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Synthesis of novel polyamidoamine (PAMAM) side chain dendritic oligourethane architecture

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Summary:

A convenient approach to the synthesis of a novel side chain dendritic oligourethane (SCDOU) (**1**) derived from ester terminated polyamidoamine (PAMAM) dendritic diol (G 3.5) (**1a**) with 2,4-toluene diisocyanate (TDI) was reported. Polymerization was conducted in bulk by using the catalytic amount of dibutyl tindilaurate (DBTD). The PAMAM dendritic diol as well as the side chain dendritic polyurethane were thoroughly characterized by means of IR, NMR spectroscopy.

Introduction:

Dendrimers are unique synthetic macromolecules with highly branched, compartmentalized structures, making them attractive for use as nanoscopic building blocks for the design and synthesis of novel functional materials [1-2]. In recent years particular interest arose in dendrimers which do not have the commonly observed spherical but rather cylindrical shape in solution [3-4]. In this context, side chain dendritic polymers (SCDPs) have received much attention in various fields including supramolecular chemistry and may act as potential giganto constituents of new generation of micells, vesicles, membranes, etc.

However a number of attempts have been made to obtain polymers with pendant dendritic units [5-8] by the groups of Frechet, Tomalia, Percec, Schluter, Ritter, and others. In this connection, the majority of the side chain dendritic polymers (SCDPs) reported in the literature are commonly produced by chain polymerization of dendritic macromonomers equipped with functional groups such as styrene or methylacrylate.

However, the polyamidoamine (PAMAM) family of starburst dendrimers (SBDs) [9-10] is a novel class of macromolecules which possess a definite molecular composition and constitution. In this regard, a challenging target is the construction of well-defined PAMAM side chain dendritic polymers possessing polymeric core units.

Therefore, in this article we wish to report a simple, efficient and novel synthetic approach based on copolymerization of ester terminated PAMAM dendritic diol (**1a**) with TDI, leading to the development of ester terminated PAMAM side chain dendritic oligourethane (SCDOU) architecture. To our knowledge, this is the first esterterminated PAMAM side chain dendritic oligourethane reported so far.

Experimental

Materials:

Methyl acrylate was shaken with a 5% NaOH solution, washed with water, dried on Na_2SO_4 and distilled. Other reagents were used as received without further purification.

Characterization

IR spectra were recorded with a SHIMADZU IR- 470 spectrometer by KBr disk/ KBr pallets method. UV/VIS spectrum of SCDOU was recorded with SHIMADZU UV-2100 spectrometer using DMF solvent. NMR spectra were recorded on a Branker AM200 spectrometer using $CDCl_3$ / DMSO- d_6 as solvent. XRD pattern of the SCDOU was obtained from cobalt source using PW-1729 X-ray diffractometer with a scan speed of 0.05°/sec. CHN-analysis of the polymer was obtained from 2400 Series II CHN Analyser, Perkin Elmer, USA, using helium as driving gas and oxygen as combustion gas.

Synthesis of dendritic diol (1a)

Our strategy for the divergent synthesis (Scheme 1) of the ester-terminated PAMAM dendritic diol involves the exhaustive Michael addition of diethanolamine with methylacrylate (1:6 mole ratio) followed by exhaustive amidation of the resulting ester with large excess of ethylenediamine to afford the next generation dendrimer with reactive amine groups. Repetition of this two step procedure ultimately leads to the targeted PAMAM dendritic wedge with two hydroxyl groups at the focal point.

IR (KBr): ν = 3345 (OH, NH stretching), 2930, 2895 (CH stretching), 1728 (ester C=O stretching), 1647 (amide I), 1557 (amide II), 1032 cm^{-1} (CO-O-C). ^1H NMR ($CDCl_3$, 200MHz): δ = 6.7 (bs, 7H, all –CONH-), 3.64 (s, 28H, $-COOCH_3$, OH-$\underline{CH_2}$-), 3.32 – 3.27 (m, 14H, -CONH-$\underline{CH}_2$-), 2.77- 2.70, (m, 30H, -CONHCH$_2$C$\underline{H}_2$N-, -$\underline{CH}_{\underline{2}}$-COOCH$_3$), 2.59- 2.37 (m, 50H, all other –CH$_2$-, HOCH$_2$-). ^{13}C NMR (CDCl$_3$, 50 MHz) δ: 172.6 (NC=O; out), 171.7 (NC=O; in) 170.7 (ester C=O), 68.3, 59.2, 58.2, 55.9, 52.5, 51.8, 51.4, 51.2, 51.1, 50.0, 49.7, 49.0, 36.7, 36.4, 35.5, 32.2, 31.80.

