Architectural Copolymers of PAMAM Dendrimers and Ionic Polyacetylenes

Lajos Balogh,*[⊥] Agnes de Leuze-Jallouli,[†] Petar Dvornic,[†] Yoshihito Kunugi,[‡] Alexandre Blumstein,[#] and Donald A. Tomalia[⊥,†]

University of Michigan Center For Biologic Nanotechnology, Ann Arbor, Michigan 48109-0533; Michigan Molecular Institute, Midland, Michigan 48640; Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431; and Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts 01854

Received June 9, 1998; Revised Manuscript Received December 15, 1998

ABSTRACT: Novel, star-shaped copolymers have been prepared to study the resulting properties of the core−shell copolymers. While the shell was formed from rigid, conductive ionic polyacetylene (PAc) arms, semiflexible, spheroidal aliphatic poly(amidoamine) (PAMAM) dendrimers served as initiator cores. The synthesis was carried out at room temperature by reacting the primary amino terminal groups of the generation three and four PAMAM dendrimers with *N*-methyl-2-ethynylpyridinium triflate in DMSO at different monomer/initiator ratios. Full surface functionalization of the amino groups was achieved at the 2EPyMeTf/PAMAM−NH_2 = 4 monomer/terminal amino group ratio when the whole surface was found to be completely covered with short rigid ionic acetylene chains giving macromolecular "sea urchins". Depending on the chain length of the polyacetylene arms and the degree of dendrimer surface coverage, these core−shell polymers may be considered as functionalized dendrimers or dendrimer-initiated ionic polyacetylenes. The resulting products were characterized by FTIR, UV−visible, ^1H and ^{13}C NMR spectroscopy, capillary electrophoresis, TEM, TGA, DSC, and conductivity measurements. Solid-state conductivity of the doped copolymer was found to be in the 10^{-4}−10^{-5} S/cm range due to the shorter conjugation length in the ionic polyacetylene shell. However, thermal stability of the PAMAM dendrimer interior improved dramatically as a result of copolymer formation.

Introduction

The present study describes the first synthesis and characterization of dendrimer—ionic acetylene copolymers. These polymers are new representatives of highly functionalized, tailored, globular macromolecules in which the "soft" or "semirigid" internal dendrimer[1−4] part is surrounded by a "crust" of ionic, rod-shaped, rigid oligomeric chains.

Dendritic polymers represent the fourth and the most recently discovered general class of macromolecular architecture.[5] Due to their high symmetry, dendrimers display unique physical properties and simple spectral characteristics. When the surface branch cells contain chemically reactive groups, these groups may be used for modification of dendrimer molecular exteriors. Poly(amidoamine) PAMAM dendrimers are prepared via divergent synthesis performed by the excess reagent method.[6,7]

This process, which consists of a reiterative sequence of a Michael addition and amidation reaction, routinely yields products containing high relative amounts of ideal dendritic structures up to generation 7.

Several different dendrimer-based multiarm copolymers have been reported in the literature.[8−14] Peripheral modification of generations 1−5 of poly(amidoamine) dendrimers with cationically substituted naphthalene diimides was also described.[15−17] Reduced forms of these dendrimers displayed isotropic conductivity in the range 10^{-2}−10^{-3} S cm^{-1}. Near-infrared (NIR) spectroscopy showed that in D_2O or formamide solutions the anion radicals aggregated into π-dimers and π-stacks. The results were explained by a charge-hopping mechanism.

Homopolymers of *N*-alkyl-2-ethynylpyridinium salts are unique with respect to their ionic nature, high degree of substitution, and extensive backbone conjugation. Doped ionic polyacetylenes display conductivity in the range 10^{-3}−10^{-2} S/cm. These polymers may be prepared by thermal polymerization or by using free radical or nucleophilic initiators.[18−22]

Our recent investigation of the nucleophile-initiated polymerization of *N*-alkyl-2-ethynylpyridinium trifluoromethanesulfonates (2EPyRTf) indicated that the first step of this process involves a Michael addition to a nucleophilic center followed by a complex zwitterionic−anionic chain-growth mechanism.[23,24] On the basis of these studies, several novel amphiphilic block copolymers of ionic polyacetylene[25−28] and polystyrene, polybutadiene, or polyisoprene have been synthesized and characterized. These block copolymers consisted of conjugated, rigid, charged, strongly hydrophilic backbone and flexible hydrophobic chains and displayed a strong tendency for nanolayer self-assembly.[25, 27]

The surface of the amine terminated PAMAM dendrimers is nucleophilic enough to enter Michael addition with the electrophilic center of the acetylenic monomer and thus serve as a multifunctional macroinitiator for the ionic polymerization of *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate (2EPyMeTf). We have investigated how the properties of these very different

---

* To whom correspondence should be addressed.

[⊥] University of Michigan Center For Biologic Nanotechnology.

[†] Michigan Molecular Institute.

[‡] University of Minnesota.

[#] University of Massachusetts Lowell.

