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Synthesis & characterization of novel silicone dendrimers as base stock for high performance lubricants

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ABSTRACT

The silicone core G_I dendrimers having terminal Si-H groups reacted with maleic anhydride in presence of Speier's catalyst to afford anhydride terminated dendrimers. These anhydride dendrimers were further reacted with long chain aliphatic alcohols in presence of lower valent tin oxide as catalyst to synthesize novel second generation complete neutral silicone ester dendrimers. These high performance silicone esters dendrimers can be used for different avionic applications and also as base stock material for lubricants. Characterizations of the dendrimers were carried out by elemental analysis; Fourier transforms infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR spectroscopy). Physical properties like density, viscosity, flash point and pour point of the dendrimers were also studied. Vapor pressure osmometery (VPO) and gel permeation chromatography (GPC) were used for measuring the molecular weight and molecular weight distribution of the dendrimers.

1. Introduction

Dendrimers being regularly branched and three-dimensional macromolecules have attracted scientific attention exceptionally, because of their size, shape, dimension, flexibility, and functionality, which can be controlled at molecular level [1–5]. Being an era of technological miniaturization, a need felt to develop multifunctional materials so that the diversified properties could be inculcated in one material. Henceforth, the dendrimers have attracted the attention of researchers to a great extent. Aliphatic polyesters with well defined architectures such as star polymers [6,7], star-block polymers [8–12], comb like polymers [13,14] hyper-branched polymers [15] and dendrimers [16,17]are attracting interest because of their unique structures and properties. During recent past the ester group bearing dendrimers have been explored for various applications of diversified nature because of their unique structure property relationship e.g., Bertino et al. [18] reported the synthesis of two new families of poly (ester amine) dendrimers, designed to be considered as flexible non-cytotoxic nano carrier of poorly water soluble drugs, like methotrexate which was widely used in chemotherapy. Polyester scaffold based dendrimers has been shown to be non-toxic even at very high concentration [19,20]. The polyester dendrimers are promising biodegradable candidate as safe and efficient delivery device because they contain multiple ester bonds. Polyesters have excellent high temperature properties and in general have improved properties over the diesters [21] including long term hydrolytic stability. Recently pyrene –based ester dendrimers were synthesized for application in dye-sensitized solar cells [22]. Polyhedral oligomeric silsesquioxanes (POSS) and polyhedral oligomeric silicate (POS) was used as lubricants, mold release agent and additives to control the viscosity, lubrication, wear and thermal properties of conventional lubricous materials [23]. Dendrimers with ester linkage [24,25] provides easy access, facile branching, versatility, solubility, applicability, and processability from inexpensive raw materials. Few biodegradable esters have been synthesizing using polyols and carboxylic acids (C_6-C_{12}) their lubrication performance were evaluated, these products were found to have good potential for use as a base stock for formulation as fire resistant hydraulic fluids of VG-22grade [26]. The use of various diesters, polyesters and complex esters as lubricating oil is well known to the art and has been described in various patents [27]. Because of their utility over extremely wide temperature range, the synthetic esters lubricating oils are widely used in the formation of lubricants for aircraft engine such as “turbo-jet”, “turboprop” and “pure-jet” aircraft.

In our previous work we have synthesized some novel branched

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chain complete neutral organosilane, organosiloxane esters [28], novel silane (Si-H) and oxirane functional first generation silicone dendrimers [29] using divergent approach. To extend it further, in the present work we have synthesized and characterized some novel second generation silicone ester functional dendrimers. And evaluate their different physical properties.

2. Experimental section

2.1. General remarks

All manipulations and reactions were performed under a purified nitrogen atmosphere using standard Schlenk technique. Maleic anhydride (LR grade, SD Fine Chemicals) and stannous oxide (SnO) (99.99%, Aldrich) were used as received. 2-Ethylhexanol (LR grade, SD Fine Chemicals), 1-octanol (LR grade, SD Fine Chemicals), isodecyl alcohol (LR grade, Ranbaxy) were used after distillation. Tetrahydrofuran (LR grade, Ranbaxy), hexane (LR grade, E. Merck), petroleum ether 60–80 °C (AR grade, Samir Tech-Chem Pvt Ltd) and ethyl acetate (LR grade, Ranbaxy) were purified and dried before use as reported [30]. Speier's catalyst was synthesized in laboratory [31].

First generation Si-H functional G_IA and G_IB dendrimers were prepared according to reported method [29].

