Full Paper: Solid-supported hyperbranched polymerisation of 4-(5-hexynyloxy)-β,β-dibromostyrene was modelled using MM2 force field. The results show that at least up to the 6th generation there is no excessive strain due to the steric hindrances in the molecule. Moreover, it seems that steric energy per atom tends to a limit with the number of generation. Steric hindrance between a single bound hyperbranched molecule and the support are far less than the attractive van der Waals interactions, independent of the nature of the polymeric support and the generation number of dendritic molecule. The only important steric hindrance was found between two bound hyperbranched molecules attached to adjacent active sites of the polymeric support. In this particular case the distance separating two attached hyperbranched molecules is strongly affected by the steric interactions.

Molecular modelling of solid-supported polymerisation of 4-(5-hexynyloxy)-β,β-dibromostyrene

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Introduction

In recent years there has been considerable interest in macromolecules with architectures differing from classical linear polymers such as dendrimers and hyperbranched polymers. Some advantages of hyperbranched structures are better solubility compared to linear analoguos and a high concentration of the end groups even for high molecular weight polymers. While the perfectly branched dendritic structures synthesised by a laborious multi-step synthesis, the hyperbranched polymers are prepared by a one step synthetic process, yet they maintain many of the architectural features of perfectly branched dendrimers. However, the lack of control over molecular weight, polydispersity, and degree of branching in hyperbranched polymers is the price paid for their easy preparation[1–6]. Solid-supported hyperbranched polymerisation was found to improve the control over the structure of the hyperbranched polymers. Moore et al. found[7] that the use of solid support reduces polydispersity of hyperbranched polymers and provides the control over molecular weight in the range of 5000–25000. The present authors reported a similar effect of solid-supported hyperbranched polymerisation on polydispersity and found that all other things being equal the molecular weight of the hyperbranched polymer found in solution is always higher than that formed on solid support and the molecular weight depends on the nature of the support[8, 9]. Although the clear understanding of the mechanism of the influence of the solid support on hyperbranched poly-

merisation is of vital importance for synthetic chemists no consistent explanation of this phenomenon has been provided up to date.

The goal of this work is to model the effect of polymeric solid support on hyperbranched polymerisation using mixed molecular mechanic and semiempirical methods approaches to gain some understanding of this effect.