10.1021/ma980904t CCC: $18.00

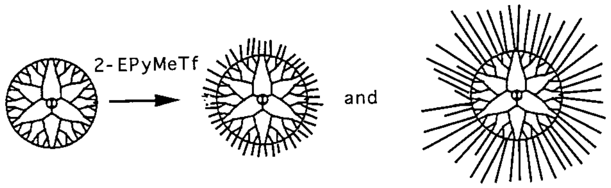
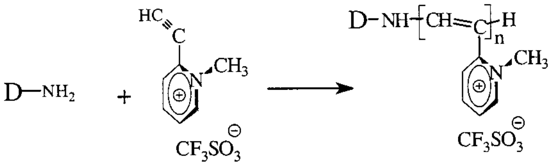


Figure 1. Generalized scheme of the PAMAM−PAc copolymer formation.

Scheme 1. Reaction of 2-Ethynylpyridinium Triflate with a Primary Amino Group of the PAMAM Dendrimer



homopolymers interact and coexist when they are covalently connected into a core−shell architecture.

Since generation 3.0 and generation 4.0 ethylenediamine−core PAMAM dendrimers are semiflexible macromolecules containing 32 and 64 primary $-NH_2$ terminal groups, respectively, the PAMAM−PAc products are multiarm macromolecules composed of two distinctly different architectural components. They might be described as a “nanoscopic sea urchin”, in which the soft interior (“body”) is provided by the aliphatic dendrimer while the conjugated rigid ionic polyacetylene chains represent the “spikes”, as shown in Figure 1. In addition, these novel architectural copolymers also provide a rare example of a multiarm star-shaped inverted micelle-like macromolecule in which both the core and the shell are hydrophilic but to a different degree.

It was expected that a variable degree of surface functionalization will allow tuning of properties between the flexible, aliphatic, nonionic, low-T_g dendrimers and rigid, conjugated, ionic, high-T_g polyacetylenes. Preliminary results have been reported in a preprint.[29]

In this paper, we focus on the effects of architecture hybridization on the thermal and conductive properties of the investigated copolymers.

Experimental Section

Materials. 2-Ethynylpyridine was purchased from Farchan Laboratories and was distilled in a vacuum under nitrogen before use. Methyltrifluoromethanesulfonate, anhydrous DMSO, and diethyl ether were purchased from Aldrich and were used as received. Common solvents were purified by standard methods. 2EPyMeTf was synthesized according to the literature.[23] PAMAM dendrimers were purchased from Dendritech as 20 w/w % solutions in methanol.

Synthesis. Dendrimer−ionic acetylene copolymers (PAMAM$_G$−PAc$_n$, where *G* refers to the generation used for initiation and *n* refers to the 2EPyMeTf/PAMAM−NH_2 ratio in the reaction mixture) were synthesized at room temperature by reacting generation 3.0 (M_w = 6909) and 4.0 (M_w = 14 215) PAMAM dendrimers carrying 32 and 64 primary amino groups, respectively, with 2EPyMeTf in DMSO (Scheme 1). Both PAMAM dendrimers possessed narrow polydispersity of $M_w/M_n = 1.06$ and $M_w/M_n = 1.10$ as measured by SEC. The length of the ionic polyacetylene blocks was adjusted by varying the monomer/macroinitiator functionality ratios in the reaction mixture. The acetylene monomer *per* terminal primary amine ratio (2EPyMeTf/PAMAM−NH_2) was set as to 0.5, 1, 4, and 16. Consequently, the resulting copolymers consisted of conjugated charged PAc chains attached to the dendrimer surface. (PAMAM contents of the products described herein were 63%, 46%, 16%, and 5%, respectively.) Thus, a typical procedure is described as follows: The methanol was evaporated from 5.0 mL of PAMAM generation 3 solution by a gentle stream of nitrogen followed by dynamic vacuum for 5 days at room temperature. The resulting 1.0470 g of G3 dendrimer was dissolved in 10.00 mL (11.010 g) of anhydrous DMSO. In a screw-cap reaction tube 2.20 mL of the PAMAM G3 stock solution (dendrimer content 0.2120 g, 3.068×10^{-5} mol, terminal amine concentration 9.819×10^{-4} mol) was mixed with the solution of 0.2642 g (9.887×10^{-4} mol) of 2EPyMeTf in 5.00 mL of anhydrous DMSO (2EPyMeTf/PAMAM−NH_2 ratio = 1.007). The reaction mixture immediately turned to deep brown. After initiation, the reactants were allowed to react for 24 h in sealed tubes at room temperature. The acetylene polymerization was terminated by addition of 1 mL of dry methanol, which converted the unreacted 2EPyMeTf into methoxyvinyl-(*N*-methylpyridinium) triflate that is soluble in diethyl ether while the polymeric product is insoluble.[23] After precipitation in 60 mL of diethyl ether, the precipitated dark solid was washed by 3 × 25 mL of ether, and the yellowish ethereal phase was separated. The precipitate was redissolved in 5 mL of methanol and repeatedly precipitated by 60 mL of ether. Finally, the product was dissolved in methanol, and the solvent was evaporated in vacuo. Drying under reduced pressure yielded 0.449 g (90.9%) of dendrimer−polyacetylene copolymer. This workup procedure was effective in removing both the methoxyvinyl-(*N*-methylpyridinium) triflates from the reaction product as well as some unattached low molecular weight oligoacetylenes. Copolymer yields were increasing with increasing 2EPyMeTf/PAMAM−NH_2 ratio; i.e., using G3 initiator yields were 86.8, 90.9, and 98% and with G4 initiator 86.6, 94.2, and 97.7%, respectively. Yields in the 2EPyMeTf/PAMAM−NH_2 = 16 reactions were practically quantitative. This phenomenon was probably due to a minor protic contamination in the system, which deactivated some acetylene monomer by chain transfer.[23] Unreacted macroinitiator was absent in the samples according to polyacrylamide gel electrophoresis (PAGE).