Perkin Elmer FTIR Spectrometer RX1 was used to record IR spectra using NaCl pellets in the range of 400–4000 cm^{-1}. A Bruker Avance 400 MHz NMR spectrometer was used for NMR studies using deutrated chloroform as solvent and TMS as standard reference. Vapour pressure osmometer (VPO) knauer instrument model K-7000 was used to measure molecular weight of dendrimers with polystyrene as standards. Polydisperse index (PDI) of dendrimers was determined by gel permeation chromatography (GPC) on C-R2AX instrument (Shimadzu, Japan) with polystyrene for calibration. A Vario EL III CHNOS elemental analyzer was used for elemental analysis. Silicon element analysis was carried out according to reported [29] methods. Density, pour point and flash point were evaluated according to ASTM D-1480, ASTM D-97 and ASTM D-3828 [30] methods respectively. Viscosity was measured by using Brookfield Viscometer (DV-II + PRO viscometer).

2.2. Synthesis of dendrimers

2.2.1. G_IA^p dendrimer

The solution of Si-H functional G_IA dendrimer (2.5 g, 1.72 mmol) and speier's catalyst (0.03 mol %) in dry THF (50 ml) was taken in a three necked round bottom flask (100 ml) fitted with a dropping funnel containing maleic anhydride (2.02 g, 20.6 mmol) was gradually added drop wise within 30 min to carry out hydrosilation reaction. The volatile substances were removed by evaporation to give pot residue. The pot residue was column chromatographed (silica gel and n-hexane) to afford yellow transparent liquid G_IA^p ($C_{88}H_{148}O_{52}Si_{21}$) dendrimer, yield 4.52 g, 89%. IR (KBr): υ 2952 (−CH_3), 2923 (−CH_2−), 2871 (−CH−), 1850 and 1781 (−CO−O−CO−, asym and sym), 1252 (−Si−CH_2−, −Si−CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, δ): −0.02 (s, −Si−CH_3), 0.84 (t, −Si−CH_2−), 3.60 (d, −CH_2−CO−), 4.72 (t, −Si−CH−CO−); Anal. Calcd for $C_{88}H_{148}O_{52}Si_{21}$: C 40.18, H 5.68, Si 22.44; found: C 40.17, H 5.68, Si 22.41. Mol Wt (VPO): 2509.16 (calcd 2627.87). GPC: PDI value (Mw/Mn), 1.01 (1268/1249); Rt, 17.15 min.

2.2.2. G_IB^p dendrimer

Hydrosilation reaction of the G_IB dendrimer (2.8 g, 1.27 mmol) with maleic anhydride (1.49 g, 15.2 mmol) in presence of speier's catalyst were carried out same as the hydrosilation of G_IA^p dendrimer, to afford the yellow transparent liquid G_IB^p ($C_{148}H_{172}O_{52}Si_{21}$) dendrimer, yield 4.28 g, 91%. IR (KBr):υ 2960 (−CH−), 2922 (−CH_2 −), 1841 and 1781 (−CO−O−CO−, asy and sym), 1495 (−Si−Ph), 1261 (−Si-CH_3), 1054 (−Si-O-Si−); ^{1}H NMR (400 MHz, $CDCl_3$, δ): −0.01 (s, −Si−CH_3), 0.82 (t, −Si−CH_2 −), 7.3–7.5 (m, aromatic protons), 2.82 (d, −CH_2−CO−), 5.2 (t, −Si−CH−CO−); Anal. Calcd for $C_{148}H_{172}O_{52}Si_{21}$: C 52.70, H 5.13, Si 17.49 found: C 52.69, H 5.14, Si 17.50. Mol Wt (VPO): 3257.43 (calcd 3372.74). GPC: PDI value (Mw/Mn), 1.01 (2366/2325); Rt, 17.12 min.

