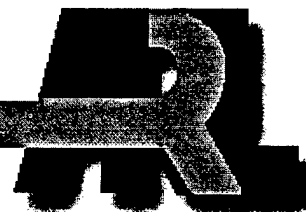


ARMY RESEARCH LABORATORY



The Properties of Dendritic Polymers I: Generation 5 Poly(amidoamine) Dendrimers

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ARL-TR-1606

MAY 1998

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Abstract

Dendritic polymers, or dendrimers, represent a new class of macromolecules characterized by an ultra-branched molecular architecture generated by a novel synthetic route developed in the mid-1980s. As the synthetic science of these molecules matures, the search for ways to use them in military and commercial technologies is becoming increasingly active. However, a lack of physical property data has made the identification of suitable application and technology areas that are ripe for exploitation of dendrimers difficult. The purpose of this series of reports is to compile, in the most concise form possible, some fundamental physical property information about dendrimers. The focus is on the behavior of poly(amidoamine) or PAMAM dendrimers, which are produced domestically by Dendritech, Inc., of Midland, Michigan. In this first report, the properties of mid-size, "Generation 5," PAMAM dendrimers are highlighted. The second and third reports will focus on the generation or size dependence of the physical properties of PAMAM dendrimers and on the end-group chemistry dependence of PAMAM dendrimers, respectively.

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THE PROPERTIES OF DENDRITIC POLYMERS I: GENERATION 5 POLY(AMIDOAMINE) DENDRIMERS

1. INTRODUCTION

Beginning in 1996, the U.S. Army Research Laboratory (ARL) partnered with the Michigan Molecular Institute in a new venture aimed at scientifically exploring dendritic polymers, an emerging technology in polymer science growing from a breakthrough in chemistry that allowed for the synthesis of polymers having novel, ultra-branched macromolecular architecture. This novel architecture lends unusual properties to dendritic polymers, such as low viscosity and high reactivity, and makes the dendritic polymers, or dendrimers, attractive for a variety of technologies. Specific application areas in which dendrimers have been identified as having potential for exploitation include chemically resistant coatings, fiber-matrix coupling agents, adhesives, compatibilizers for polymer blends, toughening agents for brittle polymers, sensors, environmental remediation, catalysis, molecular organic devices, fire suppression agents, antibacterial delivery agents, and medical diagnostic tools.

Although the synthesis of dendritic polymers is taking place throughout the world at universities and other research institutions, the commercialization of this technology is in its infancy. As a result, dendritic polymers are available only in research quantities and from only three commercial sources world wide, one of which is domestic. Because of the limited availability of these materials, very little is known about their general physical properties. As a first step toward the successful integration of dendritic polymers into useful materials systems, we endeavored to compile some fundamental chemical and physical property information about these materials and the unique behavior they display as a result of their unusual molecular structure.

In this report, the first in a series, we focus on the general chemical and physical properties of a single type of dendritic polymer, a Generation 5, Poly(amidoamine) dendrimer, produced domestically by Dendritech, Inc., of Midland, Michigan, and marketed under the trade name "Starburst®". A general introduction to the synthesis of poly(amidoamine) dendrimers and the associated nomenclature has been included, followed by a compilation of the properties related to their synthesis (purity, chemical structure, molecular weight), and finally, some physical properties of the materials in solution and bulk forms. The information contained herein has been compiled in a format that stresses brevity, and the document is intended for use primarily as a guide to general properties. References have been included when available. Future reports in this series will focus on the dependence of the physical properties of dendritic polymers on their size

and end-group chemistry and on a comparison of the properties of dendritic polymers produced from different commercial sources.

2. SYNTHESIS OF POLY(AMIDOAMINE) DENDRIMERS

2.1 Nomenclature

A generalized structural formula of Starburst[®] poly(amidoamine) (PAMAM) dendrimers may be represented as follows [1]:

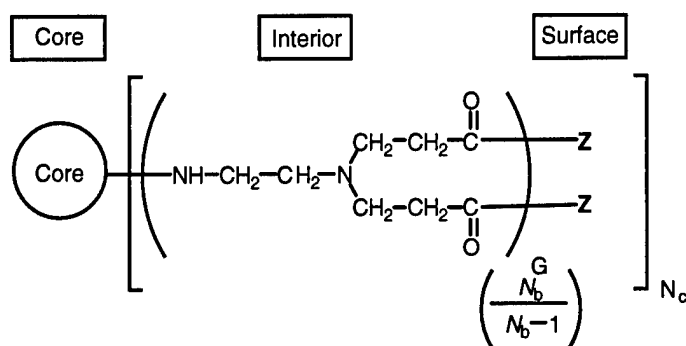


Figure 1. Structural Representation of the PAMAM Dendrimer Chemistry.

in which core is ethylenediamine residue $-\text{[CH}_2\text{N[CH}_2\text{CH}_2\text{CO]}_2\text{]}_2$. The functionality of the core, N_c , is 4, the functionality of the branch junctures, N_b , is 2, and G is the number of generations surrounding the initiator core and containing the repeating units $[\text{NHCH}_2\text{CH}_2\text{N[CH}_2\text{CH}_2\text{CO]}_2]$. Z represents the terminal groups, which for PAMAM dendrimers are $-\text{OCH}_3$ or $-\text{NHCH}_2\text{CH}_2\text{NH}_2$.

2.2 Synthetic Procedure

The preparation of PAMAM dendrimers involves a typical divergent synthesis via a two-step growth sequence that consists of two reiterating reactions: the Michael addition of amino groups to the double bond of methyl acrylate (MA) followed by the amidation of the resulting terminal carbomethoxy, COCH_3 , with ethylenediamine (EDA) [1]. When ethylenediamine is used as the initiator core reagent, this synthesis is represented in Figure 2.