Characterization. Materials and compounds were characterized by different analytical techniques. IR spectra were recorded on a Nicolet 20DBX FT-IR spectrophotometer between CaF_2 plates. UV−visible spectra were obtained on a Cary 1E spectrophotometer at room temperature between 200 and 900 nm. ^{1}H and ^{13}C NMR measurements were carried out on a Varian Unity 300 multinuclear spectrometer equipped with a temperature controller. Size exclusion chromatography of PAMAM dendrimers was performed on three TSK gel columns (4000, 3000, and 2000) using a Waters 510 pump with a multidetector system consisting of a Wyatt Technology Dawn DSP-F MALLS, a Wyatt Technology 903 interferometric refractometer, and a Waters 410 differential refractometer, respectively. A DB-17 μSil quartz capillary (L = 100 cm, d = 0.1 μm) filled with 0.5% hydroxypropylmethylcellulose (HPCE) was used for capillary gel electrophoresis on a Beckman P/ACE system 2050. Polyacrylamide gel electrophoresis (PAGE) was performed with a BioRad model 500/200 power supply. Thermal analyses were carried out by DSC (Perkin-Elmer DSC 7 series) and TGA (Du Pont TGA 910 thermogravimetric analyzer). A Phillips EM301 instrument and Formvar-coated carbon grids were used for transmission electron microscopy (TEM). Cyclic voltammograms[30] (CV) were measured at room temperature using a potentiostat/galvanostat (Princeton Applied Research, model 173) and universal programmer (Princeton Applied Research, model 175). An acetonitrile or acetonitrile:methanol = 3:1 mixture containing 0.1 M lithium perchlorate, saturated with nitrogen, was used as electrolyte in all experiments. The redox characteristics of the copolymers were measured at a highly polished glassy carbon working electrode (GC disk, diameter 3 mm) with respect to an SCE reference electrode, while scanning the potential at a speed of 50 mV s^{-1}. The graphite electrode served as the counter electrode in all these experiments. Conductivities of the films (10 μm thickness) were measured by the four-probe method. In the case of iodine oxidation, neutral films were cast from

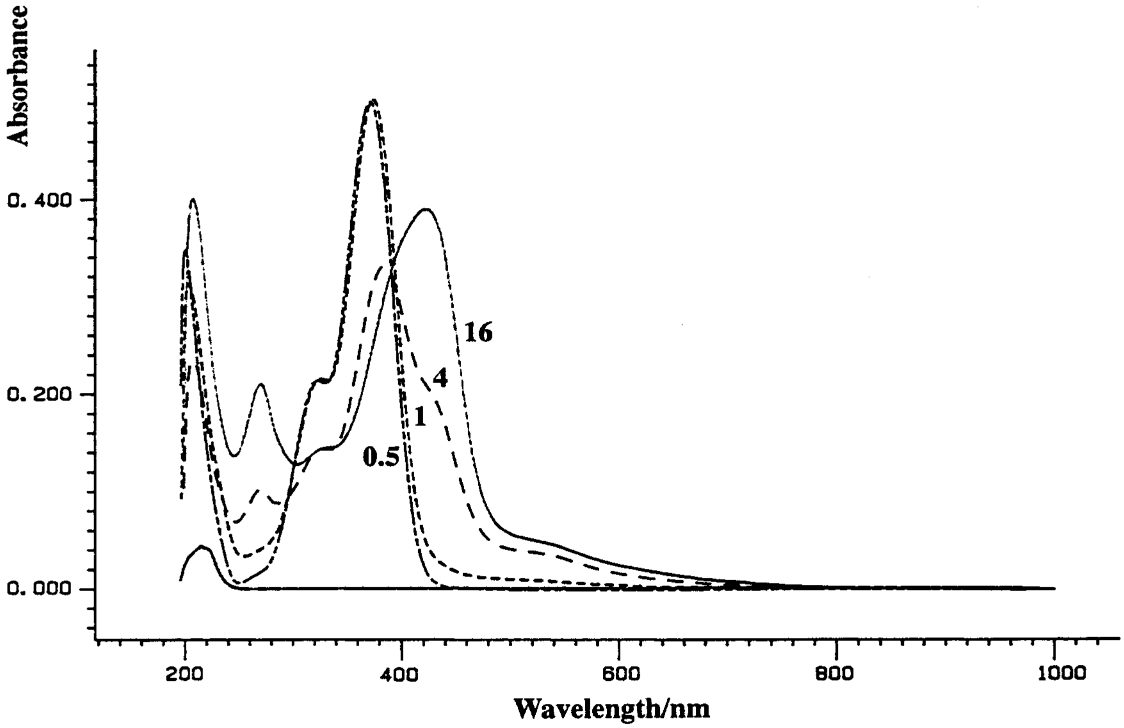


Figure 2. UV−visible spectra of $PAMAM_{G3}$−PAc copolymers with increasing 2EPyMeTf/PAMAM−NH_2 ratios. Solvent: methanol. Spectra are normalized to 1×10^{-2} g/L concentration.

acetone solution and exposed to iodine vapor. In the case of $NOPF_6$ oxidation, the films were cast from a mixture of PAMAM−PAc and $NOPF_6$ in hexafluoropropan-2-ol.

