Distribution of Dendritic, Terminal and Linear Units and Relationship between Degree of Branching and Molecular Weight of AB$_2$-Type Hyperbranched Polymer: A ^{13}C-NMR Study

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Degree of branching (DB) of AB$_2$-type hyperbranched polymer has been studied using ^{13}C-NMR spectroscopy. For this purpose, a series of hyperbranched polyamides based on 3,5-bis(4-aminophenoxy)benzoic acid differing in molecular weight was prepared by adopting a fractional precipitation technique. A model compound mimicking exactly the terminal and dendritic units present in the hyperbranched polymer (HBP) was also synthesized in high yield. ^{13}C-NMR spectra of the polymers and the model compound were recorded under exacting experimental conditions. With the help of ^{13}C-NMR spectrum of model compound and the integration values, peaks for terminal (T) units, dendritic (D) units and linear (L) units present in the HBP have been assigned. The spectra of low molecular weight fractions clearly showed that the linear unit is first formed and then the dendritic unit. Plots of mole fraction of individual unit against molecular weight (M$_w$) and DB against molecular weight (M$_w$) are constructed. For the first time, it is found that there is a critical molecular weight (the value calculated is between 3200–3500 for the chosen real system) below, which DB is dependent on molecular weight and above which it becomes independent. A new term T + D/L, which has a maximum value of 20 and minimum of 1, characterizing all AB$_2$-type hyperbranched polymers in general, has been introduced.

Keywords ^{13}C-NMR spectroscopy, degree of branching, hyperbranched polymers

Introduction

Dendritic and hyperbranched polymers (HBPs) are a new class of macromolecules upon which numerous research groups are now working. Several reviews (1–9) have been published which describe the preparative methods and properties of dendrimers and HBPs. These materials show unusual properties compared to their linear analogues (1). The effect of DB of HBPs on the rheological and thermal properties has been studied and found that the DB significantly affected these properties in the molecular weight range of 1500–3300 g mol^{-1} (10). As a result of the presence of a large number of

terminal reactive functional groups, high solubility and low viscosity, HBPs have potential application in crosslinking processes (11), toughening process (12), rheology modifications (13) and coating industries (14, 15). Recently we reported the use of amine terminated HBPs with molecular weight (M_w) 2337 to 13063 as crosslinkers in the preparation of polyurethane elastomer and found that a very low amount (0.01 equivalent relative to 1.0 equivalent of co-monomer) of hyperbranched polymer with DP approximately equal to 11 is sufficient to improve tensile strength to a great extent (16).

HBPs consists of three kinds of units namely linear (L), dendritic (D), and terminal (T) groups. Based on the mole fraction of these units, DB can be determined. For perfect dendrimers, the linear unit is absent, hence, the DB is unity. Whereas, for HBPs the DB varies from 1 to 0.5, research groups working on HBPs invariably report that the DB of AB_2-type HBP is around 50%. This is possible because all the researchers are aiming at a high conversion and high molecular weight. However, high molecular weight HBPs possess an extremely large number of terminal functional groups, which cause gelation immediately with co-monomer and thus, they are not suitable for crosslinking applications (16). HBPs to be used as crosslinkers must have as many low end functional groups as possible, i.e., polymers based on AB_2-type monomers with low degree of polymerization (DP) find use in the crosslinking processes.

Frey and co-workers (17) studied theoretically the DB of HBPs based on AB_m (m is ≥ 2) monomers employing simple topological considerations and concluded that the maximum value for DB achievable in a statistical AB_2-type and AB_3-type (assume B groups are equally and independently reactive) polyreactions is 0.5 and 0.44, respectively. Few experimental (18, 19) and theoretical (17, 20–22) studies dealing with the relationship between DB and conversion of functional groups are reported. Correlation of DB with molecular weight, especially with M_w is more difficult since it requires the use of a branching theory; hence, the relation between DB and molecular weight is not yet experimentally studied. It is believed that the DB is independent of molecular weight (1). Since the mole fraction of (D) and (T) units becomes equal only for high molecular weight species, it is envisaged that there will be a dependence of DB on molecular weight, the range of this molecular weight being rather low. This is an essential parameter for HBP to be used as a crosslinker in crosslinking processes. With this objective, it is our aim to identify and establish the relation between mole fraction of individual (T), (D) and (L) units and molecular weight (M_w), as also between DB and molecular weight (M_w) of HBP of a real system using the best analytical tool.