2.2.3. $G_{II}A^x$ dendrimer

Esterification reaction of the G_IA^p dendrimer (2.4 g, 0.9 mmol) with 2- ethylhexanol (3.43 ml, 21.9 mmol) in petroleum ether (30 ml) in presence of metal oxide (SnO) as catalyst (3% of G_IA^p) was carried out in a round bottom flask (250 ml) fitted with Dean's Stark and refluxed for 6 h and cooled to room temperature. The solution was filtered under reduced pressure using millipore filters (11 μm) to remove catalyst. The filtered solution was vacuum distillated (~4 mbar, 70 °C) to remove volatile solvent and unreacted alcohols. The yellow transparent liquid product $G_{II}A^x$ ($C_{280}H_{556}O_{64}Si_{21}$) dendrimer was purified by column chromatography using silica gel (50.0 g for 1 ml) as stationary phase and a mixture of petroleum ether (60–80 °C) and ethyl acetate (9: 1) as mobile phase. Yield 4.82 g, 95.3%. IR (KBr):υ 2958 (−CH_3), 2925 (−CH_2−), 2872 (−CH−), 1736 (−COOR), 1250 (−Si−CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.05 (s, −Si−CH_3), 0.53 (t, −Si−CH_2 −), 0.83–1.60 (m, −Si−CH_2−CH_2−CH_2−CH_3 and alkyl chain), 2.56 (d, −CH_2−CO−), 4.01 (t, −O−CH_2 −), 4.15 (t, −Si−CH−CO−); Anal. Calcd for $C_{280}H_{556}O_{64}Si_{21}$: C 60.73, H 10.12,Si 10.65; found: C 60.74, H 10.12, Si 10.66. Mol Wt (VPO): 5454.92 (calcd 5537.32). GPC: PDI value (Mw/Mn), 1.02 (4072/3982); Rt, 16.25 min.

Following the same procedure other esterification reactions as mentioned below were carried out.

2.2.4. $G_{II}A^y$ dendrimer

Reaction of the G_IA^p dendrimer (2.4 g, 0.9 mmol) with 1-octanol (3.45 ml, 21.9 mmol) in presence of SnO catalyst gives a yellow transparent liquid $G_{II}A^y$ ($C_{280}H_{556}O_{64}Si_{21}$) dendrimer. Yield 4.9 g, 97%. IR (KBr):υ 2956 (−CH_3), 2928 (−CH_2−), 2854 (−CH−), 1736 (−COOR), 1253 (−Si−CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.07 (s, −Si−CH_3), 0.58 (t, −Si−CH_2 −), 0.86–1.63 (m, −Si−CH_2−CH_2−CH_2−CH_3 and alkyl chain), 2.59 (d, −CH_2 −CO−), 4.07 (t, −O−CH_2 −), 4.18 (t, −Si−CH−CO−); Anal. Calcd for $C_{280}H_{556}O_{64}Si_{21}$: C 60.73, H 10.12, Si 10.65; found: C 60.72, H 10.13, Si 10.65. Mol Wt (VPO): 5420.62 (calcd 5537.32). GPC: PDI value (Mw/Mn), 1.02 (4089/3998); Rt, 16.24 min.

2.2.5. $G_{II}A^z$ dendrimer

Reaction of the G_IA^p dendrimer (2.4 g, 0.9 mmol) with isodecyl alcohol (4.13 ml, 21.9 mmol) in presence of SnO catalyst gives a yellow transparent liquid $G_{II}A^z$ ($C_{328}H_{652}O_{64}Si_{21}$) dendrimer. Yield 5.33 g, 94%. IR (KBr):υ 2957 (−CH_3), 2928 (−CH_2−), 2871 (−CH−), 1736 (−COOR), 1259 (−Si−CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.05 (s, −Si−CH_3), 0.55 (t, −Si−CH_2 −), 0.83–1.60 (m, −Si−CH_2−CH_2−CH_2−CH_3 and alkyl chain), 2.53 (d, −CH_2−CO−), 4.06 (t, −O−CH_2−), 4.17 (t, −Si−CH−CO−); Anal. Calcd for $C_{328}H_{652}O_{64}Si_{21}$: C 63.43, H 10.56, Si 9.48; found: C 63.43, H 10.56, Si 9.48. Mol Wt (VPO): 6140.79 (calcd 6210.52). GPC: PDI value (Mw/Mn), 1.02 (5153/5049); Rt, 16.23 min.

2.2.6. $G_{II}B^x$ dendrimer

Reaction of the G_IB^p dendrimer (2.9 g, 0.85 mmol) with 2-ethylhexanol (3.19 ml, 20.4 mmol) in presence of SnO catalyst gives a product $G_{II}B^x$ ($C_{340}H_{580}O_{64}Si_{21}$) dendrimer. Yield 5.07 g, 95%. IR (KBr):υ 3050–3070 (aromatic protons), 2960 (−CH_3), 2930 (−CH_2), 2873 (−CH−), 1736 (−COOR), 1461 (Si-Ph), 1261 (Si−CH_3),