In the first step of this process, ethylenediamine is allowed to react under an inert nitrogen atmosphere with a three-fold molar amount of MA at 25°C for about 48 hours. The resulting compound is referred to as “generation -0.5 PAMAM tetra ester.” The next step involves reacting

tetra ester with excess EDA to produce generation 0 PAMAM tetramine. This amidation reaction is performed under inert nitrogen in methanol and requires about 48 hours at 0° C for completion.

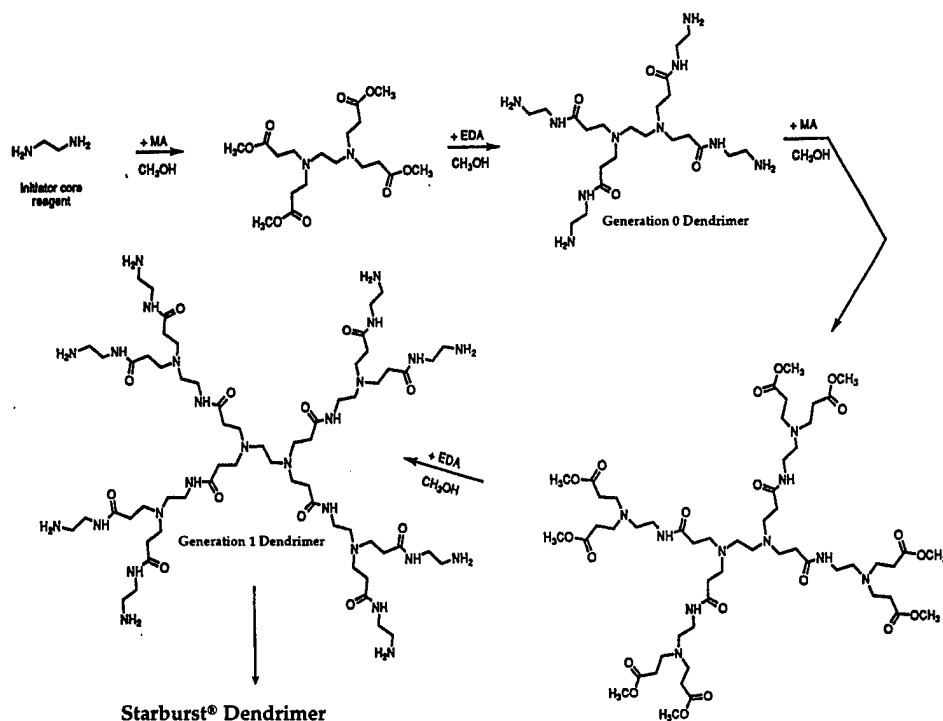


Figure 2. Reaction Scheme 1: Synthesis of PAMAM Dendrimer.

The preparation of tetramine completes the first full sequence employed in the divergent synthesis of PAMAM dendrimers. Reiteration of this reaction sequence results in the synthesis of half and full generation intermediates (i.e., ester- and amine-terminated intermediates, respectively). For example, the second iteration of this sequence produces generations 0.5 and 1, the octoester and octoamine, respectively. The same reactions are performed in the same way as for generations -0.5 and 0. They yield essentially quantitative amounts of the generational products through generation 5. Selected molecular characteristics of generation 5, EDA core PAMAM dendrimer are listed in Table 1.

Table 1. Molecular Characteristics of G5 PAMAM Dendrimers

NOMINAL PROPERTY	VALUE
Number and type of surface groups	128 NH ₂ groups
Molecular weight	28,826
Core	>NCH ₂ CH ₂ N<
Repeat unit	-[CH ₂ CH ₂ CONHCH ₂ CH ₂ N]<
End groups	-NH ₂

3. MOLECULAR PROPERTIES

3.1. Purity [2]

Purity was determined using a reverse phase, ion pair chromatography, on a Beckman Pump 126 Detector 168 Instrument operated with System Gold software. Purity is defined as the percent area of the main peak in the chromatogram, and it corresponds to the amount of pure monodendrimer in the sample. Data from Generation 5 PAMAM dendrimer samples indicate a 95.82% monodendrimer content, or 95.82% purity (see Figure 3).

