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RESEARCH ARTICLE

NEWDENDRONIZED POLYMERSFROMTRIS ANDETHYLENEDIAMINE DERIVATIVES

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Amphiphilic dendronized monomers and polymers from tris (hydroxymethyl) amino methane (TRIS) and N-Boc-ethylene diamine were synthesized following adivergent path way starting from TRIS and N-Boc-ethylenediamine. There action with acrylonitrile, after methanolysis, produced the desired dendrons. The monomers were obtained by there action of acryloyl chloride with the ester-terminated dendrons. The monomers and polymers were characterized by FT-IR, 1H-NMR, and13C-NMR spectroscopic measurements. The spectroscopic results were in good agreement with the expected chemical structures. The polymers were characterized by Size Exclusion Chromatography (SEC), Thermo gravimetric Analysis (TGA)and Differential Scanning Calorimetry (DSC). Thermal analysis of the samples indicated that both polymers were thermally stable and behaved as semi crystalline polymers with melting temperatures of 34.0 and 42.0°C. The results suggest that dendronized polymers of this family can be prepared with several chemical modification sintheside group. These structures enable the preparation of materials with different cavities in their architecture that canentrap small molecules for various purposes and modify theamphiphilicity. A new syntheticroute for the preparation of new amphiphilic monomers and polymers is reported and discusse dinterms of the chemical structure.

INTRODUCTION

The development to fwell-defined molecular structures to generate new compound sand obtains new types of architectures is still of great interest in the field of macro molecular science. Dendritic structures are considered one of the most innovative classes of compounds of the past twenty years because of their potential applications in fields ranging from biochemistry to electronics and because of the various structures that can be built from these compounds.

Since Hawkeretal. and Tomaliaetal. Synthesized the first dendritic compounds - for example, dendronized polymers (DP), i.e., polymers with dendritic side chains- interest in developing a wide range of such composites has grown considerably. General synthetic strategies are *graft-to*, *graft-from* and *macro monomeric route strategies.*

Dendronized polymers are a new family of branched polymers that can entrap and receive small molecules as guests; therefore, they can be used as matrices for drug delivery, catalyst delivery, dye delivery, and compatibilization of small molecules, etc. in a host-guest interaction. The chemical structure of this type of molecule should have some pseudocavities, which can be constructed following a path way of frequent repetition of similar steps and can be advantageous for these purposes. In general, synthetic methods for the preparation of branched architectures relyon two similar procedures described as *divergent* and *convergent*. Both procedures usually rely on mutually compatible and complementary protection and deprotection sequences. In this type of synthesis and these chemical products, it is necessary to mention the accepted terminology and concepts such as *core*, *monomer*, *generation*, *termini*, *focalsite*, *spacer*or *connector*, *periphery* and *voidregion*. Furthermore, in contrast with the notable differences inherent in the divergent and convergent techniques, one similarity also exists. The convergent protocol can be considered a “higher order” divergent method where by “complex” monomers are attached to a central unit whether it is a formally final core or simply another self-similar monomer. However, this “higher order” nature is the extent of the similarity because the outcomes of using each technique differ substantially.

Previous reports have demonstrated that these compounds can be useful for drug delivery, thermal response and in optoelectronics. The aim of this work is the synthesis of dendrons and new dendronized polymers derived from the known compounds poly (amidoamine) (PAMAM) and tris (hydroxymethyl) amino methane (TRIS). Dendronized polymers containing hydro phobic and hydro philicresidues

(amphiphilic dendrons) on the dendritic side chain are important for elucidating the physico-chemical behaviour of these materials. To achieve this objective, were port the divergent synthesis of two types of dendronized polymers from TRIS and *N*-Boc-ethylene diamine (**Scheme 1Aand1B**). The solution properties and surface behaviors of these polymers will be part of another project.