Experimental

Materials

3,5-Dihydroxy benzoicacid (Lancaster), lithium chloride (Lancaster), 10% palladium-charcoal (Lancaster), 4-fluoronitrobenzene (Aldrich) and triphenyl phosphite (TPP) (Aldrich) were used as received. Aniline, thionyl chloride and pyridine were distilled under reduced pressure before use. N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide (DMAc), N,N-dimethylformamide (DMF) were refluxed with calcium hydride and distilled under reduced pressure before use. 3,5-bis(4-nitrophenoxy) benzoic acid **1** (starting compound for the synthesis of model compound), and 3,5-bis(4-aminophenoxy)benzoic acid (monomer used for the preparation of hyperbranched polyamides) were prepared using the reported procedure (23).

Measurements

Infrared (IR) spectra were recorded using a Thermo Mattson Satellite model FTIR spectrophotometer. ^{1}H-NMR spectra were recorded using a JEOL GSX 400 instrument. EI mass spectra and MALDI-TOF mass spectrum were recorded using a JEOL DX−303 and Voyager-DE PRO−6316 instrument, respectively. ^{13}C-NMR spectra of polymer and model compound were recorded on a JEOL JNM-AL300 and BRUKER amx 300 NMR spectrometer, respectively; the solvent used was DMSO-d_6. Gel permeation chromatography (GPC) was performed on a JASCO HPLC 880PU fitted with polystyrene-divinyl benzene columns (two Shodex KD-806M and KD-802) and a Shodex RI-71 refractive index detector. DMF containing $0.01 \, mol \, L^{-1}$ of lithium bromide was used as an eluent. The absolute molecular weights of HBPs were determined by light scattering measurement using a mini DAWN apparatus (Wyatt Technology Co.) and a Shimadzu RID-6A refractive index detector. A specific refractive index increment (dn/dc) of the polymer in DMF at 690 nm was determined to be $0.2109 \, ml \, g^{-1}$ using an Optilab 903 apparatus (Wyatt Technology Co.).

Synthesis

3,5-Bis(4-nitrophenoxy)phenyl Benzamide (2). In a 100 ml three-necked flask, 3.0 g (7.5 mmol) of 3,5-bis(4-nitrophenoxy)benzoic acid **1** and 0.69 ml (7.5 mmol) of aniline were dissolved in 50 ml of NMP. To this solution, 4.3 ml of pyridine, 4.5 ml of TPP and 0.87 g of lithium chloride were added under nitrogen atmosphere. The reaction mixture was heated at 100°C for 3 h. The temperature was reduced to 30°C and then the reaction mixture was poured into 1.5 L of water containing 5% sodium chloride to precipitate the product, filtered, washed the precipitate with water and dried at 100°C under vacuum. The crude product was recrystallized in acetone. Yield: 3.12 g (89%); m.p.: 215−218°C. IR (KBr) (cm^{-1}): 3271 (s, amide N-H), 1651 (s, C=O), 1569 and 1330 (-NO$_2$), 1230 (C−O−C). ^{1}H-NMR (400 MHz, Acetone-d_6) (δ): 9.52 (s, CONH), 8.15 (d, 4H), 7.65 (d, 2H), 7.60 (d, 2H), 7.50 (d, 1H), 7.20 (d, 4H), 7.15 (t, 2H), 7.0 (t, 1H). MS (70 eV): $m/z = 471.4$ (M$^+$). Nitrogen content for C$_{25}$H$_{17}$N$_3$O$_7$: Calcd. 8.9%; Found 9.1%.

3,5-Bis(4-aminophenoxy)phenyl Benzamide (3). In a 100 ml flask, 1.0 g (2.1 mmol) of 3,5-bis(4-nitrophenoxy)phenyl benzamide **2** was dissolved in 15 ml of DMF. 0.0625 g of 10% palladium-charcoal catalyst was added and stirred under hydrogen at room temperature for 48 h. The reaction mixture was poured into 1 L of ice water to precipitate the product, filtered and vacuum dried at room temperature. The crude product was then dissolved in methanol, filtered through celite 540 to remove the catalyst. The solvent evaporation of the filtrate under rotary evaporator yielded the product at 90 % (0.79 g) Yield. M.p.: 81−83°C. IR (KBr) (cm^{-1}): 3463 (amine −NH$_2$), 3367 (amide N-H), 1662 (C=O), 1207 (C−O−C). ^{1}H-NMR (400 MHz, Acetone-d_6) (δ): 9.60 (s, CONH), 7.80 (d, 2H), 7.25 (d, 2H), 7.15 (s, 1H), 7.10 (t, 2H), 6.90 (d, 4H), 6.75 (d, 4H), 6.60 (d, 1H). MS (70 eV): $m/z = 411.4$ (M$^+$). Nitrogen content for C$_{25}$H$_{21}$N$_3$O$_3$: Calcd. 10.2 %; Found 9.9%.