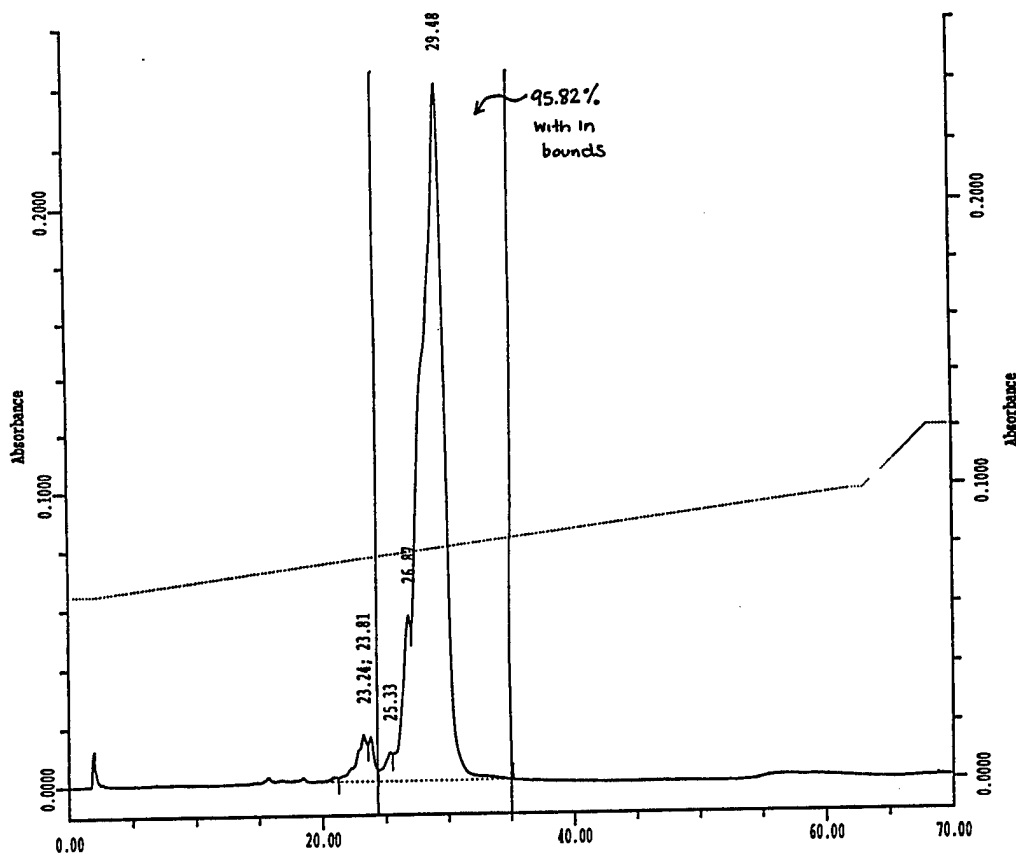


Figure 3. High Performance Liquid Chromatogram of G5 PAMAM Dendrimer in Aqueous Solution.

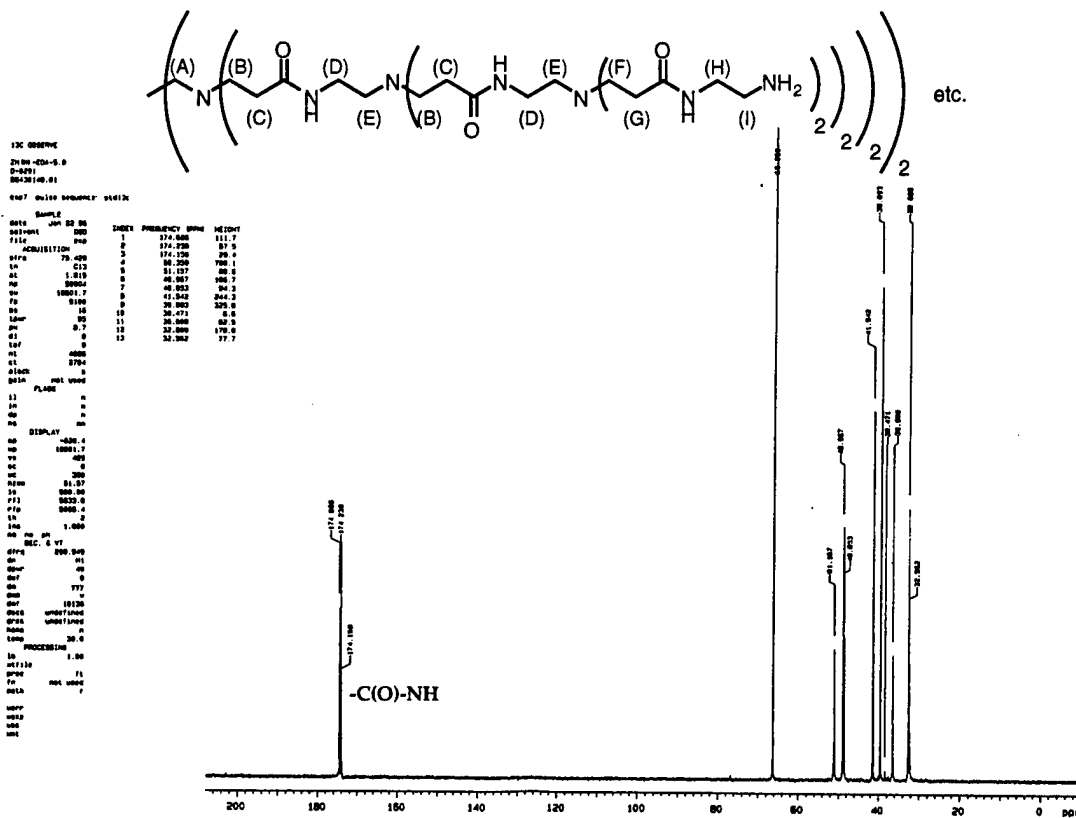
3.2 Compositional Identification

3.2.1 *Nuclear Magnetic Resonance (NMR)* [3]

NMR spectra were obtained in D_2O using 1,4 *p*-dioxane as the reference on a Varian 300-MHz superconducting magnet at 30° C. Representative spectra and associated peak assignments are given in Tables 2 and 3 and Figures 4 and 5.

Table 3. Features From the ^{13}C NMR Spectra of G5 PAMAM Dendrimer Illustrated in Figure 5 [3a]

PEAK LABEL	PEAK POSITION, d ppm
A	Core carbon cannot be seen on the spectrum beyond generation 2.
B	48.967
C	32.562
D	36.608
E	51.157
F	48.967
G	32.689
H	41.542
I	39.693
Amide Carbon	174.566, 174.238, 174.158