***Scheme 1.*A**

Structures of a) tris (hydroxy methyl) amino methane (TRIS) and b) *N*-Boc- ethylene diamine. **B.** Structure of a) Polymer 5a (poly (*N*-tris [((methoxy carbonyl) ethoxy) methyl]methyl acrylamide)) and b) Polymer 5b (poly(*N*-acrylamide-*N*,*N*-bis((methoxy carbonyl) ethyl)-ethane amine)

MATERIALS AND METHODS

MATERIALS

TRIS, *N*-Boc-ethylene diamine, triethyl amine (TEA), and acrylonitrile were purchased from Sigma-Aldrich, Inc. Potassium hydroxide, sodium chloride, sodium carbonate and sulphuric acid were obtained from Merck. ’-Azoisobutyronitrile(AIBN)was acquired from Fluka. All of the commercial chemicals were used without further purification. The solvents were obtained from Merck.

Synthesis of Dendrons and Monomers

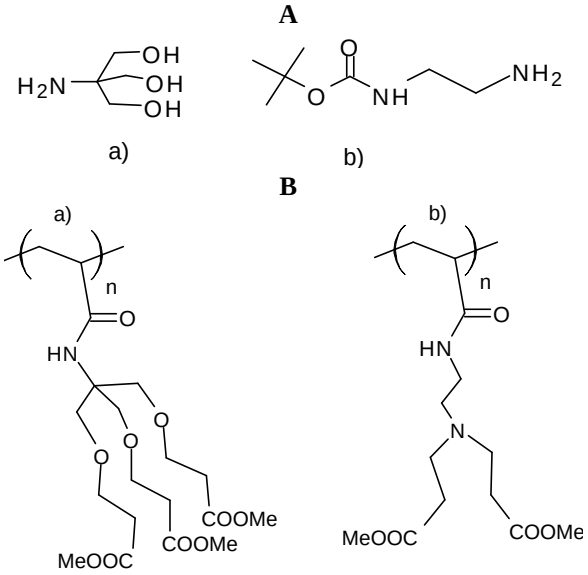
Dendrons 2a and 3a were synthesized according to a previously reported procedure. In addition, dendrons 2b and 3b were prepare dusing the same procedure used to prepare dendrons 2a and 3a.

Synthesis of Monomer 4a (N-tris[((methoxycarbonyl) ethoxy) methyl]methylacrylamide)

Dendron 3a (1.00g, 2.64 mmol) was dissolved in dry THF, and TEA (0.324mL) was added to the solution. After 30 min of stirring, 0.352 mL (15%excess) of acryloylchloride was added drop wise to the solution. After one week, the solution was filtered by vacuum, washed with dry THF and then washed with $CHCl_3$ and aqueous 10% $NaHCO_3$. The organic layer was dried ($MgSO_4$), filtered, concentrated under vacuum and purified by liquid chromatography on silicagelusingethyl acetate as the eluent. The yield was 80.0%.

Synthesis of Monomer 4b (N-acrylamide-N,N-bis((methoxy carbonyl) ethyl)- ethaneamine)

Dendron 3b (0.44g, 1.894 mmol) was dissolved in dry THF, and 0.233 mL of TEA was added to the solution. After 30 min of stirring, 0.253mL (15%excess) of acryloyl chloride was added drop wise to the solution. After one week, the solution was filtered by vacuum, washed with dry THF and then washed with $CHCl_3$ and 10% aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$), filtered, concentrated under vacuum and purified by liquid chromatography on silicagelusingethyl acetate as the eluent. The yield was 86.7%.



Synthesis of Polymers

Synthesis of Polymer 5a (poly (N-tris [((methoxy carbonyl) ethoxy) methyl] methyl crylamide))

Monomer 4a (0.41g, 0.95mmol) was polymerized at 65° Cinbulk under an N_2 atmosphere and in the presence of AIBN (0.6mol%) as an initiator. The reaction mixture was stirred for 72h, and the obtained polymer was dissolved in $CHCl_3$. Hexane was carefully added to precipitate the polymer, and the supernatant was extracted. The polymer (5a) was dried under vacuum for24 hat room temperature to obtain 5a.The yield was 45.0%.