Results and Discussion

The lack of unreacted initiator demonstrated the high initiator efficiency of the dendrimers due to the high local concentration of reactive amino groups on the exterior of the macromolecule. However, the competition between initiation and propagation steps clearly was observable.

With increasing 2EPyMeTf/D−NH_2 ratio, increasing degree of the dendrimer amino surface groups was utilized in the initiation process. Comparison of FT-IR spectra of the initiator and the products revealed a gradual decrease in the intensity of the 3300 cm^{-1} N−H valence stretching (ν_{NH}), which almost perfectly disappeared from the spectra of $PAMAM_{G3}$−PAc_4 and $PAMAM_{G3}$−PAc_4 (not shown). Increase of the PAc/PAMAM ratio in the copolymers was also confirmed by the concomitant intensification of the −C═C− backbone valence stretching (conjugated backbone) at 1620 cm^{-1} and the symmetric and asymmetric S═O valence stretchings at 1279 and 1174 cm^{-1}.

The color of bulk copolymers changed from orange-yellow (PAMAM−$PAc_{0.5}$) to dark brown (PAMAM−PAc_4 and PAMAM−PAc_{16}), indicating an increase in the conjugation length (Figure 2) with the increasing relative amount and length of the acetylenic component.

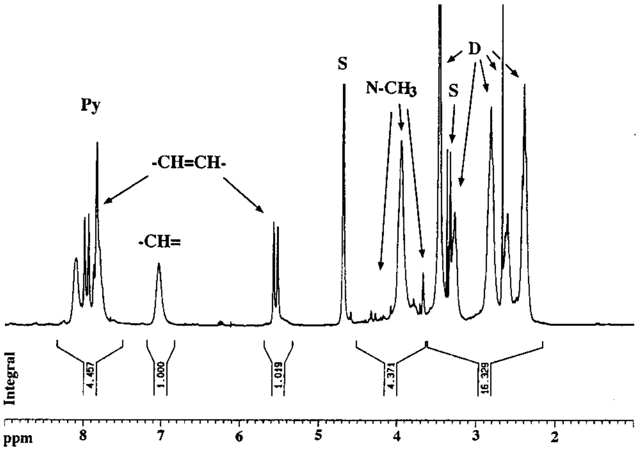


Figure 3. ^1H NMR spectrum of $PAMAM_{G3}/PAc_1$ in deuteriomethanol. S = solvent peaks; D = PAMAM proton signals; Py = pyridinium nucleus. For structural details see Scheme 2.

A more detailed analysis and standard deconvolution displayed the presence of distinct peaks at 270, 330, 380, 420, and 540 nm. The 270 nm peak is due to the pyridinium ring in the 2EPyMeTf monomer. (When there is no other peak present in the UV−visible spectrum, the ultimate unit of the dendrimer must be a pyridinium-substituted and nonconjugated ethylene.) The consecutive peaks at 330, 380, and 420 nm therefore indicated two, three, and four conjugated acetylenic units on the dendrimer, respectively, while higher absorptions suggest the presence of longer linear oligoacetylene chains attached to the PAMAM surface. Obviously, the number of conjugated units indicates only the minimum length of the “spikes”, because the conjugation length may be less than the length of the polyacetylene chain. At 2EPyMeTf/PAMAM−NH_2 = 0.5 and 2EPyMeTf/PAMAM−NH_2 = 1 reagent ratios, both the 270 and 330 nm peaks were observed, indicating the formation of some pyridiniumacetylene dimers and trimers on the surface (Figure 3). A similar tendency was also observed for the higher PAc/PAMAM ratios where a whole series of peaks was found. It is probable that in this particular system the rate of polymerization is comparable to the rate of initiation, which occurs at random locations of the dendrimer surface. This mechanism seems to be somewhat similar to the polymerization of 2EPyMeTf in protic solvents.[23] It should also be noted that for 2EPyMeTf/PAMAM−NH_2 = 16 the

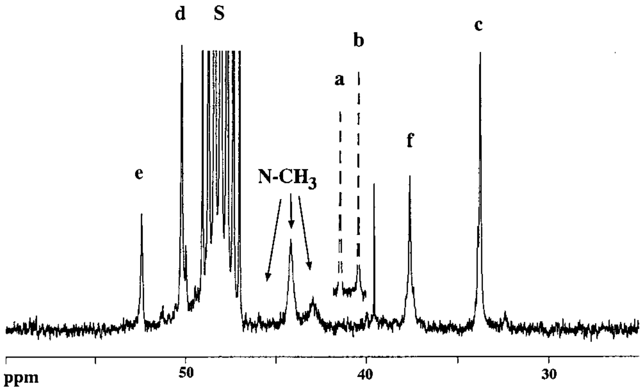
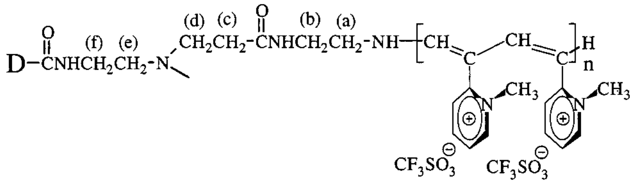


Figure 4. ^{13}C NMR spectrum of PAMAM$_{G3}$/PAc$_1$ in CD$_3$OD. S = solvent; (a) and (b) peaks are characteristic of the unsubstituted $-NH_2$ terminal groups of the PAMAM dendrimer. For peak identification and assignments see also Schemes 1 and 2.