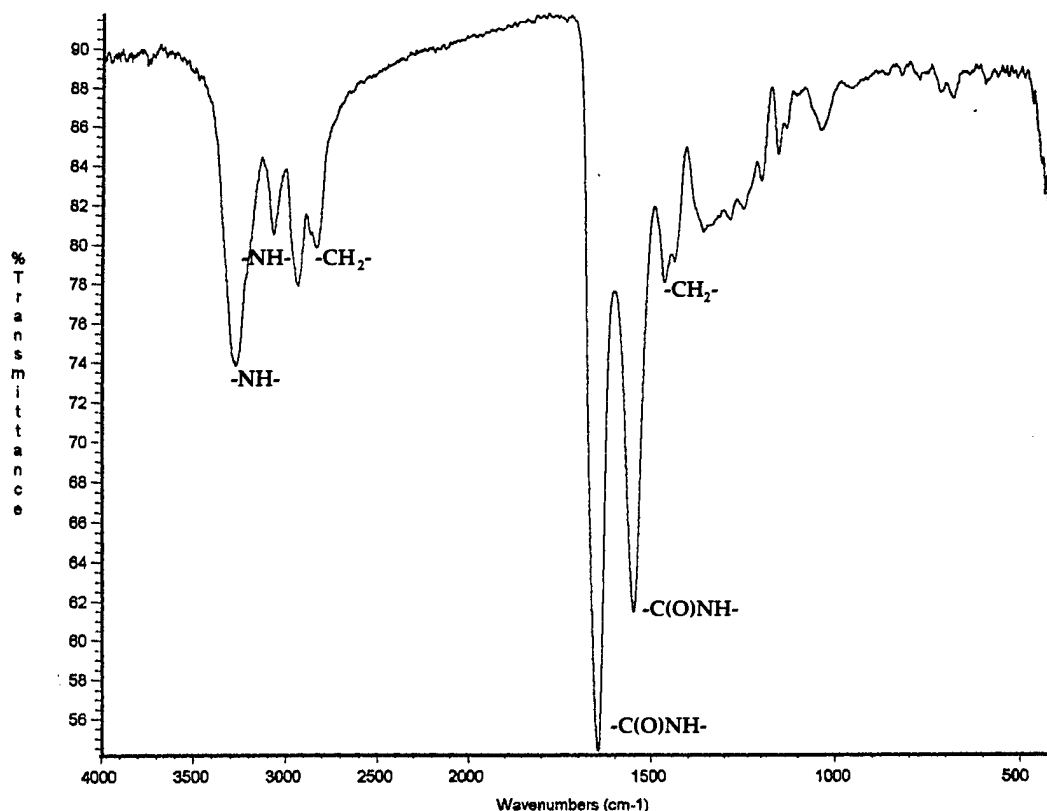


Figure 6. Fourier Transform Infrared Spectrum of G5 PAMAM Dendrimer.

3.3. Molecular Weight and Polydispersity

The molecular weights of the G5 PAMAM dendrimers were determined by size exclusion chromatography (SEC) [5] and by matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF) [6]. SEC was conducted using a Waters Model 410 differential refractometer during acidic conditions (citric acid buffer, pH = 2.7) at 30° C. MALDI-TOF spectra were obtained using a Vision 2000 Finnigan instrument. Samples were prepared using dihydroxy benzoic acid matrix. Representative data and molecular weight measurements are given in Table 5 and Figures 7 and 8.

Table 5. Molecular Weight and Polydispersity From the Chromatograms Shown in Figures 7 and 8

PROPERTY	METHOD	VALUE
Molecular Weight	MALDI-TOF (Peak MW)	28,175 g/mole
Polydispersity	MALDI-TOF (Polydispersity of the main peak*)	1.017
Molecular Weight	SEC (M_{peak})	24,956 g/mole
Molecular Weight	SEC (M_n)	25,323 g/mole
Molecular Weight	SEC (M_w)	26,589 g/mole
Polydispersity	SEC (Polydispersity), M_w/M_n	1.05

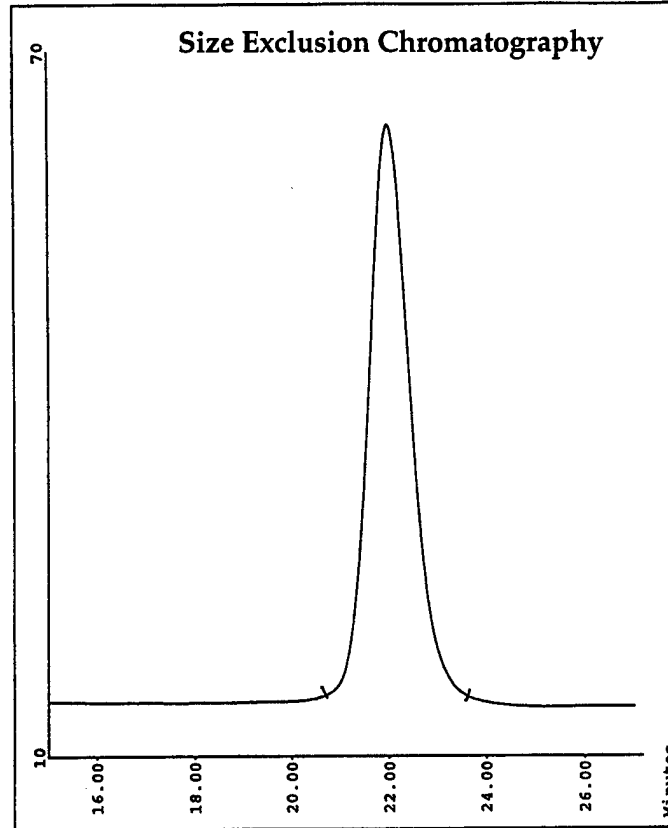


Figure 7. Size Exclusion Chromatogram From G5 PAMAM Dendrimer Measured in Buffered Aqueous Solution.