Methods

To model the effect of polymer support on hyperbranched polymerisation the following approach has been chosen: The polymeric supports used in the polymerisation of AB_2 type monomer 4-(5-hexynyloxy-)β,β-dibromostyrene[8] are represented by model oligomers shown in Fig. 1. Supports **7S1** and **14S1** differ only in the chain length thus allowing the estimation of the effect of the molecular weight of the model molecules while in the case of **14S′3** and **7S′1** models the steric hindrance caused by dendritic molecules attached to the adjacent active sites can be evaluated. **7S2** differs from the others by the nature of active sites (dibromovinyl). The hyperbranched polymer at different stages of growth is modelled by a set of perfect dendrimers from first to sixth generations as shown in Fig. 2. In addition to intramolecular steric hindrances affecting the solution polymerisation of AB_2 type monomer arising from crowded architecture of hyperbranched polymer, there are two more factors needed to be consid-
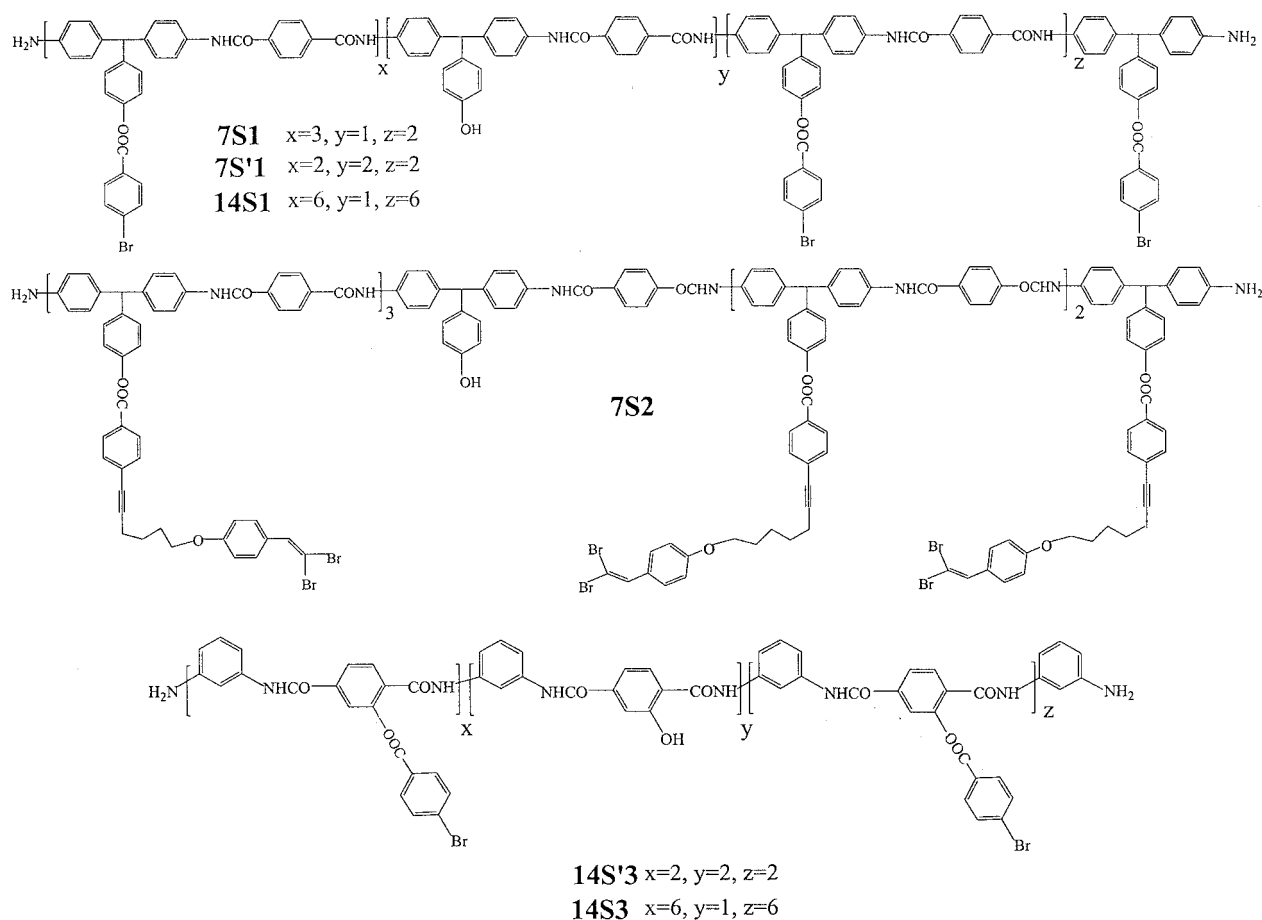
Fig. 1.   Model molecules representing different kinds of polymeric supports

ered in the case of solid-supported hyperbranched polymerisation. The first is the interaction betwen the bound hyperbranched molecule and polymeric support and the second is the interaction between the hyperbranched molecules attached to the adjacent active sites of solid support. To take into account these features of solid-supported hyperbranched polymerisation the method of isodesmic reaction was used (Fig. 3). The reactions **1–6** represent the methanolysis of bound dendrimers to form free supports and the dendrimers. Since the number and the type of chemical bonds and atoms are not changed during the transformation, ΔE of the reactions should be entirely due to non-bond interactions between the dendrimer and support with additional terms including interactions between two adjacently bound dendrimer molecules for reactions **2** and **5**. Due to the size of the systems under the study (many thousand of atoms) it seems that the only practical method for their modelling is molecular mechanics (MM). Although MM can not properly predict the energetics of the reactions, in the case of the reactions **1–6** MM should perform reasonably well since ΔE of those reactions is mainly due to non-bonded interactions.

The modified Allinger's MM2 force field[10], as implemented in Chem3D-pro (Version 5.0) package, was used for the modelling. The principal additions made to Allinger's MM2 force field are: (1) A charge-dipole interaction term. (2) A quartic stretching term. (3) Cutoffs for electrostatic and van der Waals terms with 5th order polynomial switching function. (4) For models containing π systems, it performs a Pariser-Parr-Pople π orbital SCF[11]. The SCF computation yields bond orders which are used to the scale of the bond stretching force constants, standard bond lengths, and twofold torsional barriers. (5) Torsional and non-bonded constraints.