Scheme 2. Surface Structure of PAMAM−PAc Copolymers (D = Dendrimer)



UV−visible absorption of the copolymer was trailing to 800 nm, indicating a broad distribution of the conjugated double-bond sequences.

Large variations were observed in the solubility of the PAMAM−PAc products as a function of composition. While PAMAMs are insoluble in acetonitrile and acetone but are soluble in water, DMSO, DMF, and methanol, the resulting core−shell copolymers were also soluble in acetonitrile and acetone in addition to water, DMSO, DMF, and methanol, similarly to the homopoly(pyridiniumacetylenes). For example, although both PAMAM and PAc are soluble in methanol, PAMAM−PAc$_{0.5}$ copolymers dissolved only very slowly, over the period of 12 h in this solvent. The dissolution was preceded by swelling, but finally a 10% methanol solution could be obtained at room temperature.

^{1}H NMR spectra of the obtained products further confirmed the reaction of the dendrimer surface $-NH_2$ groups with the acetylenic monomer (Scheme 2, Figure 3). However, in PAMAM−PAc$_{16}$ only peaks characteristic of ionic polyacetylene could be observed although the relative PAMAM dendrimer amount was more than 5 wt % in the product. Disappearance of the characteristic PAMAM proton signals was already noted at 4/1 reagent ratio (23% dendrimer). Due to the low intensity of the subsurface PAMAM proton signals, interpretation of the ^{1}H NMR spectra clearly became a complex task in the case of these core−shell macromolecules.

In contrast to the ^{1}H NMR, ^{13}C NMR spectra of the copolymers showed no unexpectedly disappearing peaks (see Figure 4) and were consistent with the proposed structures. The absence of the peaks indicated by (a) and (b) of Scheme 2 shows that in the PAMAM−PAc$_1$ copolymers almost all of the surface $-NH_2$ groups have already reacted with the acetylenic monomer.

Capillary gel electrophoresis (CGE) showed electropherograms similar to homopolyacetylene in the case of PAMAM$_{G4}$−PAc$_{16}$ copolymer as a consequence of the ionic polyacetylene exterior. The large number of peaks observed is a manifestation of the many possible combinations of multiple charges. Comparison of CGE traces confirms that a near complete surface coverage has already been achieved at 2EPyMeTf/PAMAM−NH$_2$ = 1, indicating fast initiation. Comparison of electropherograms (Figure 5A−E) indicates the preference of the surface initiation followed by limited acetylene chain growth.

An unexpected increase in thermal stability of the PAMAM−PAc copolymers was observed with increasing PAc content. It is known that poly(methylpyridinium) triflates are thermally stable$^{9-12}$ up to 360 °C, while thermal degradation^7 (usually involving retro-Michael processes and transamidation) and simultaneous weight loss of PAMAMs starts around 120 °C.

The decomposition temperature under nitrogen (Figure 6A−C) has increased from approximately 100 to 240 °C. A plausible explanation is offered by the decreased mobility of the semiflexible PAMAM branches and the strong ionic interactions between the ionic oligoacetylene rods on the dendrimer surface.

Differential scanning calorimetry (DSC) showed traces illustrated in Figure 7. A higher apparent T_g with a relatively large relaxation overshoot was observed on the first heating of PAMAM$_3$−PAc$_4$ and PAMAM$_4$−PAc$_4$ copolymers. The overshoot disappears (after a quick quenching) on the second heating. The observed T_g values of PAMAM−PAc architectural copolymers (second heating) were by about 10−15 °C higher than those reported for the pure PAMAM dendrimers. It needs to be emphasized that according to the corresponding TGA curves no weight loss occurs at the temperatures of the first T_g values. These data are consistent with a more rigid primary structure of these core−shell copolymers, which is probably due to the expected electrostatic interactions between the PAc rods.

Due to the increased electron contrast of the polyacetylene chains, it was possible to acquire transmission electron micrographs (TEM) of these architectural copolymers without staining. TEM images indicated the presence of single and multiple spherical objects. Single objects displayed a diameter of 100 Å, which may correspond to a single copolymer molecule (calculated diameter is 65 Å in solution). Figure 8 illustrates that single macromolecules dominate the image because of the electrostatic repulsion between charged surfaces, although dimers and trimers can also be observed.

All samples provided good quality films when cast on hydrophilic glass plates as opposed to PAc homopolymers. The color of the spin-coated films changed from yellow through red to dark brown with increasing film thickness while visible adsorption of light shifted toward higher wavelengths. The copolymers were stable; iodine or NOPF$_6$ did not oxidize them well. No significant change of the vis−NIR spectra of the films was observed after iodine or NOPF$_6$ treatment. Electrochemical oxidation of PAMAM$_{G3}$−PAc$_{16}$ occurred only at 1.2 V vs SCE, and it was irreversible. This oxidation peak corresponds to the oxidation of the oligoacetylene, as core PAMAM$_{G3.0}$ shows no oxidation peak in this range. The conductivity of undoped polymers was less than 10^{-7} S cm^{-1}, while iodine doping brought the conductivity of both PAMAM$_{G3}$−PAc$_4$ and PAMAM$_{G4}$−PAc$_{16}$ films up to the (2−3) × 10^{-5} S cm^{-1} range. The measured conductivity with NOPF$_6$ doping was 4 × 10^{-4} S/cm.