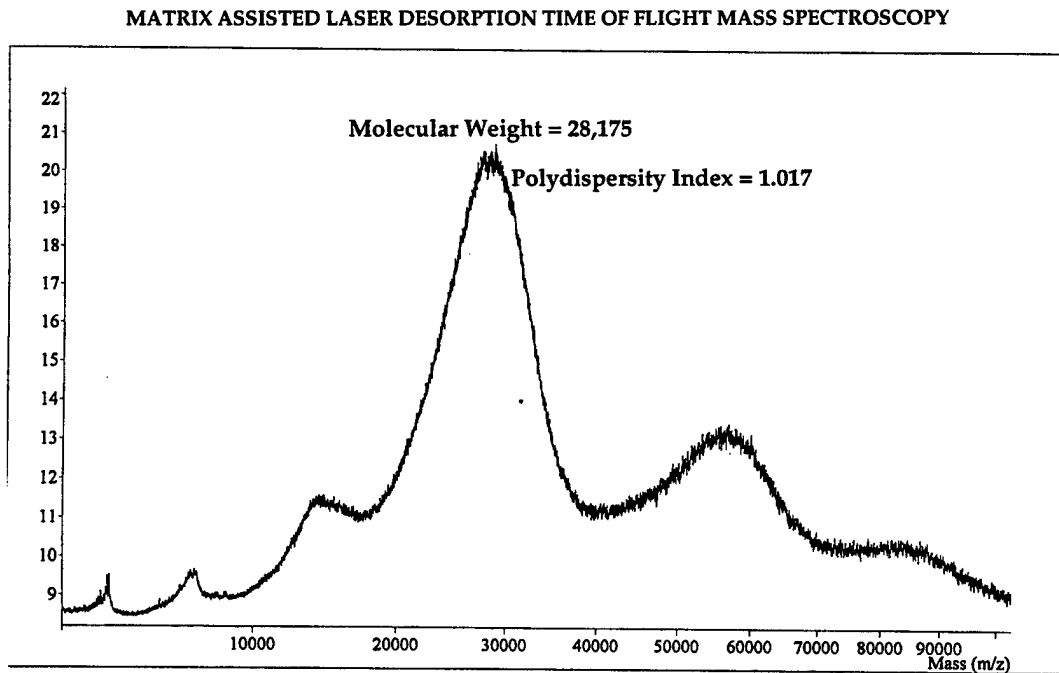


Figure 8. MALDI Spectrum From G5 PAMAM Dendrimer From Dihydroxy Benzoic Acid Matrix.

3.4. Molecular Size and Shape

Molecular size and shape of Generation 5, PAMAM dendrimers have been probed using a variety of experimental and computational techniques. The results are summarized in Table 6.

Table 6. Molecular Size and Shape of G5 PAMAM Dendrimers

METHOD	CONDITIONS	PARAMETER	VALUE
Size Exclusion Chromatography	Citric Acid Buffer in Water at 30° C	Hydrodynamic Radius	27.2 Å
Dilute Solution Viscometry [7]	5 wt % NaCl in water at 20° C	Hydrodynamic Radius	30.0 Å
Small Angle Neutron Scattering [8]	Deuterated Methanol at 20° C	Radius of Gyration	23.0 Å
Modeling	Molecular Dynamics "Polygraph" software	Ratio of the Moduli of Inertia (I_z/I_x) [9]	1.3
Modeling	Monte Carlo on Diamond Lattice	Asphericity Parameter [10]	0.21

4. SOLUTION PROPERTIES

4.1. Solubility [11]

Solubility parameters were determined according to the standardized American Society for Testing Materials (ASTM) D 3132-84 procedure. In all cases, concentrations were 1 weight percent (wt %), and tumbling was performed for 24 hours. The solubility was checked visually (see Table 7).

Table 7. Solubility of G5 PAMAM Dendrimer in Common Solvents

SOLVENTS	2-Methyl-2-butanol, 2-Ethyl-2-butanol, 2-Methyl-2-propanol, 2-Methyl butanol, Hexanol, 2-Pentanol, 2-Butanol, 2-Ethylhexanoic acid, 3-Methyl butanol, 2-Methyl propanol, Nitromethane/Acetonitrile (60/40), 1,2-Propanediol, Ethanol/Methanol (50/50), Dimethylacetamide, 1-Butanol, 1-Propanol, Dimethylformamide, Ethanol, Methanol, Ethylene glycol, Water, Acetic acid, Phosphoric acid, Hydrochloric acid, Citric acid buffer, Dimethylsulfoxide
NON-SOLVENTS	Aliphatic hydrocarbons, Aromatic hydrocarbons, Diethyl ether, Cyclohexane, Methyl cyclohexane, Cyclohexanone, Toluene, Toluene/Acetonitrile (50/50), Acetonitrile, o-Xylene, Styrene oxide, Pyridine, Dimethyl maleate, Nitromethane, Tetrahydrofuran, Chloroform, Morpholine

4.2 Refractive Index [12]

Refractive indices of dendrimer-methanol solutions were measured using an Abbe refractometer at room temperature. Solutions of desired concentrations (wt %) were prepared and immediately transferred onto the refractometer for these measurements. The results are summarized in Table 8 and Figure 9.

Table 8. Refractive Index of (G5 PAMAM Dendrimer)-Methanol Solutions

Concentration (Wt %)	Refractive Index
0	1.3276
5.00	1.3347
10.00	1.3411
13.90	1.3482
16.67	1.3540
19.45	1.3569
22.23	1.3647
25.00	1.3668
27.79	1.3747
33.35	1.3788
38.90	1.3847

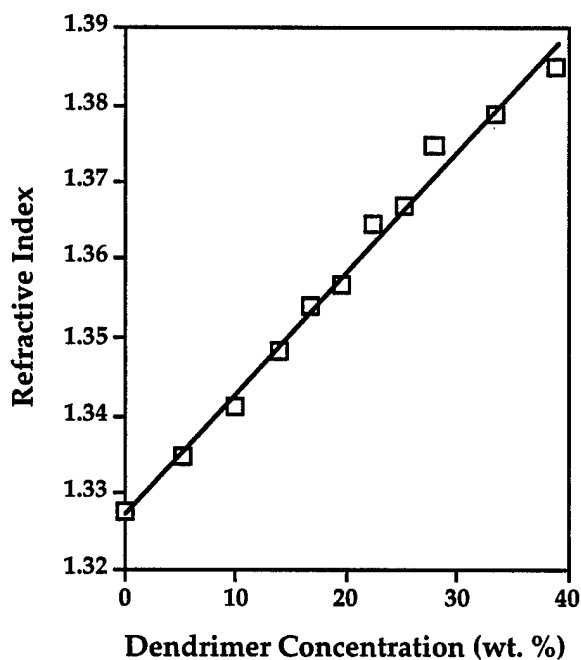


Figure 9. Refractive Index of G5 PAMAM Dendrimer-Methanol Solutions as a Function of PAMAM Concentration.