Polymrization

The polymerization reaction was conducted in bulk. For the polymerization in bulk, stoichiometric amount of dedritic diol 1a (0.77mmol, 1.237g) and TDI (0.77mmol, 0.135g) (1:1 mole ratio) were dissolved in dried chloroform. After the addition of catalytic amount of dibutyl tin dilaurate , the solvent was immediately evaporated under reduced pressure at room temperature. The polymerization was carried out 27°C for 24 hrs and then at 60-65°C for 3hrs under N$_2$ atmosphere. The polymerization reaction mixture was then washed with methanol and dried to yield the polydendron (**1**) as yellow powder.

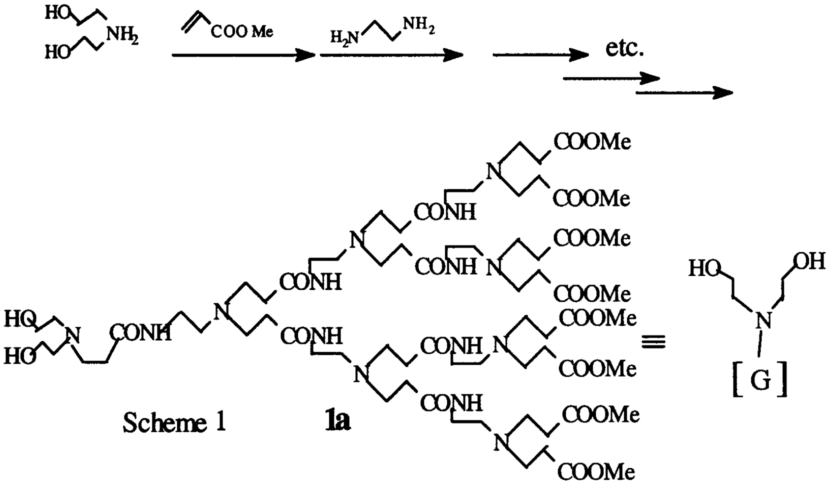
IR (KBr): ν = 3374 (OH, NH stretching), 2928, 2857 (CH stretching), 1730 (ester C=O stretching), 1638 (amide-I of dendritic wedge), 1600 (aryl C=C, aryl CH), 1537 (amide-II of dendritic wedge, -O-CO-NH-, aryl CH), 1034 (CO-O-C), 820 (aryl CH). ^{1}H NMR (DMSO-d$_6$, 200MHz) δ : 9.45 (bs, 1H, N$\underline{H}$CO para to CH$_3$ from TDI), 8.97 (bs, 1H, N$\underline{H}$CO ortho to CH$_3$ from TDI), 7.9 (bs, 1H, ArH^3), 7.04 (bs, 2H, ArH^{5,6}), 6.76 (bs, 7H, all –CONH-), 4.08 (bs, 4H, -N(-CH$_2$CH$_2$O-)$_2$), 3.55 (bs, 6H, -HNOCCH$_2$C$\underline{H}_2$-N(C$\underline{H}_{\underline{2}}CH_2$O)$_2$, 3.32 (s, 24H, -COOCH$_3$), 3.05 (bs, 14H, -CONH-C$\underline{H}_2$), 2.64 (bs, 30H, -CONHCH$_2$C$\underline{H}_2$N-, -C$\underline{H}_2$COCH$_3$), 2.37-2.19 (CH$_3$ of TDI,and all other –CH$_2$-). ^{13}C NMR (50 MHz, DMSO-d$_6$)δ : 172.56 and171.37 (CONH-,COOCH$_3$); 154.3,154.1 and 153.1(-OCONH-); 138.0, 137.8, 130.3, 125.4,120.8,112.2,68.0, 63.5,59.2,58.2,56.0,52.3, 51.6, 51.2, 49.6, 49.2, 48.9,48.6,36.8,33.4,32.1,31.3,29.0,17.4 ($\underline{C}$H$_3$ of internal TDI unit), 12.7 ($\underline{C}$H$_3$ of terminal TDI unit) UV/VIS (DMF): $\lambda_{max/nm}$ = 268. ($C_{80}H_{135}N_{17}O_{27}$)$_n$ (1767.02)$_n$ Calc. C 54.37 H 7.69 N 13.47 Found._ C 53.25 H 6.15 N 14.83 [η] = 0.061 in dl/g, at 40°C in DMF; M$_n$ (from ^{13}C NMR) = 6360.