Synthesis of Model Compound (5)

0.57 g (1.43 mmol) of 3,5-bis(4-nitrophenoxy)benzoic acid **1** and 20 ml of thionyl chloride were taken in a flask and refluxed for 30 min. The excess thionyl chloride was distilled off

and the product was washed carefully with 15 ml of hexane. This product was then mixed with 30 ml DMAc solution of 3,5-bis(4-aminophenoxy)phenyl benzamide **3** (0.29 g; 0.71 mmol), maintained at $-10°C$ and stirred for 15 min. The stirring was continued to 2 h at $0°C$ and then further extended to an additional 13 h at room temperature. The reaction mixture was poured into 1 L of water containing 5% sodium chloride to precipitate the precursor **4** for the model compound. The precipitate was filtered, washed with water, vacuum dried at $100°C$, and recrystallized in THF. Yield: 1.35 g (85%); m.p.: 197–199°C. IR (KBr) (cm^{-1}): 3305 (amide N-H), 1662 (C=O), 1577 and 1342 (-NO$_2$), 1226 (C–O–C). ^{1}H-NMR (400 MHz, Acetone-d_6) (δ): 9.8 (s, CONH, 2H), 9.6 (s, CONH, 1H), 8.2 (d, 8H), 7.8 (s, 3H), 7.65 (s, 6H), 7.25 (s, 14H), 7.0 (d, 6H), 6.75 (s, 1H). Nitrogen content for $C_{63}H_{41}O_{17}N_7$: Calcd. 8.3%; Found 8.7%. 0.2 g (0.17 mmol) of this precursor **4** was reduced under hydrogen in the presence of 0.04 g of 10% palladium-charcoal catalyst in 4 ml of DMF at room temperature for 48 h. The reaction mixture was diluted with 15 ml of DMF. After the catalyst was removed by filtration through celite 540, the product was precipitated in 1 L of water containing 5% of sodium chloride, filtered, washed with water and vacuum dried at $100°C$. Yield: 0.165 g (85%); m.p.: >275°C. IR (KBr) (cm^{-1}): 3379 (free NH$_2$), 3232 (amide N-H), 1650 (C=O), 1203 (C–O–C). ^{1}H-NMR (DMSO-d_6) (δ): 10.20 (s, CONH, 2H), 10.18 (s, CONH, 1H), 6.4–8.3 (m, 38H), 5.0 (br, NH$_2$). MS (MALDI-TOF): $m/z = 1050$ (calculated 1047). Nitrogen content for $C_{63}H_{49}O_9N_7$: Calcd. 9.3%; Found 9.5%.

Preparation of Hyperbranched Polyamides

A three-necked glass reaction kettle charged with 3.0 g of monomer was fitted with a mechanical stirrer and a heating device. The kettle and the heating device were inter-connected through a temperature indicator. The kettle was evacuated and filled with nitrogen repeatedly for three times. The sample was heated to $100°C$ for 1 h to remove the moisture and solvents if present. Then, the sample was heated to $235°C$ for 4 min. The heating was stopped and the heating device was removed immediately. The transparent product was dissolved in 30 ml of DMF and precipitated in 2 L of methanol containing 0.1% of lithium chloride. The high molecular weight fraction was separated out and the filtrate was collected carefully. Low molecular weight fractions were separated by the subsequent addition of 1 L of water each time to the filtrate. Totally three fractions were separated. Identical experiments were carried out for the reaction time of 10 min and 30 min.