To assure that modified the MM2 model performs reasonably well on these systems the energy difference of model reaction **6** was calculated using AM1[12], PM3[13], and MM2 methods. The geometry obtained after optimisation with MM2 force field was used for optimisation with semiempirical AM1 and PM3 methods. ΔE calculated for reaction **6** with MM2, AM1, and PM3 were 4.9, 1.3, and 4.8 kcal/mol, respectively. As can be seen there is a good agreement between MM2 and PM3 models which is known to be the best in prediction of heats of
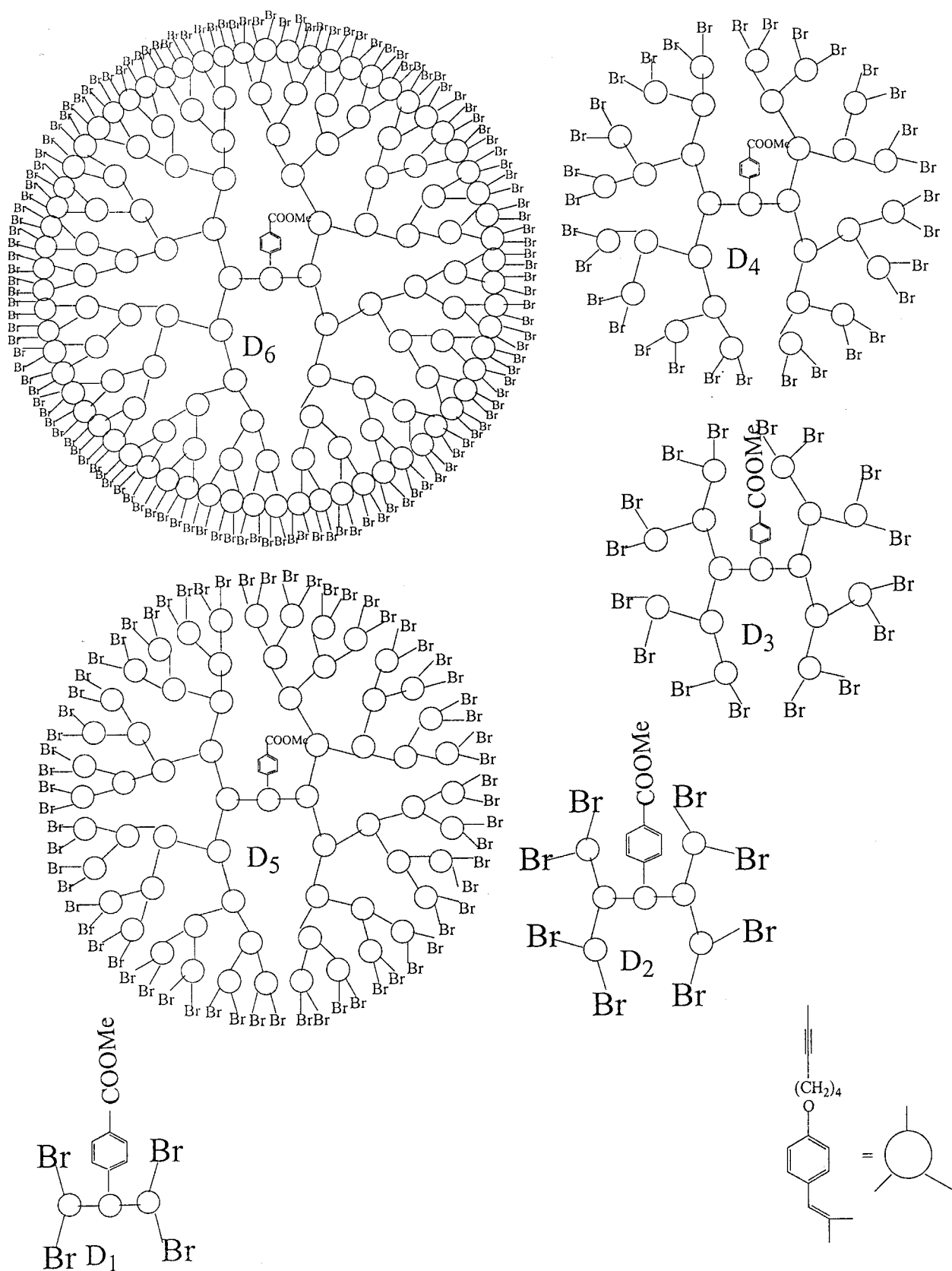
Fig. 2.   Dendritic model molecules representing hyperbranched poly-[4-(5-hexynyloxy)-β,β-dibromostyrene] at different stages of growth