Synthesis of Polymer 5b (poly(N- acrylamide-N,N-bis((methoxycarbonyl)ethyl)-ethaneamine)

Monomer 4b (0.30g, 1.05mmol) was polymerized at 65°Cinbulk under an N_2 atmosphere and in the presence of AIBN (0.6mol %) as an initiator. The reaction was stirred for 72h, and the obtained polymer was dissolved in $CHCl_3$. Hexane was carefully added to precipitate the polymer, and the supernatant was extracted. The polymer (5b) was dried under vacuum for24 h at room temperature to obtain 5b. The yield was 18.9%.

Spectroscopic Characterization

The products were characterized by Fourier-trans form infra red spectros copy (FT-IR) using a Bruker Vector 22 FT-IR spectrometer and liquid KBr films. They were also characterized by ^{1}H-NMR and ^{13}C-NMR in $CHCl_3$-*d* using a Bruker Avance 400MHz Ultra shield spectrometer.

Molecular Characterization

The weight-average molecular weight (Mw) and poly dispersity (Mw/Mn) values of the polymer were determined using a Viscotek (VE1122solventdelivery system) size-exclusion chromatograph equipped with a VE3580 RI refractive index detector. The mobile phase was THF, and separation was conducted using aT600 M column. Anelution

rate of 1mL/min at 30° C and 1wt% solutions of the polymer in $CHCl_3$ were used. The molecular weight distribution was calculated on the basis of a calibration curve constructed using mono disperse poly (styrene) standards.

Thermal Analysis

Thermo gravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA 851 thermo gravimetric analyzer. The scans were performed at temperatures ranging from 25°C to 700°Cata heating rateof10°/min under a dry N_2 atmosphere. The sample masses were 2–4 mg, and the samples were placed into 40μL aluminapans. The data were processed using the STAR^e softwareversion8.1fromMettler-Toledo.The thermal transitions of the polymer were studied by differential scanning calorimetry (DSC) ona Mettler-ToledoDSC821-700 differential scanning calorimeter; the samples were measured under dry nitrogen an data heating rate of 10°C/min. The thermal curves of the samples were obtained using the following heating method: a 5 min hold at 300°C, at temperature decrease to-100°Cat 10°/min, a2minholdat-100°C and at temperature increase to 300°C at 10°/min. The second heating cycle was used for analysis. The data obtained were processed using the STAR^{e}software (version 8.1) from Mettler-Toledo

RESULTS

Synthesis of Polymers and Spectroscopic Characterization

The synthesis of the Dendron's was carried out in a series of steps with different yields. The first step was the reaction of TRIS (1a) with acetonitrile in a dioxane/water mixture in a basic medium at room temperature. A yellowish oil, tris[(cyanoethoxy)methyl]amino methane (2a), was obtained in a good yield of 92.4%.This product, via methanol sis, allowed us to obtain the dendrontris [((methoxycarbonyl) ethoxy)methyl] aminomethane (3a).This product was obtained in a good yield of 83.1%,and it was the first Dendron(3a)of the series. The monomer (4a) containing the Dendron (3a) was obtained in a good yield of85.5%by the reaction of 3a with acryloyl chloride in THF in the presence of tri ethylamine as an acid acceptorat0°C. The spectroscopic characterization showed that the spectra of the Dendron, monomers and inter mediate structures were in good agreement with the expected chemical structures. The assignation of the spectroscopic signals provided an account of the real chemical structures.

This synthetic sequence (**Scheme 2**) resulted in a good method to obtain these types of monomers containing very bulky side groups with dendrite structures; the semonomers could be polymerized to obtain new dendronized materials.

