperature range as that of PSS. An initial weight loss profile of polyaniline-containing PSSB4–PANi1 (Fig. 9d) prior to 400 °C was consistent with the thermal behavior of PSS–PANi complex reported.[38] The overall 45% weight loss of PSSB4–PANi1 at temperatures of 400–700 °C is almost the same as that of PSSB4, consistent with the high thermal stability of polyaniline moieties.
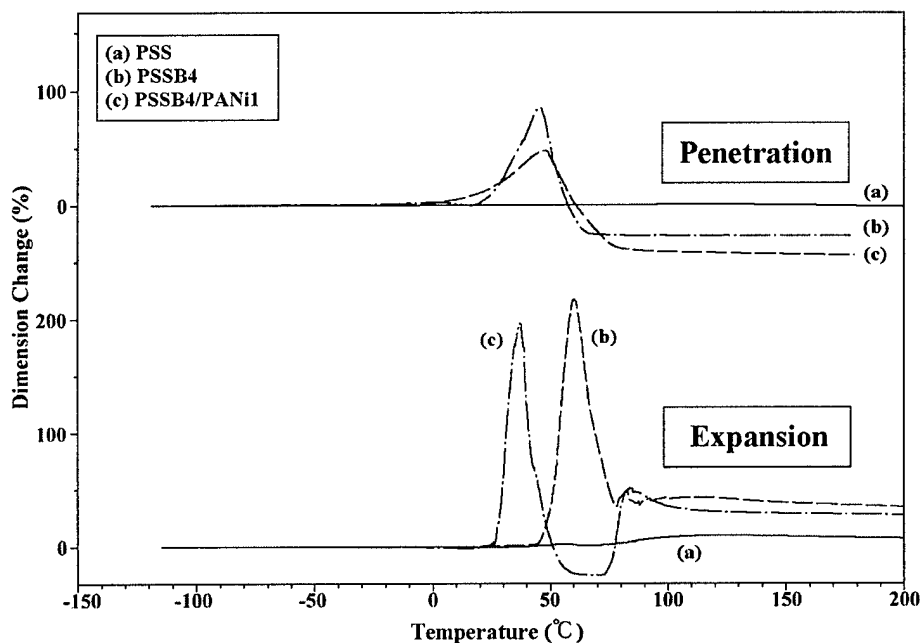

Fig. 10. Softening temperatures measured by thermal mechanical analysis (TMA) with a penetration probe (top curves) with a pressure of 66 psi at a heating rate of 10 °C/min under N_2. Film samples were dried at 100 °C in vacuum oven for overnight.

A weak glass transition temperature of PBD at roughly –90 °C was detected on samples of PSSB4 and PSSB4–PANi by differential scanning calorimetry (DSC). The low intensity of signal is, presumably, due to the domination of PSS in the materials composition with a low content of PBD. Thermal mechanical analysis (TMA, Fig. 10a) of glassy polyelectrolyte PSS

showed essentially no any significant thermal dimensional change in both penetration and expansion modes of the measurement. Upon the incorporation of PBD as the core material, a softening temperature near 45 °C was observed in both cases of PSSB4 and PSSB4–PANi1 samples. This softening point higher than the typical melting temperature of poly(1,4-butadiene) at 2.0 °C bears a similar trend to what was obtained on other PBD-containing copolymers, such as styrene-butadiene thermoplastic elastomers. In the expansion mode, the dimensional change of PSSB4 at a slightly higher temperature (57 °C) than that of PSS-PANi1 (36 °C) was detected. These TMA results clearly indicated retention of rubbery properties of the elastic PBD core, even though it was covered and blocked by the semi-rigid conductive shell of PSS-PANi complexes. The elastic core-shell structure is, therefore, established.

Conclusion

Facile synthesis of starburst oligoanilines was made using dodecaethyl-hexakis(methano)[60]fullerene hexamalonate and decaethyl-pentakis(methano)[60]fullerene pentamalonate as precursor molecules with the C_{60} acceptor as a molecular core. Similarly, synthesis of starburst hexanilino, hexa(dianilino), hexa(tetraanilino), and hexa(hexadeca-anilino)[60]fullerenes was demonstrated using hexanitro[60]fullerene (HNF) as a reactive precursor molecule. Hexanitro[60]fullerene was prepared by direct nitration of the C_{60} molecules using gaseous nitrogen dioxide as the nitration agent. The tertiary nitro groups of nitrofullerene compounds can be located at allylic or benzylallylic carbon atoms in the structure of HNF. This type of nitro function was found to act as excellent leaving group readily for replacement by a nucleophilic substituent. Utilization of this reactivity towards electron-donor nucleophiles, a synthetic approach was developed for producing oligoanilinated fullerenes as intramolecular donor–acceptor A–(D)$_6$ analogous starburst macromolecules with a well-defined arm number and chain length. Reactivity of HNF with oligomeric anilines increases with the increasing number of the repeating aniline units. Therefore, only an equal molar quantity of tetraaniline and hexadecaaniline was necessary for a complete reaction with HNF under mild conditions.

The conductive elastomer composite samples of PDMS-(F5A$_{16}$)$_2$ were prepared by the reaction of bis(aminopropyl)poly(dimethylsiloxane) (BAPDMS) in a medium molecular weight of M_n 27,000 with hexadecaniline as the structural components. Successful incorporation of elastic polysiloxane segments on the structures of semi-rigid starburst oligoanilines with variable rubbery properties was made. High incompatibility between hexadecaniline and

polydimethylsiloxane moieties makes intermolecular self-assembly of hydrophobic polydimethylsiloxane possible. Interestingly, spherical core-shell particles with a size of 2.0–5.0 μm in diameter were readily detectable in microscopic investigation of the particle morphology of these PDMS-(F5A$_{16}$)$_2$ (PDMS M_n 27,000) samples casted directly from the DMSO solution. We demonstrated that, by using the same PDMS-(F5A$_{16}$)$_2$ (PDMS M_n 27,000) samples in a highly diluted THF solution (1.0 x 10^{-5} M), core-shell particles with a size of roughly 120–250 nm in diameter were obtained. Based on the mean dynamic volume of these core-shell particles in comparison with that of each polydimethylsiloxane and hexadecaniline moiety, the outer surface of the particle should be well packed with penta(hexadecanilino)C$_{60}$ derivatives.

Conductive polybutadiene (PBD)–polysulfostyrene (PSS)–polyaniline (PANi) core-shell microparticles were synthesized in an aqueous solution. Covalent bonding between PBD rubber and PSS–PANi complex stabilizes the particle and minimizes the inter-particle aggregation. Conductivity of these materials was found to be in the range of 0.1–1.0 S/cm. Core-shell structure of rubber-polyaniline latex may provide significant modification possibilities with respect to the thermal processability and the improvement in mechanical properties, including impact strength.

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