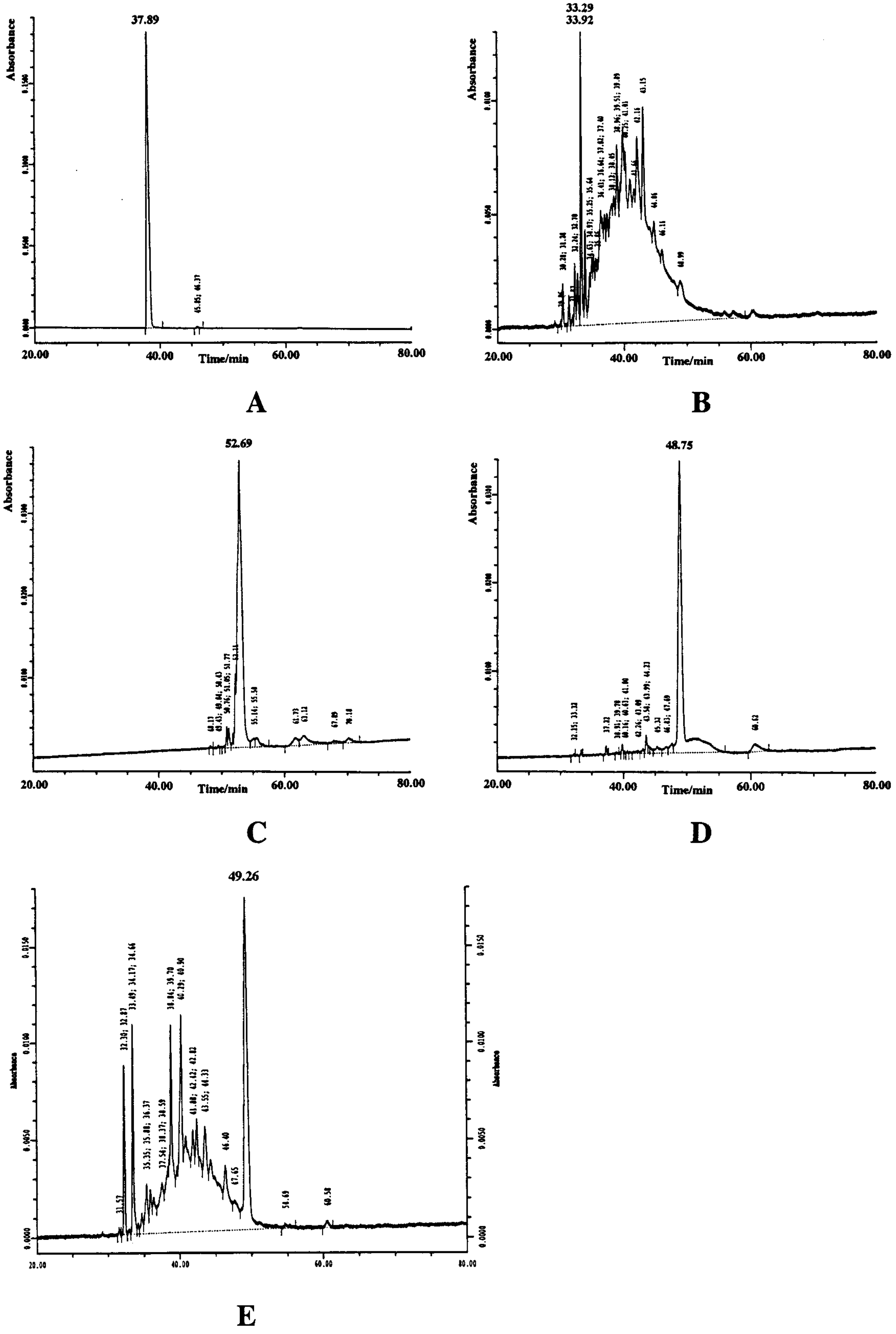


Figure 5. Capillary electropherograms of the 2EPyMeTf (A, $t_R = 37.89$ min), the homopolyacetylene (B, $t_R = 30-60$ min), PAMAM G4 (C, $t_R = 52.69$ min), PAMAM$_{G4}$–PAc$_1$ (D, $t_R = 48.75$ min), and PAMAM$_{G4}$–PAc$_4$ (E, $t_R = 31-55$ and 49.26 min). Conditions: μSil DB-17 column, $L = 100$ cm, i.d. = 0.1 mm, pH = 2.7, 0.1 M phosphate buffer, 0.5% HMPC gel, pressure injection, 7.5 kV, UV detection at 214 nm.