Polymerization of the monomer was achieved by radical polymerization in bulk using AIBN as radical initiate or under vacuum at 65°C. The polymer was obtained in 33% yield, which was similar to the common yield for this type of radical polymerization when the bulkiness of the side groups that have an important sterichindrance and are therefore unfavorable for the polymerization process is taken in to account.[22-26] The characterization of the polymer was achieved by spectroscopic techniques such has FT-IR, ^{1}H-NMR and ^{13}C-NMR. The results of the spectroscopic characterization were in good agreement with the suggested polymeric chemical structure. One of the most important results in this type of analysis was the disappearance of the signals corresponding to the vinyl protons in the ^{1}H-NMR spectra.

The synthesis of the second dendronized polymer5b (**Scheme3**) was performed using a similar syntheticroute. The reaction of *N*-Boc-ethylenediamine(1b)with acrylonitrilein dioxaneina basic medium afforded *N*-Boc-*N*,*N*-bis (cyano-ethyl)- ethylenediamine (2b) in 87.5 % yield, which, inturn, afforded *N*,*N*- bis ((methoxycarbonyl) ethyl))-ethylenediamine (3b) in 27.3 %yield by methanolysis. The low yield was due to the deprotection of the Boc group in the dendron. There action of 3b with acryloyl chloride resulted in the corresponding monomer(4b)containing the dendronized side group(3b)inagoodyieldof86.7%.Asinthe first case, this synthetic route was a good way to obtain this type of functionalized monomer containing a dendronasalateral group. Radical polymerization of 4 busing AIB Nasan initiator resulted in the dendronized polymer 5bina low yield of 19%.This slow yield was attributed to steric hindrance, together with some intra molecular interactions of the monomer; these effects prevented the free exposure of the vinyl group for radical formation in the vinyl segment. Sever all assays of polymerization were performed to improve the yield taking into account different amounts of initiator and polymerization times; however, the results were the same.

These results suggested that different chemical modifications could be performed on the side chain of the polymers; thus, a macromolecular structure could be designed to obtain polymers with different types of cavities and/or hydrophilic ties, depending on the on the nature of the substituent.

The following results confirm the presence of the desired products, characterized by means of FT-IR, ^{1}H-NMR and ^{13}C-NMR.

Monomer 4a FT-IR (cm^{-1}): 3368.6 (m, N-H stretching); 2954.4 and 2878.6 (s, C-H stretching); 1739.6 and 1679.9 (s, C=O stretching); 1625.3 (m, C=C stretching).

^{1}H-NMR (ppm): 7.40 (s, CON*H*); 6.60 (m, C*H*-vinyl); 6.12 and 5.88 (m, H_2Cvinyl); 3.75 (broad s, 2H, CCH_2O); 3.72 (t, 2H, OCH_2CH$_2$); 3.69 (s, 3H, COOCH_3); 2.57 (t, 2H, CH_2COOCH$_3$).
^{13}C-NMR (ppm): 172.2 (*C*OOCH$_3$ ester); 165.4 (*C*ONH amide); 131.7 (*C*H-vinyl); 125.5 (H_2*C*vinyl); 69.1 (C*C*H$_2$Oether); 66.5 (OCH_2CH$_2$ ether); 59.9 (*C*CH$_2$O); 51.6 (COO*C*H$_3$); 34.7 (*C*H$_2$COOCH$_3$ ester).

Monomer 4b FT-IR (cm^{-1}) =3459.0(m, N-H stretching); 2953.5 and 2871.7 (s, C-Hstretching); 1736.1 and 1648.4 (s, C=O stretching); 1617.6 (m, C=C stretching

^{1}H-NMR(CHCl3-*d*)(ppm)=7.31(s,CON*H*);6.41(m,C*H*-

vinyl); 6.12 and 5.90 (m,H_2C vinyl); 4.05 (t,2H,NCH_2CH$_2$COOCH$_3$); 3.73 (t,2H,NHCH_2CH$_2$N); 3.69 (s,3H,COOCH_3); 2.58(t, 2H, CH_2COOCH$_3$); 2.31(t, 2H, NHCH$_2$CH_2N).