Results and Discussion

Though the model compound synthesized for this study is apparently similar to that reported by Kakimoto and co-workers (24), it differs in the following two aspects. The first aspect is that there was a structural heterogeneity in the reported model compound, whereas, for this study a change was made at the focal group to make the compound structurally homogeneous and fully suitable for this study. The second aspect is that the yield of the model compound was extremely low and it was very difficult to get a pure compound adopting the reported procedure (24). Hence, a simple, new route was adopted in this study to obtain the model compound with the yield of 85% (Scheme 1). Though all the analytical data confirmed the structure of 3,5-bis(4-aminophenoxy)phenyl benzamide **3**, the
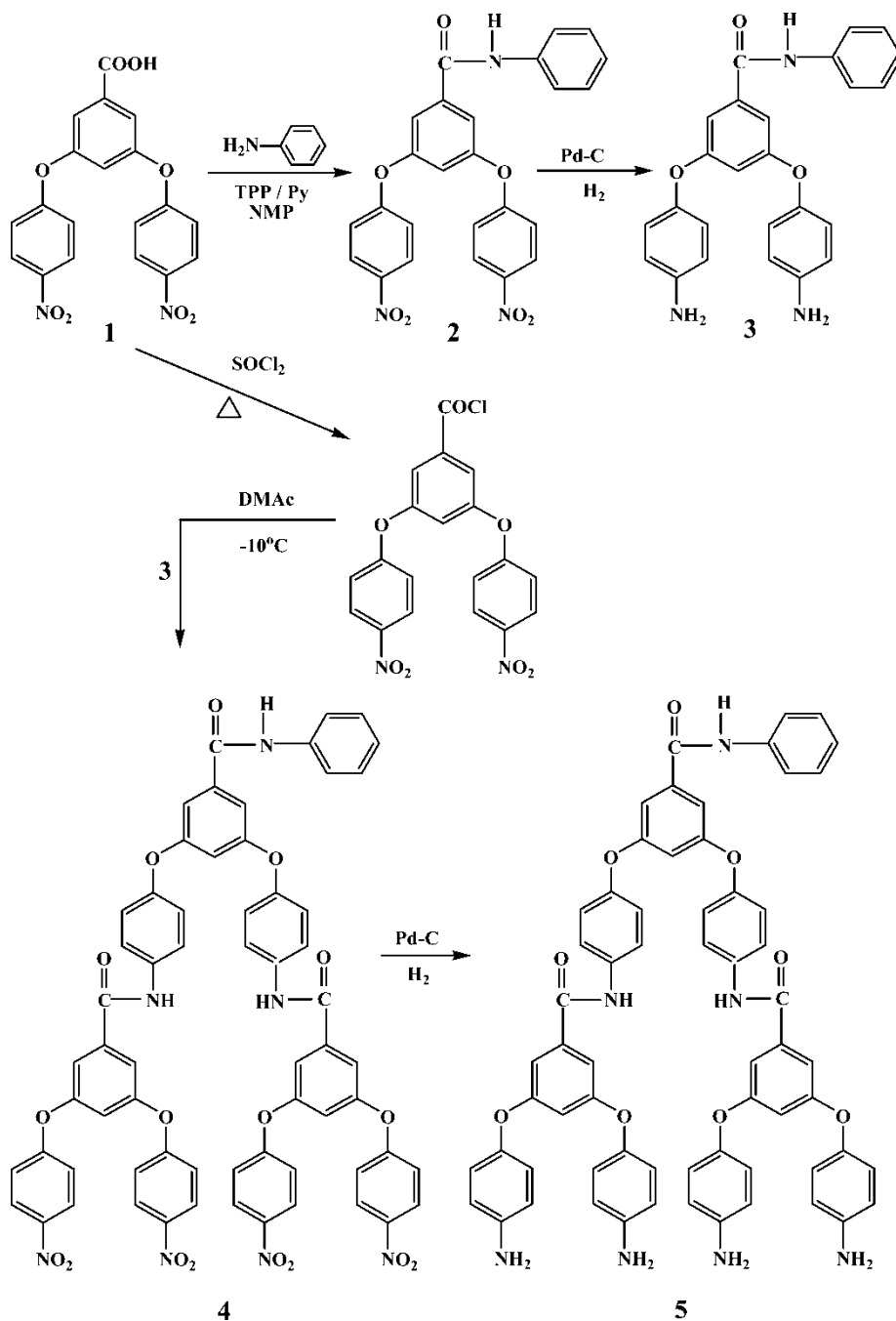
Scheme 1. Synthesis of model compound for the calculation of degree of branching.

^{1}H-NMR spectrum did not show a peak for free amine protons. The presence of amino group was confirmed indirectly by the reaction of the compound **3** with ethylchlorofor-mate to prepare the corresponding dicarbamate derivative, the structure of which was confirmed unambiguously by the ^{1}H-NMR spectroscopy.

Among the nine polymers obtained from three polymerization experiments, only seven polymers were used for the ^{13}C-NMR experiment; their molecular weight and polydispersity values are given in Figure 2. The remaining two polymers have been omitted since one of them showed a molecular weight close to 19950 and the other one showed a molecular weight close to 13060, which are already part of the seven polymers used for ^{13}C-NMR study.