4.3 Solution Viscosity

4.3.1 Intrinsic Viscosity [7]

Reduced viscosities of dendrimer solutions were measured using an Ubbelohde semi-micro viscometer within a concentration range from 1 g/dL to 0.1 g/dL. Intrinsic viscosities were determined by extrapolation to zero concentration. The solvent was 5% by weight sodium chloride in water and the temperature was 20° C. The intrinsic viscosity of generation 5, EDA core, PAMAM dendrimer during these conditions was found to be 0.059 dL/g.

4.3.2 Zero-Shear Viscosity [7, 13, 14]

Zero-shear viscosities of dendrimer solutions in EDA were measured using a controlled stress low inertia (CSL) 100 Carri-Med stress controlled cone-and-plate rheometer. The cone angle was 2° and the radius was 4 cm. All measurements were performed in nitrogen atmosphere, and a trap was used to minimize evaporation of the solvent. The results are given in the Table 9 and Figures 10 and 11.

Table 9. Zero-Shear Viscosity of G5 PAMAM Dendrimer-Ethylenediamine Solutions

CONCENTRATION, wt %	TEMPERATURE, °C	VISCOSITY, Poise
30	10	1.01
30	25	0.58
30	40	0.43
50	10	22.61
50	25	12.14
50	40	7.67
75	10	5274
75	25	971.1
75	40	257.2

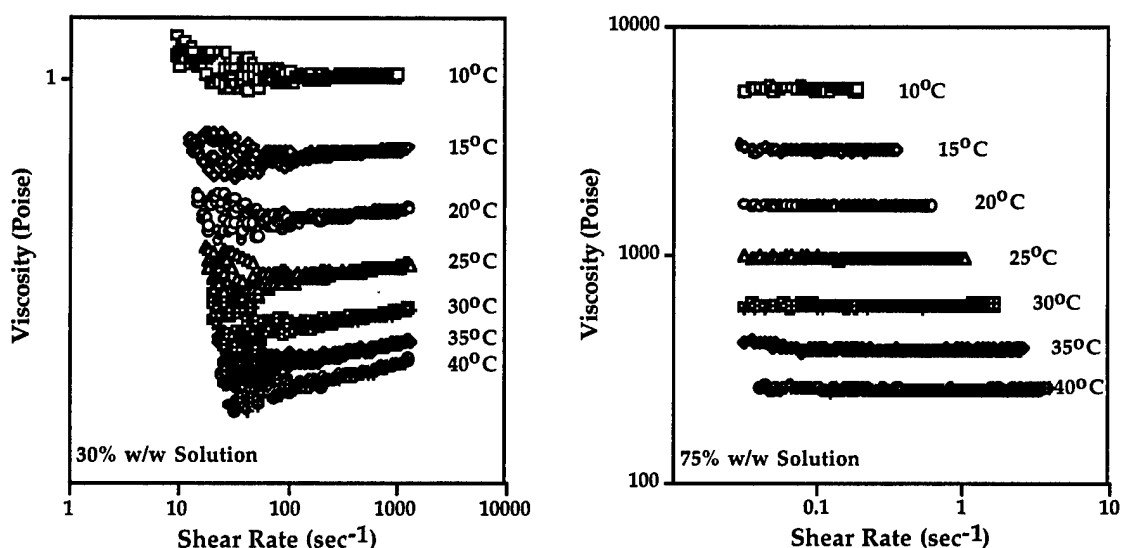


Figure 10. Zero-Shear Viscosity of G5 PAMAM/EDA Solutions at Constant Temperatures. [14]

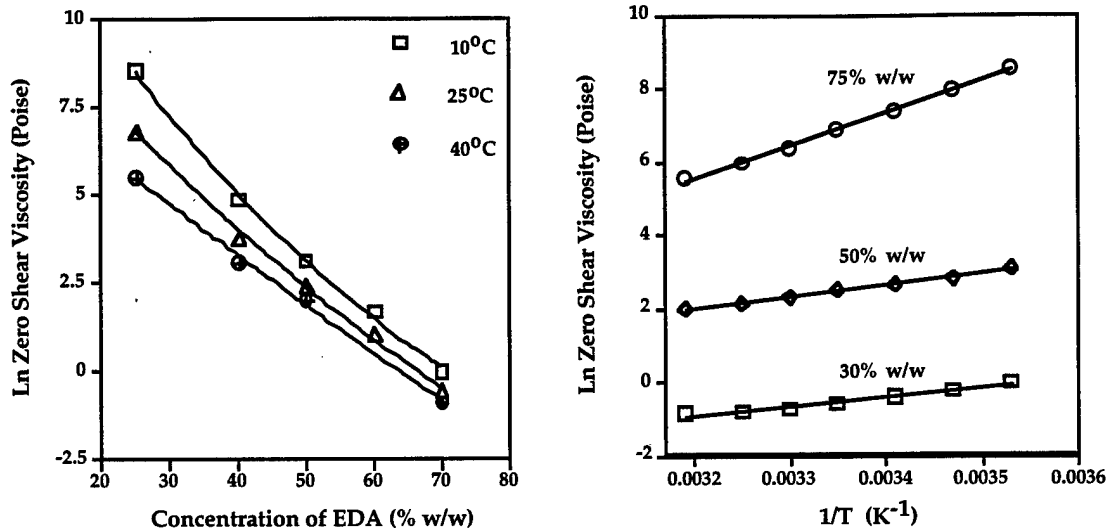


Figure 11. Zero-Shear Viscosity of G5 PAMAM/EDA Solutions at Constant Shear Rate. [14]

5. BULK PROPERTIES

5.1 Density [7, 15]

Densities of dry, neat dendrimer were measured pycnometrically in a hydrophobic non-solvent phenetole. A water bath was used for temperature equilibration, and densities were determined from the weights of dendrimer, volume of the non-solvent and volume of the pycnometer at specified temperatures. Results are given in Table 10.