^{13}C-NMR(CHCl$_3$-*d*) (ppm)=173.6 (*C*OOCH$_3$ester); 171.9(*C*ONHamide); 131.5(*C*H-vinyl) 128.5(H$_2$*C* vinyl); 66.3(NHCH$_2$*C*H$_2$N); 64.1(N*C*H$_2$CH$_2$COOCH$_3$); 51.7 (COO*C*H$_3$); 34.8; (NH*C*H$_2$CH$_2$N); 34.1 (CH$_2$COOCH$_3$).

Polymer 5a FT-IR (cm^{-1}) =3365.0 (m, N-H stretching); 2953.5 and 2879.1 (s, C-Hstretching); 1738.7 and1678.4 (s, C=O stretching).

^{1}H-NMR(CHCl$_3$-*d*)(ppm)=7.23(s, CON*H*);3.66(broads,2H, CC*H*$_2$O);3.62(t,2H, OC*H*$_2$CH$_2$); 3.60 (s, 3H, COOC*H*$_3$); 2.47 (t, 2H, C*H*$_2$COOCH$_3$). The signals of thevinyl protons disappeared.

^{13}C-NMR(CHCl$_3$-*d*)(ppm) =172.1(*C*OOCH$_3$ester); 165.5 (*C*ONHamide); 69.0(C*C*H$_2$Oether); 66.7 (OC*H*$_2$CH$_2$ether); 59.9 (*C*CH$_2$O); 51.6 (COO*C*H$_3$); 34.6 (*C*H$_2$COOCH$_3$ester).

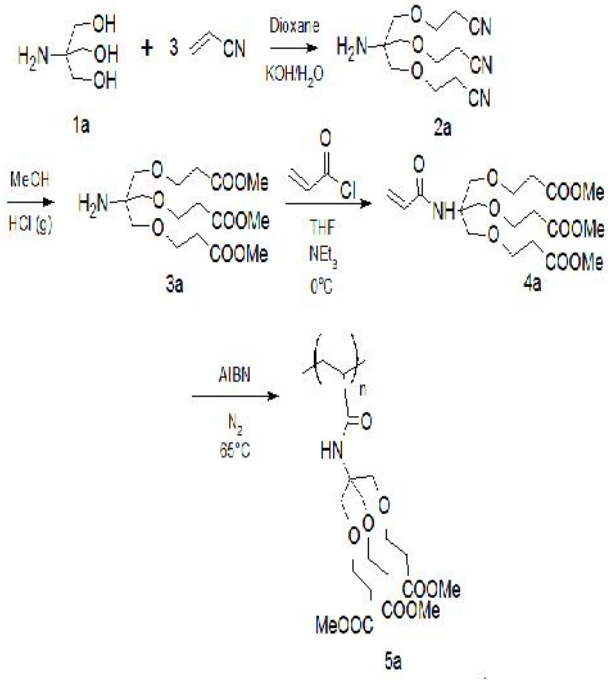
Polymer 5b

FT-IR (cm^{-1}) =3436.4(m, N-H stretching); 2946.6 and 2865.9 (s, C-Hstretching); 1725.8 and1643.6 (s, C=O stretching).

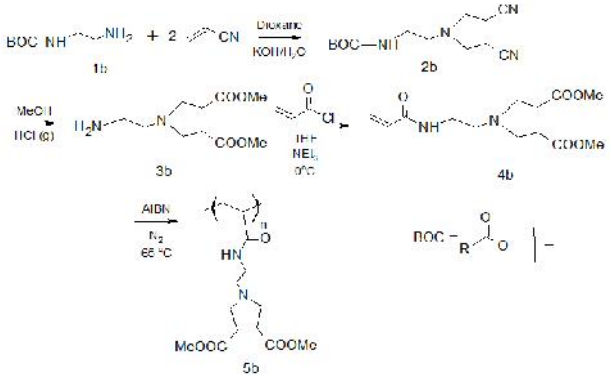
^{1}H-NMR(CHCl$_3$-*d*)(ppm)=7.32 (s,CON*H*); 4.06 (t,2H,NC*H*$_2$CH$_2$COOCH$_3$); 3.69 (overlapped, t,2H,NHC*H*$_2$CH$_2$N); 3.69(s,3H,COOC*H*$_3$); 2.60 (t,2H,C*H*$_2$COOCH$_3$); 2.31 (t, 2H, NHCH$_2$C*H*$_2$N). The signals of the vinyl protons disappeared.