Viscosity Measurement

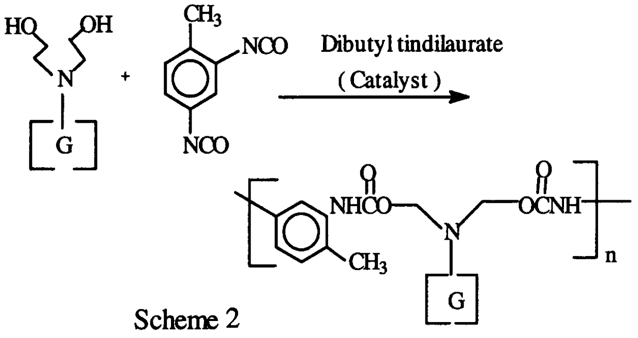
The intrinsic viscosity of the SCDOU was determined in DMF using Ubbelohde viscometer thermostated at 40°C. In this study, the intrinsic viscosity [η] of the SCDOU was determined by using the equation derived by Raju et. al [11].

$$\log [\eta] = \log [(\eta_{rel} - 1)/ C] - K [\eta_{rel} - 1]$$
$$= \log (\eta_{sp}/C) - K\eta_{sp}$$

Where C is concentration in g/dl. This equation was reported by Raju et al. to have a good fit when K= 0.14 for (η_{rel}-1) < 0.3 and K= 0.12 for 0.3 < (η_{rel}-1) < 0.8.



Scheme 1 **1a**



Scheme 2

SCDOU (1)

Results and Discussion

We have recently reported [10] the synthesis of ester terminated PAMAM dendritic wedge having one hydroxyl group in its focal point. Using the similar approach we have reported herein the ester terminated PAMAM dendritic wedge (**1a**) having two hydroxyl groups in its focal point (scheme-1). It is well known that isocyanates react with every active hydrogen of the reaction partner, and so it is with hydroxyl groups containing esterterminated PAMAM dendritic wedge in its focal point. In the reaction of ester-terminated PAMAM dendritic wedge with the isocyanate, a linear side chain dendritic polymer is produced with urethane bonds. The polymerization reaction was carried out at 27°C by monitoring the IR spectra in order to quantify the progress of polymerization reaction.

In the IR spectrum, the peak assignable to the isocyanate group (-NCO) i.e, 2308 cm^{-1} was clearly observed by admixing both the dendritic diol and the TDI. This peak intensity gradually decreases with reaction time until about 24hrs and completely disappeared, as shown in fig. 1, on raising the reaction temperature to 60-65°C for 3hrs. The SCDOU, obtained in fairly good yield, soluble in the organic solvents such as DMF, DMSO, NMP etc, but insoluble in methanol, ethanol, chloroform, carbontetrachloride etc. The structural characterization of both the dendritic wedge (**1a**) and the SCDOU (**1**) was carried out by IR, NMR spectroscopy. The ^1H NMR spectrum of SCDOU (Fig. 2), derived from dendritic diol and TDI shows the signals