This is less than the conductivity of doped ionic homopolyacetylenes, which is in the $10^{-3}-10^{-2}$ S/cm range.[31]

These observations suggest that the PAc chains are in interaction with each other. However, both the conjugation length is shorter and the effective cross

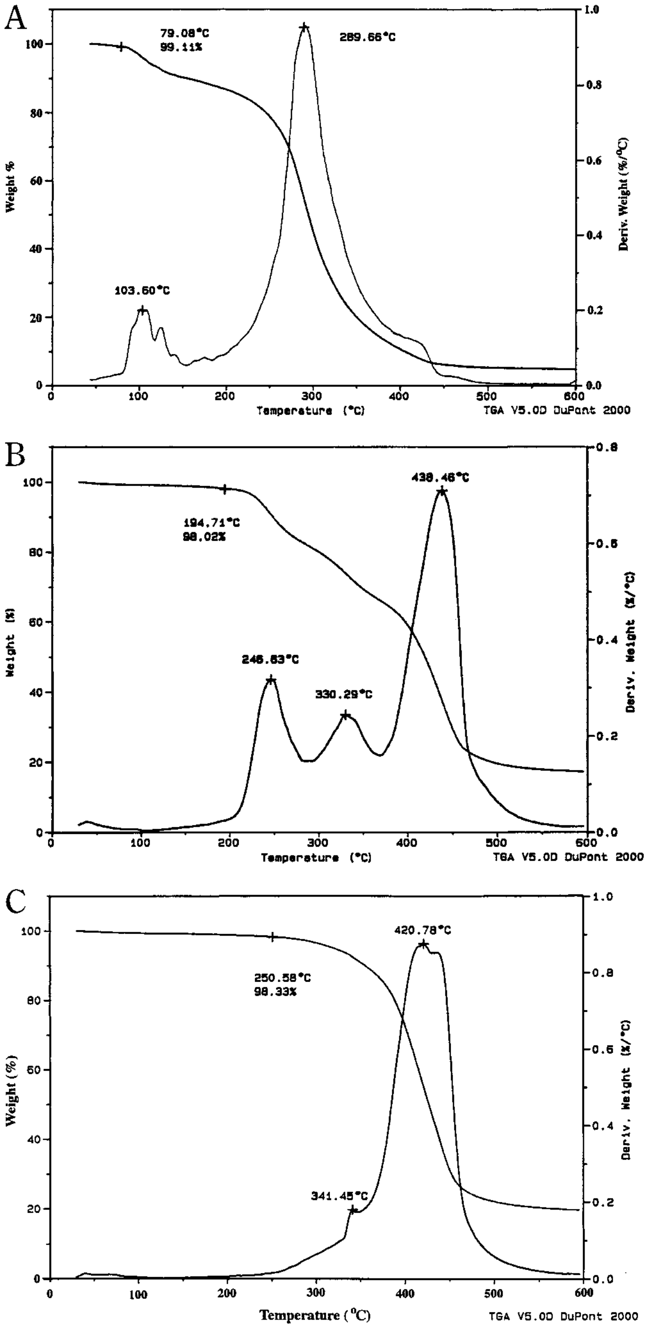


Figure 6. (A) TGA response and its derivative of PAMAM G3 dendrimer at a rate of 20 °C/min, in nitrogen. (B) TGA response and its derivative of $PAMAM_{G3}-PAc_1$ copolymer (dendrimer content 43 wt %) at a rate of 20 °C/min in nitrogen. Degree of polymerization of acetylene $DP_{PAc} = 1-2$, estimated surface coverage ≈90%. (C) TGA response and its derivative of $PAMAM_{G3}-PAc_4$ copolymer (dendrimer content 16 wt %) at a rate of 20 °C/min in nitrogen. Degree of polymerization $DP_{PAc} = 3-4$, surface coverage ≈100%.

section of the layer is smaller than in the PAc homopolymer, which result in lower conductivities.

Summary

We describe the synthesis and characterization of a special architectural copolymer formed from a semiflexible dendrimer core and rigid, conjugated ionic acetylene chains attached to the PAMAM surface through the terminal $-NH_2$ groups.

Preparation of these nanoscopic "sea urchins" was achieved by using generations 3 and generation 4 primary amine terminated PAMAM dendrimers as multifunctional spheroidal macroinitiators and 2-ethynylpyridinium trifluoromethanesulfonate as an acetylenic monomer. Initiation occurred via a Michael addition reaction, and propagation followed a zwitterionic polymerization route. The synthesis involved a simple one-step reaction, which was carried out in DMSO at room temperature.

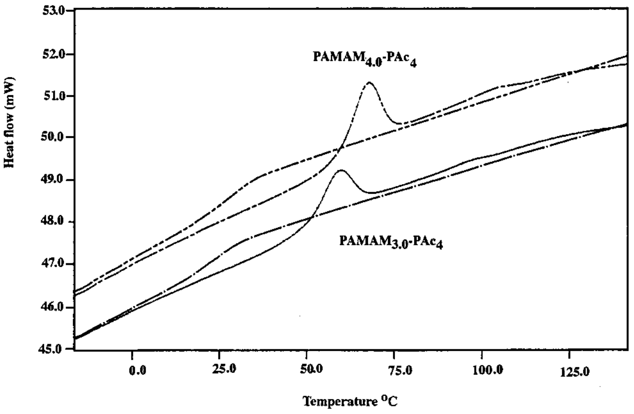


Figure 7. Comparison of DSC first and second heating curves of $PAMAM_3-PAc_4$ and $PAMAM_4-PAc_4$ copolymers. Heating rate 20 °C/min, under nitrogen.