^{13}C-NMR(CHCl$_3$-*d*)(ppm)=173.5(*C*OOCH$_3$ester and *C*ON Hamide); 64.1 (NHCH$_2$*C*H$_2$N);51.8(backbone *C*HCONH);34.1(NC*H*$_2$CH$_2$COOCH$_3$);28.3(COO*C*H$_3$);25.5 (NH*C*H$_2$CH$_2$N); 24.5 (*C*H$_2$COOCH$_3$).

Scheme 2 Synthesis of dendronized polymer 5a.



Scheme 3 Synthesis of dendronized polymer 5b.



Molecular Characterization

Molecular characterization of the polymers was performed by size exclusion chromatography (SEC) in THF and by viscosity measurements. The weight-average molecular weights of the polymers were M_W (5a) =14,000g/mol and M_W (5b)=25, 500g/mol. The low molecular weights obtained could be due to the steric hindrance for polymerization as a consequence of the bulkiness of the lateral groups**.**

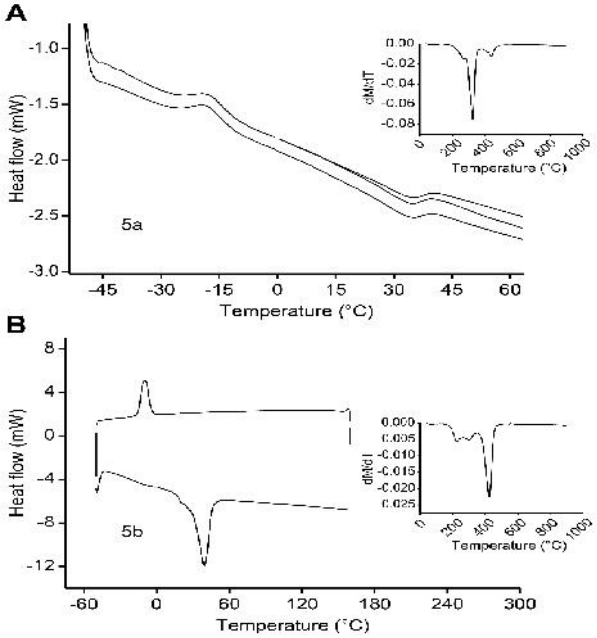


Figure 1 DSC and TGA (dm/dT) profiles for the polymers: **A**, polymer 5a and **B**, polymer 5b.

Table 1 Glass-transition temperatures (Tg), melting temperatures (Tm), crystallization temperatures (Tc) and degradation temperatures (TDT) of both polymers.

Temperatures (°C)	Polymer 5a	Polymer 5b
TDT	325	424
Tg	-27.0	-25.0
Tm	34.0	42.0
Tc	-15.3	-11.0

CONCLUSION

Dendronized polymers containing amphiphilic dendritic side chains were obtained in good yields via as implesynthetic sequence. The spectroscopic characterization of the monomers and polymers was consistent with their expected

chemical structures. These results suggested that the dendronized polymers could be chemically modified to control their amphiphilicity in order to obtain dendritic polymers with appropriate chemical structures. Therefore, the ability of these structures to entrap different types of molecules and/ or to interact with other macro molecular structures to obtain new materials with new properties could be monitored. Chemical modification of the side chain enables different cavities to be incorporated into the macromolecular structure. The thermal analysis of the samples indicated that both polymers were thermally stable and behaved as semi crystalline polymers with melting temperatures of 34.0 and 42.0°C. The DSC measurements showed that the Tg values of the polymers were very similar and that both were below zero, which was expected because of the chemical structure of the flexibleidechains and was consistent with the physical structure of the polymers, which had arubbery aspect.

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