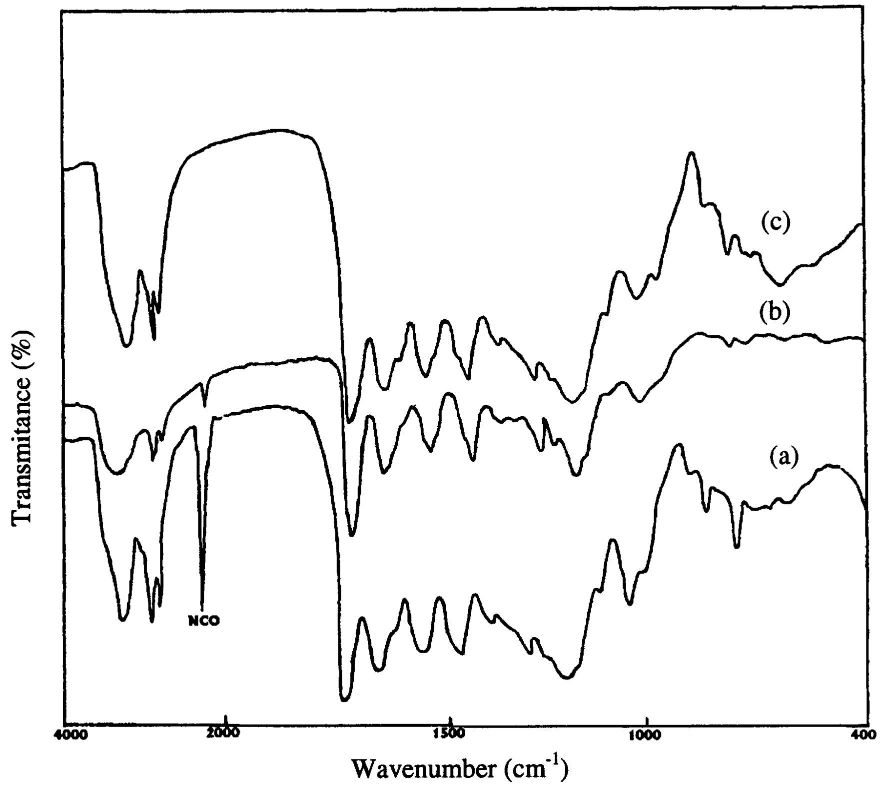


Figure 1. IR spectra of PAMAM dendritic wedge 1a – TDI mix; (a) immediately after TDI addition, (b) 15hrs after TDI addition, (c) 27hrs after TDI addition.

for the –NH protons of the urethane groups at 9.45-8.97 ppm. The resonance signals at 7.04 - 7.9 ppm are attributed to the aromatic protons. The methyl groups of the TDI unit show signals at 2.19 ppm. The methyl protons of COOMe groups of the dendritic unit of the SCDOU resonances at 3.32 ppm. These findings are also confirmed by the ^{13}C NMR and IR spectral data.

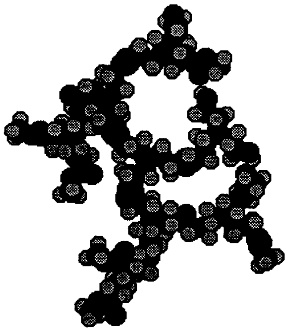


Figure 4. Computer- generated (Hyper chem lite: Molecular Mechanics) optimized geometry of dendritic diol 1a. with minimum energy of 72.757 kcal/mole.

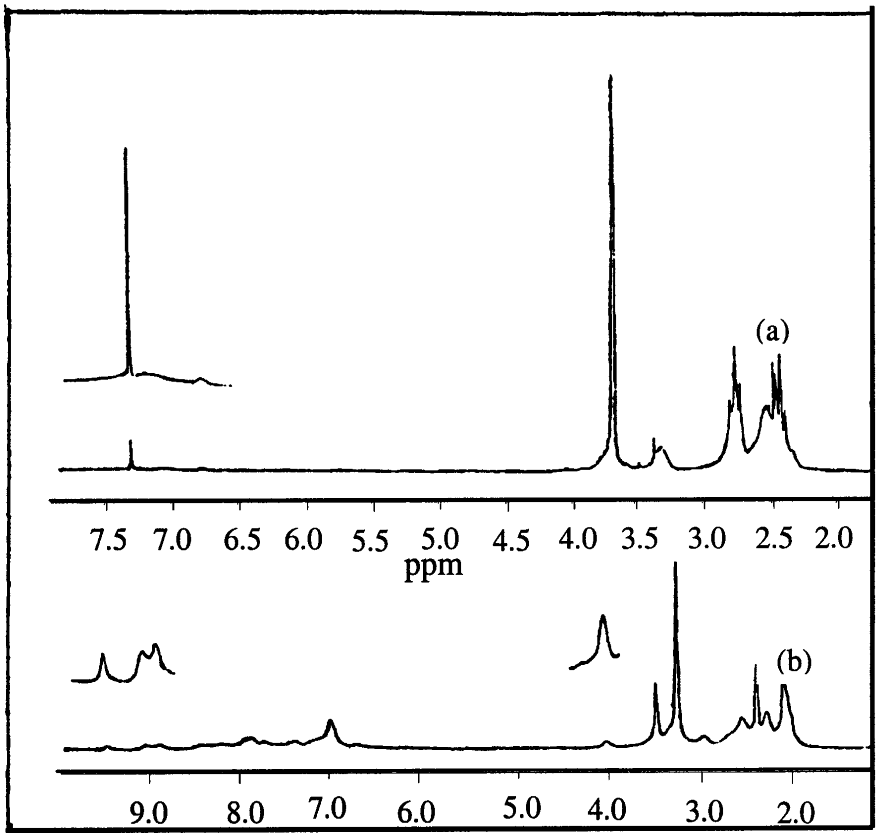


Figure 2. ^{1}H NMR spectra of (a) dendritic wedge 1a, (b) SCDOU 1.