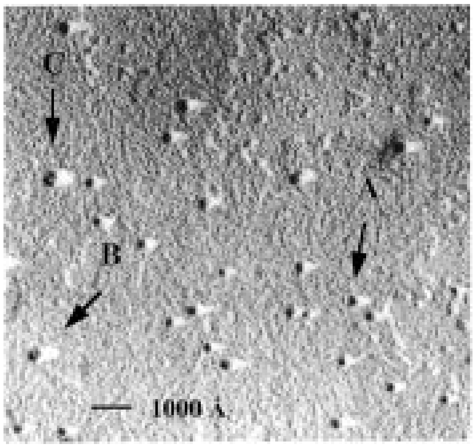


Figure 8. TEM image of the $PAMAM_4-PAc_4$ copolymer. Magnification: 100 000, unstained. Pt shadowing (4:1) A, a single nanocluster; B, a dimer; C, a trimer.

The resulting core–shell architectural copolymers consist of a maximum of 32 or 64 rigid conjugated ionic chains covalently attached to the surface of a semiflexible dendrimer core. The length of these arms ranged from DP ≈ 1 to DP > 16, depending on the macroinitiator/monomer ratio.

While ^1H NMR failed to provide quantitative integration values, ^{13}C NMR was useful. The resulting polymers gave capillary electropherograms similar to those of polyacetylenes but formed good quality films when cast on hydrophilic glass substrate. The conductivity of iodine-doped copolymer films was lower than the conductivity of the corresponding ionic homopolyacetylenes. Most interestingly, thermal stability of the PAMAM dendrimer unit in these copolymers was greatly enhanced compared to the unsubstituted PAMAM dendrimers, suggesting a protective role of the rigid ionic polyacetylene shell.

Acknowledgment. This work was supported by the National Science Foundation's Polymer Program under

Grant DMR-9201439. Thanks are expressed to Professors Larry Miller and R. B. Blumstein for their interest and helpful discussions. L.B. thanks Dr. Herb Brothers II and Kevin Battjes for their contribution with PAGE and TEM analysis.

References and Notes

(1) Tomalia, D. A.; Dewald, J. R.; Hall, M. J.; Martin, S. J.; Smith, P. B. *Proceedings of the First SPSJ International Polymer Conference, Kyoto, Japan, Aug 1984*, p 65.
(2) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J. (Tokyo)* **1985**, *17*, 117.
(3) Newkome, G. R.; Yao, Z.-Q.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003.
(4) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(5) Tomalia, D. A.; Dvornic, P. R.; Uppuluri, S.; Swanson, D. R.; Balogh, L. *Proc. ACS PMSE* **1997** (77), 95
(6) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.
(7) Dvornic, P. R.; Tomalia, D. A. In *Starburst Dendrimers, Technology Review*; Dendritech, Inc.: Midland, MI, 1995.
(8) Zhou, L. L.; Toporowski, P. M.; Roovers, J. U.S. Patent 5,276,110, 1/4/1994.
(9) Roovers, J.; Zhou, L. L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324.
(10) van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; Eilssen-Roman, C.; van Genderen, M. H. P.; Meijer, E. W. *Chem. Eur. J.* **1996**, *2* (12), 1616; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 23.
(11) Gitsov, I.; Wooley, K. L.; Frechet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1992,** *31* (9), 1200.
(12) Wooley, K. L.; Frechet, J. M. J. *Proc. ACS PMSE* **1992**, *67*, 90.
(13) Hayes, W.; Leduc, M. R.; Leon, J. W.; Fréchet, J. M. J *Proc. ACS PMSE* **1997**, *77*, 143.
(14) Leduc, M. R.; Hawker, C. J.; Dao, J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 45, 11111.
(15) Duan, R. G.; Miller, L. L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 43, 10783.
(16) Miller, L. L.; Duan, R. G.; Tully, D. C.; Tomalia, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 5, 1005.
(17) Tabakovic, I.; Miller, L. L.; Duan, R. G.; Tully, D. C.; Tomalia, D. A. *Chem. Mater.* **1997**, *9*, 3, 736.
(18) Subramanyam, S.; Blumstein, A. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 23.
(19) Subramanyam, S.; Blumstein, A. *Macromolecules* **1991**, *24*, 2668.
(20) Subramanyam, S.; Li, K. P.; Blumstein, A. *Macromolecules* **1992**, *25*, 2065.
(21) Subramanyam, S.; Blumstein, A. *Macromolecules* **1992,** *25*, 4058.
(22) Subramanyam, S.; Chetan, M. S.; Blumstein, A. *Macromolecules* **1993,** *26*, 3212.
(23) Balogh, L.; Blumstein, A. *Macromolecules* **1995,** *28*, 25.
(24) Balogh, L.; Blumstein, A. *Macromolecules* **1995**, *28*, 5691.
(25) Balogh, L.; Samuelson, L.; Alva, K. S.; Blumstein, A. *Macromolecules* **1996**, *29*, 4180.
(26) Balogh, L.; Blumstein, A. *Proc. ACS PMSE* **1995**, *73*, 312.
(27) Balogh, L.; Samuelson, L.; Alva, K. S.; Blumstein, A. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 703.
(28) Balogh, L.; Samuelson, K. S.; Blumstein, A. *Macromolecules* **1996**, *29*, 4180.
(29) Balogh, L.; Blumstein, A.; Jallouli, A.; Dvornic, P.; Tomalia, D. A. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1996**, *37* (2), 417.
(30) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.
(31) Subramanyam, S.; Chetan, M. S.; Blumstein, A.; Mil'shtein, S. *Polym. Mater. Sci. Eng.* **1991**, *64*, 186.

MA980904T