Since ^{13}C NMR spectrum is always free from peak overlap compared to ^{1}H-NMR spectrum, this technique was chosen to study the DB of HBPs using a model compound consisting of (D) and (T) units which exactly mimic the units present in the polymer chain. To identify the peak corresponding to (L) unit of the polymer, ^{13}C-NMR spectrum of model compound and that of polymers, both recorded under identical experimental conditions, are compared. Since the spin-lattice relaxation time (T_1) for the quaternary carbon and carbonyl carbon present at branching point of the polymer was measured in advance to be approximately 2.5 sec, the sum of acquisition and delay time for each measurement was set to 15 sec. It must be mentioned here, that it is necessary to set the number of scan as at least 21200 to obtain good quality spectrum for model compound, whereas in the case of polymers, the number of scans should be at least 8000. Two kinds of peak for carbonyl carbon and quaternary carbon present at branching point of model compound were observed at 164.2–164.8 ppm and 138.5–139.5 ppm, respectively. When comparing carbonyl carbon region and quaternary carbon region, there was an ambiguity in the peak counting in the region of carbonyl carbon of model compound. On the other hand, the quaternary carbon region of model compound clearly showed only two peaks. Thus, this region was considered for peak assignment and for further calculations. Based on the integration value, the peak appearing at 138.5 ppm was assigned to terminal (T) units and the peak appearing at 139.5 ppm was assigned to dendritic (D) unit (Figure 1). When comparing the ^{13}C-NMR spectrum of the model compound to that of polymers, the latter shows a discrete signal of three kinds at the same region (Figure 2a–2g). Besides, all the spectra conforms that the polymers are free from a fourth possible unit due to intramolecular cyclization. This is not a surprise since polymerization reactions were carried out in bulk (25). For peak assignment, ^{13}C-NMR spectra of polymers of high molecular weight have been considered for the reason that the linear (L) unit alone present in the relatively high molecular weight HBPs is always nearly 50%. This can be easily understood when considering statistical probability for reaction between A and B functional groups of AB$_2$ monomers and consequent topological features of the corresponding HBPs (17). Thus, the linear unit present in the hyperbranched polymer can be easily differentiated from the other two units with the help of integration values. Based on this argument, the central peak of the discrete signal is assigned to quaternary carbon present at branching point of linear units.

Based on this assignment, mole fractions in percentage of individual units were calculated and plotted against molecular weight (Figure 3). The spectrum (Figure 2a) of polymer having molecular weight (M_w) 1460 indicates that there is no formation of a dendritic unit, while there is evidence for the formation of a linear unit at the initial stage. When the molecular weight is increasing to 2335, there is evidence for the formation of a dendritic unit, but the value is only 1.3%. Here, we would like to emphasize, that at low molecular weight range, the mole percentage of the individual unit may not correspond with the value obtainable for a structure in terms of a simple, topological argument. The reason may be that the real system is not monodispersed and does not contain similar sized molecules. It is observed that the content of (D) units
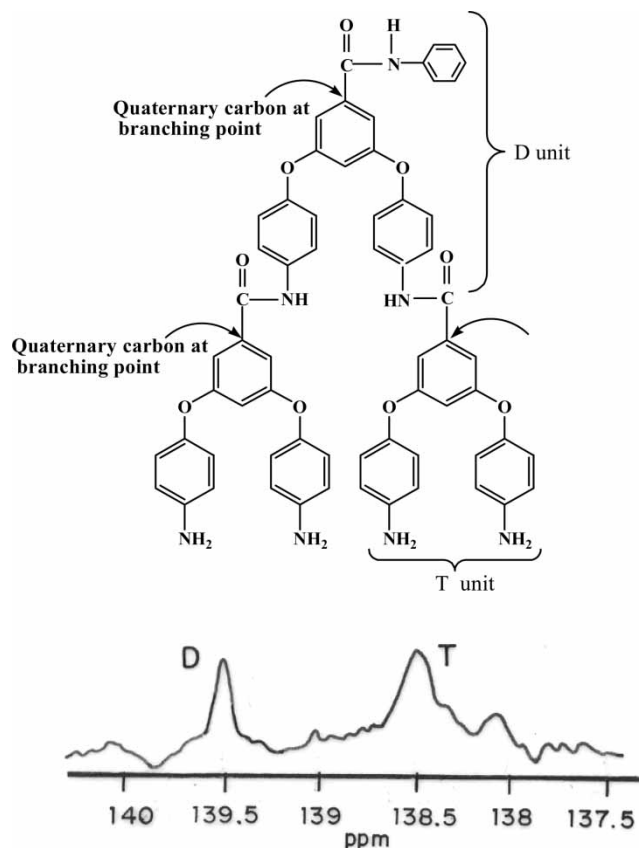
Figure 1. ^{13}C-NMR spectrum of model compound.