The X-ray diffraction pattern (Fig. 3) of SCDOU (1) shows a broad halo, meaning that the polymer is amorphous in nature. This may be due to the presence of bulky pendent dendritic group which increases the disorderliness in the chains and thereby causes the disturdance in chain packing.

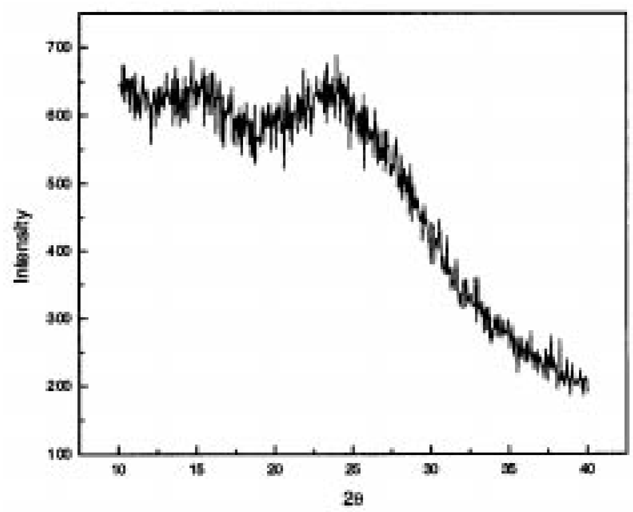


Figure 3. X-ray diffractogram of SCDOU.

The intrinsic viscosity [η] of the SCDOU was found to be 0.061 at 40°C as determined according to the method developed by Raju et al. The degree of polymerization (n) as well as the average molecular weight (M_n) of this oligourethane were determined from ^{13}C NMR spectroscopy by comparing intensities I_{CI} ($\underline{C}H_3$ of internal TDI unit) and I_{CT} ($\underline{C}H_3$ of terminal TDI unit) of both kinds of methyl carbons according to the following equations:

$I_{CI}/I_{CT} = n$; $Mn = (1590 + 176) + n \times 1767$.

It is reasonable to expect that the presence of dendritic side group (G 3.5) as well as the low degree of polymerization for this SCDPU derived from most sterrically hindered co-monomers i.e, dendritic diol (G3.5) and TDI might decrease the intrinsic viscosity [η] of this polymer.

Conclusion

We have shown that oligourethane (SCDOU) with pendant dendritic group of 3.5 generation can be produced via condensation polymerization of PAMAM dendritic diol with TDI. We anticipate that PAMAM side chain dendritic polyurethane of this type will open the exciting avenues into the biological mimicry as well as in the construction of nanoscale devices and modules. Incorporation of this ester terminated PAMAM dendritic diol in random or block fashion in the resulting dendronized copolymers (SCDPUs) using nondendritic diol as the comonomer and further investigation of the effect of dendritic pendent group on their macromolecular architecture are ongoing efforts in our laboratory.

References

1) Malenfant PRL, Groenendaal L, Frechet JMJ (1998) J. Am. Chem. Soc. 120 : 10990.
2) (a) Schenning APHJ, Elissen-Roman C, Weener J, Baars MWPL, vander Gaast SJ, Meijer EW (1998) J. Am. Chem. Soc. 120 : 8199. (b) Frey H (1998) Angew Chem. Int. Ed. Engl 37: 2193.
3) Neubert I, Amoulong-Kirstein E, Schluter A-D, Dautzenberg H (1996) Macromol. Chem. Phys. 17: 517.
4) Stocker W, Karakaya B, Schurman BL, Rabe JP, Schluter A-D (1998) J. Am. Chem. Soc. 120 : 7691. and references therein.
5) Lijin S, Andreas S, Schluter A-D (2000) Macromolecules 33: 4321. and references therein.
6) Yin R, Zhu Y, Tomalia DA (1998) J. Am. Chem. Soc. 120: 2678.
7) (a) Ji T, Zhang J, Cui G, Li Y (1999) Polym. Bull. 42 (4) : 379. (b) Jahromi S, Coussens B, Meijerink N, Braam AWM (1998) J. Am. Chem. Soc. 120 : 9753 and references therein.
8) Kaneto T, Horie T, Asano M, Aoki T, Oikawa E (1997) Macromolecules. 30 : 3118.
9) Tomalia DA, Naylor AM,Goddard WA (1990) Angew Chem. Int. Ed. Engl. 29: 138.
10) Ghosh S, Banthia AK (2001) Tetrahedron Lett. 42 : 501.
11) Raju KVSN, Yaseen M (1992) J. Appl. Polym. Sci. *45* : 677.