Table 10. Bulk Density of G5 PAMAM Dendrimer

TEMPERATURE, °C	DENSITY, g/cm ³
10	1.230±0.010
20	1.220±0.010
30	1.203±0.004
40	1.195±0.009

5.2 Glass Transition Temperature [7]

Glass temperatures were measured using a DuPont Instruments 910 differential scanning calorimeter (DSC) and a Solomat Instruments thermally stimulated current (TSC). The heating rates used in DSC and TSC measurements were 20° C/min and 7° C/min, respectively. Results are given in Table 11.

Table 11. Glass Transition Temperature (T_g) of G5 PAMAM Dendrimer

METHOD	HEATING RATE, °C/min	ONSET OF T_g , °C	MIDPOINT T_g , °C
DSC	20	7	14
TSC	7	8	20

5.3 Thermal Stability [7]

Thermal stability and degradation behavior were evaluated using a DuPont Instruments thermogravimetric analyzer Model 951. About 10 mg of the sample was loaded onto a platinum pan, and a temperature sweep was performed in both nitrogen and air between room temperature and 1000° C at the rate of 20° C/min. Results are summarized in Table 12, and sample data are shown in Figures 12 and 13.

Table 12. Results of Thermal Gravimetric Analysis on G5 PAMAM Dendrimers (graphical representation in Figures 12 and 13)

ATMOSPHERE	CHARACTERISTIC	VALUE
Nitrogen	Onset of degradation	215° C
	5% weight loss	240° C
	50% weight loss	320° C
	End of Degradation	465° C
	Maximum loss at the end of degradation	96 wt %
	Temperature for maximum rate of degradation	320° C
	Maximum rate of degradation	0.97 wt %/°C
	Weight loss at maximum rate of degradation	32 wt %
Air	Onset of degradation	215° C
	5% weight loss	250° C
	50% weight loss	325° C
	End of degradation	685° C
	Maximum loss at the end of degradation	~100 wt %
	Temperature for maximum rate of degradation	320° C
	Maximum rate of degradation	0.97 wt %/°C
	Weight loss at maximum rate of degradation	32 wt %

Note: Dry dendrimers may be effectively used without considerable degradation (< 5%) at temperatures as great as 140° C for 16 hours. The presence of residual solvent may adversely affect thermal stability.

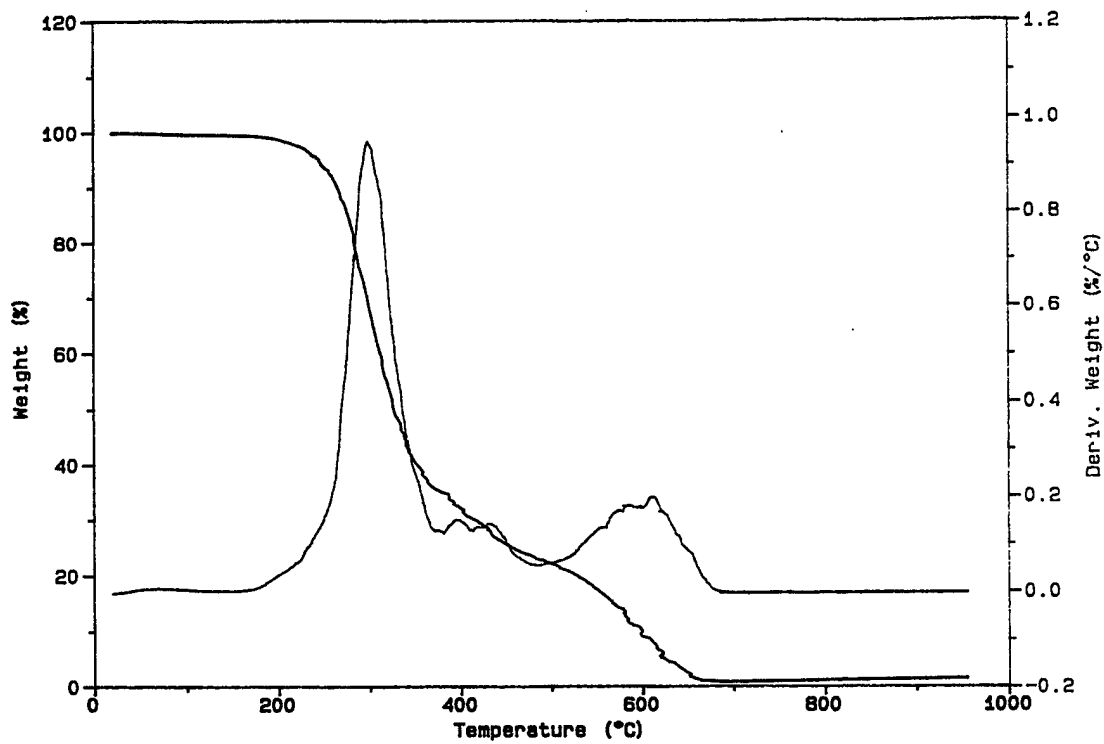


Figure 12. Results of the Thermal Gravimetric Analysis on Dry, G5 PAMAM Dendrimer (weight loss as a function of temperature, air atmosphere).