increases from 0% for molecular weight 1460 to 23.8% for the molecular weight 66525 and the content of (T) units decreases from 95.2% to 24.1% for the same molecular weight range; both (D) and (T) unit content of high molecular weight polymer is in good agreement with that estimated by a degradative procedure (26). The plot (Figure 3) also indicates that the increment in the dendritic unit is gradual up to the highest molecular weight studied, whereas the decreasing trend in the terminal unit content is very abrupt up to the molecular weight 3500 and then gradual up to the highest molecular weight studied where both the increasing and decreasing trends take a common point. It is also found that the linear unit increases rapidly as the molecular weight increases up to 3500 and then almost tends to level off at 50%. From the plot of (D), (L) and (T) units against molecular weight, it can be concluded that (1) there is a conversion of terminal (T) units to linear (L) and dendritic (D) units during polymer chain growth: this conversion is in agreement with topological argument (2) among these two conversions, terminal (T) to linear (L) conversion is predominant and (3) beyond the molecular weight 10000, the conversion of terminal (T) unit to dendritic (D) units is appreciable and reaches the ultimate value at critical molecular weight 66525 where the conversion takes place in such a way to maintain both the units in equal proportions. Presence of the critical molecular weight below 66525 could not be ruled out since we are not able to present data for the molecular weight in-between 20000 to 66525.
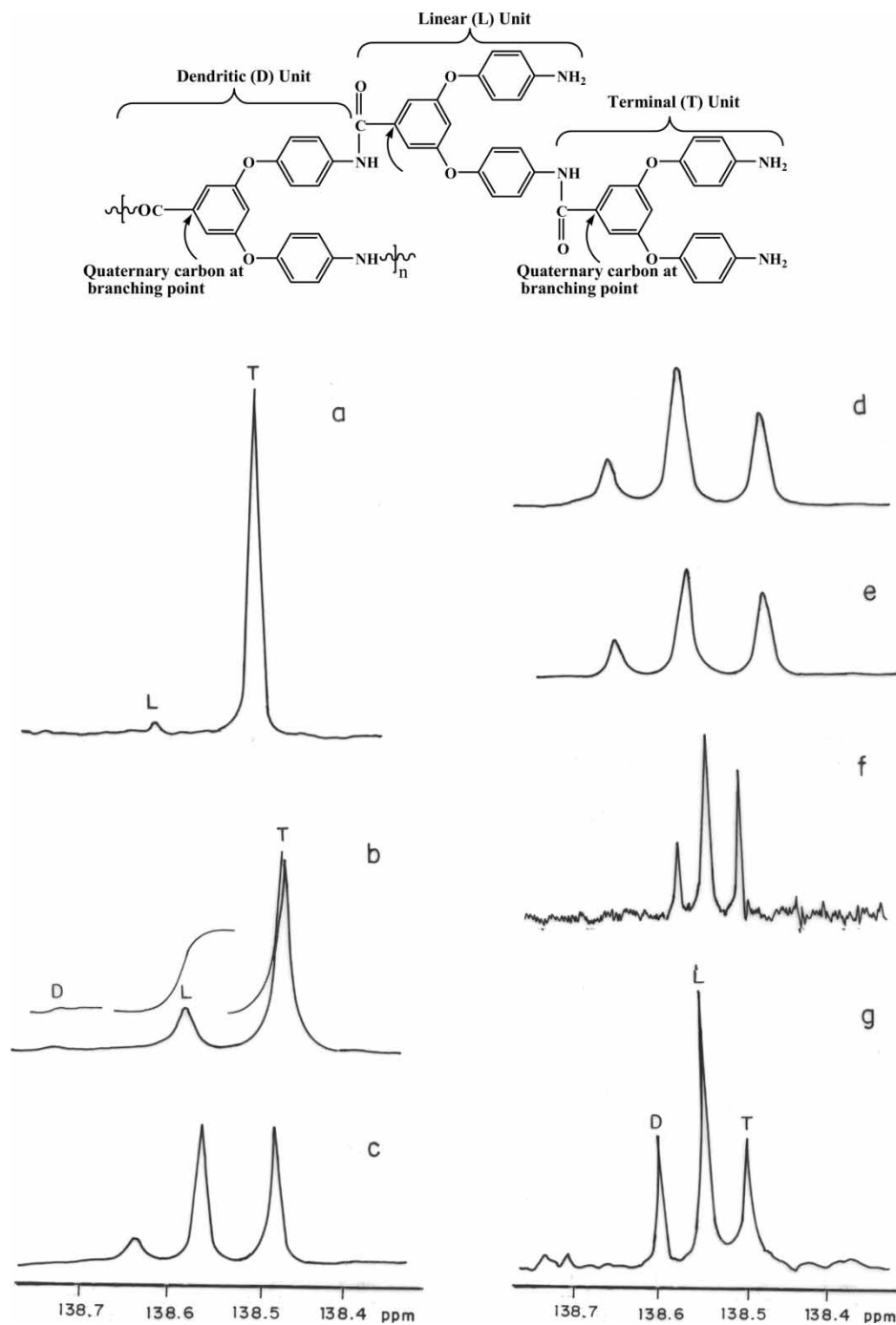
Figure 2. ^{13}C-NMR spectrum of hyperbranched polyamide having (a) molecular weight (M_w) 1460, (b) molecular weight 2335 (1.2), (c) molecular weight 3500 (1.1), (d) molecular weight 13060 (1.1), (e) molecular weight 17800 (1.1), (f) molecular weight 19950 (1.5) and (g) molecular weight 66525 (1.7). The value given in the parenthesis indicates the PD of the polymer.
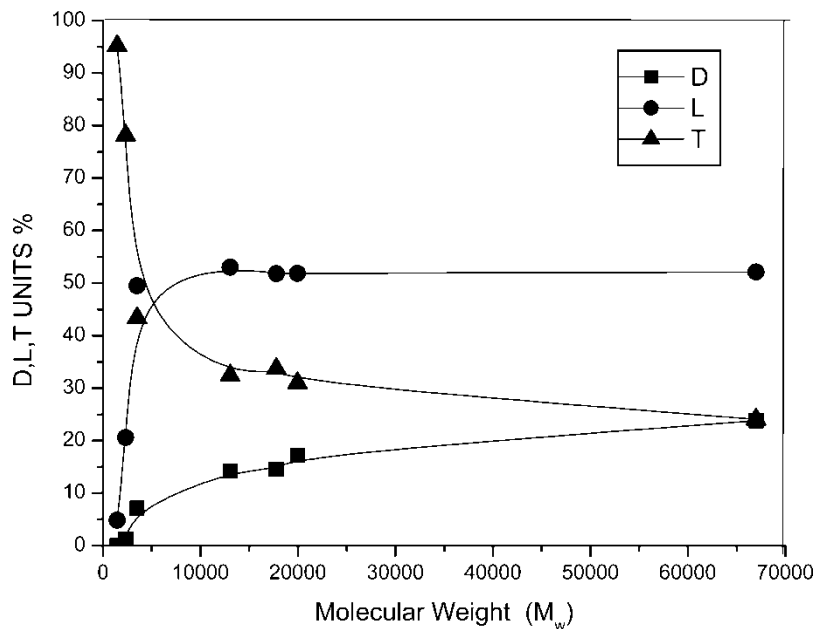
Figure 3. Mole fraction of D, L and T units of AB$_2$-type HBP in percentage vs. molecular weight.

There are two equations, equation (1) reported by Frechet and co-workers (27) and Equation (2) reported by Frey and co-workers (17), available for the calculation of DB.

$$DB = \frac{D + T}{T + D + L} \tag{1}$$

$$DB = \frac{2D}{2D + L} = \frac{2T}{2T + L} \tag{2}$$

Based on purely theoretical considerations, Frey and co-workers (17) concluded that equation (1) is suitable only for high molecular weight polymer. This is not true according to our observation since spectrum of low molecular weight ($M_w = 2335$ and above) polymer shows peaks for all the three kinds of units in different proportions. It is also claimed that the equation (2) is applicable for both low and high molecular weight polymers. This is also not in agreement with our observations. In the present study, it is found that the dendritic unit is not formed in the case of extremely low molecular weight ($M_w = 1460$) polymer, but there is evidence for the formation of linear unit as already mentioned and (D) becomes equal to (T) only at high molecular weight. Besides, the mole ratio of the individual unit is varying with respect to molecular weight even up to 66525. Thus, the DB were determined according to the Frechet method (27) using equation (1). The calculated DB are plotted against molecular weight and given in Figure 4. It is found that the DB decreases rapidly from 95.2% to 50.5% as the molecular weight increases from 1460 to 3500 and then tends to level off at 48.2%, in excellent agreement with the theoretical treatment (17). This plot clearly shows that there is a critical molecular weight; beyond this critical molecular weight the DB loses its meaning. The critical molecular weight for the AB$_2$-type HBP used in this study was calculated by extrapolating the tangent point of the DB against
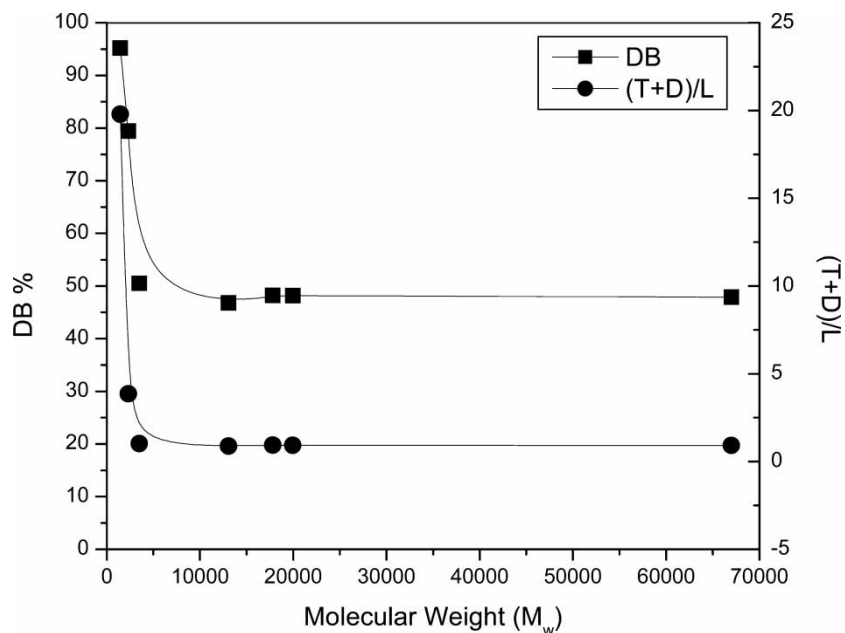
Figure 4. Degree of branching (DB) and ratio of T+D to L units of AB$_2$-type HBP vs molecular weight.

molecular weight curve to the molecular weight scale and the value lies between 3200 and 3500. In other words, it can be concluded that the DB does not vary beyond the degree of polymerization (DP) at a value of 10 to 11 for the chosen real system. This critical molecular weight or DP may vary from polymer to polymer derived from different kinds of AB$_2$-type monomers. Above the critical molecular weight, the (T) and (D) units are found to exist in such a way as to total 50% with (L) unit remaining constant at 50%, making the term T + D/L significant. This term assumes a maximum value of 20, this value decreases with increasing molecular weight and reaches unity at critical molecular weight and above for the chosen real system, and this may be applicable for all AB$_2$-type HBPs. These values are also plotted against molecular weight and presented in Figure 4. The pattern of the plot is quite like the plot of DB against molecular weight and the extrapolation of tangent point to the molecular weight scale also corresponds with that of DB against molecular weight.

Conclusions

Based on the findings of ^{13}C-NMR experiments aimed at studying the DB of AB$_2$-type hyperbranched polymers, the following are the conclusions arrived at:

Among the two equations available for the determination of DB, only the Frechet equation is found to be suitable for low and high molecular weight polymers.

It is found that there is a critical molecular weight for the DB: The value determined lies between 3200 and 3500 for the chosen system; below this value, the DB is found to be dependant on molecular weight and above this value DB is found to be independent on molecular weight i.e., DB of pure AB$_2$-type HBPs loses its significance when the molecular weight of the polymer exceeds 3500. A second critical molecular weight

($\approx$66500) pertains to the situation, wherein (T) units are converted into (L) and (D) units. Beyond this critical molecular weight, the amount of (T), (L) and (D) units present in the polymer reaches a constant value at the ratio of $1:2:1$.

Since (T) and (D) units are adjusted to each other during polymer chain growth in such a way to 50% cumulatively and (L) unit remains at 50% beyond the critical molecular weight, the term $T + D/L$ becomes significant. This term is a maximum of 20 and minimum of 1 for the chosen AB_2-type HBP.

Acknowledgements

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