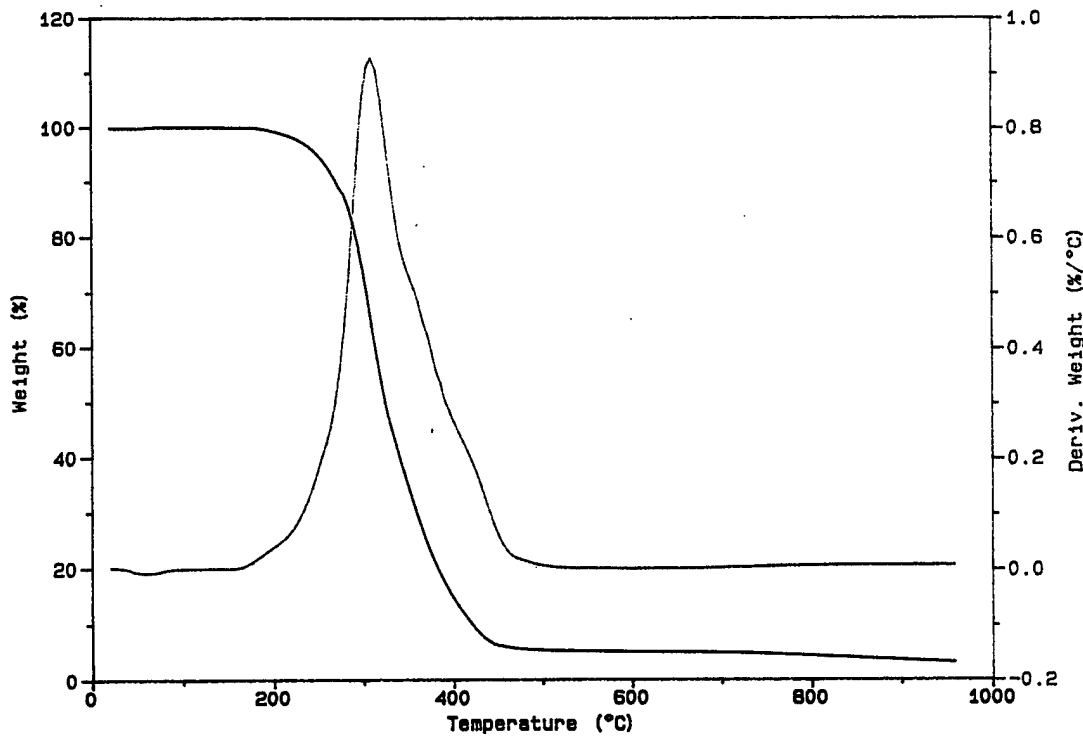


Figure 13. Results of the Thermal Gravimetric Analysis on Dry, G5 PAMAM Dendrimer (weight loss as a function of temperature, nitrogen atmosphere).

5.4 Viscosity [7]

Zero-shear viscosities of dry neat samples were measured using a CSL² 500 Carri-Med stress-controlled rheometer fitted with a cone-and-plate geometry. The cone angle was 1° and the radius was 2 cm. All measurements were performed in nitrogen atmosphere. Results are summarized in Table 13, and sample data are presented in Figure 14.

Table 13. Zero-Shear Melt Viscosity of G5 PAMAM Dendrimer

PROPERTY	TEMPERATURE, °C	VALUE, Poise
Zero-Shear Viscosity	40	10,000,000
	50	1,600,000
	60	295,000
	70	74,000
	75	37,000
	80	21,600
	85	13,500
	90	8,000

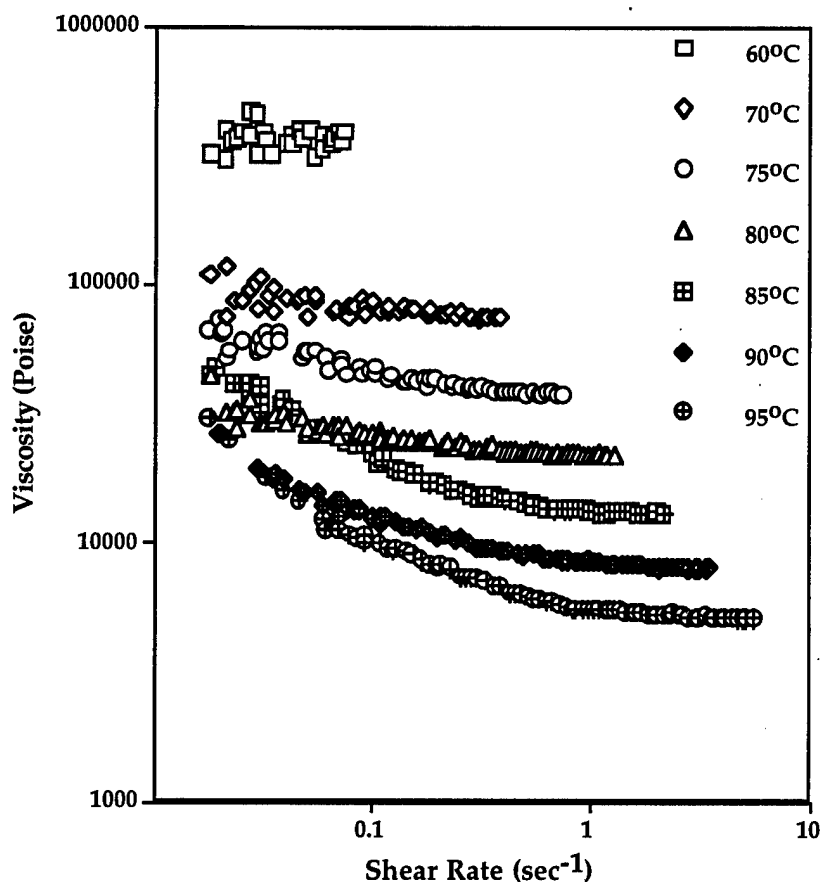


Figure 14. Dependence of the Zero-Shear Melt Viscosity of G5 PAMAM Dendrimer on Shear Rate.

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