1 $D_n\text{-}7S2 + MeOH = D_n + 7S2$
   n=1-5

2 $2(D_n)\text{-}7S'1 + 2MeOH = 2D_n + 7S'1$
   n=1-6

3 $D_n\text{-}7S1 + MeOH = D_n + 7S1$
   n=1-6

4 $D_n\text{-}14S1 + MeOH = D_n + 14S1$
   n=1-5

5 $2(D_n)\text{-}14S'3 + 2MeOH = 2D_n + 14S'3$
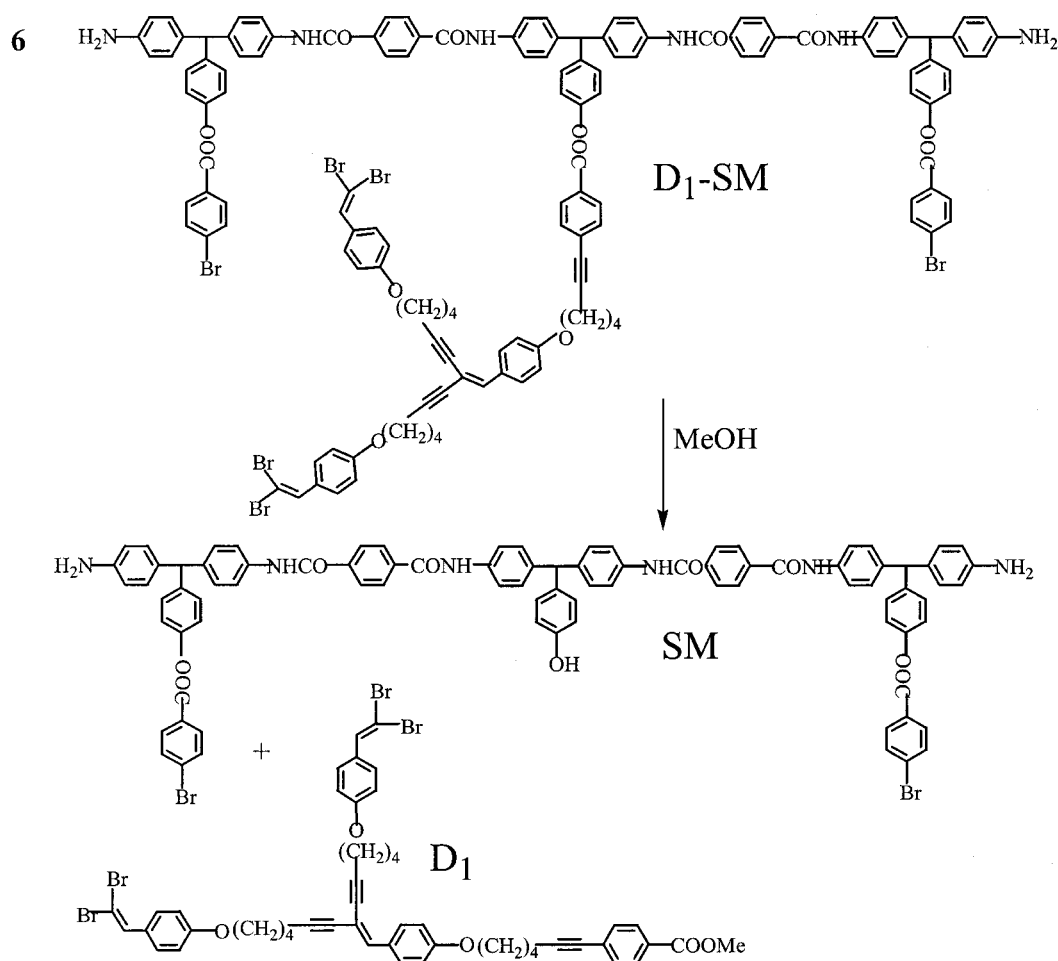   n=1-5

Fig. 3.   Isodesmic reactions of methanolysis of bound dendrimers to form free supports and dendrimers

formations among semiempirical methods[14]. Therefore, the modified MM2 model was used for all subsequent calculations.

To equilibrate the geometries of the models, the molecular dynamics (MD) was run at 370 °C for 150 ps. 25 conformations at steps of 4 ps generated during the last 100 ps were minimised using MM2 force field and their average energy was taken as the energy of the corresponding molecules. In MD simulations a step of 0.001 ps and a heating time of 2 ps were used.

Results and discussion

Fig. 4 shows the steric energy per atom for dendrimers from the 1 to 6 generation. As it can be seen the steric energy tends to a limit with the number of generations. Similar trends have been observed for $1 \rightarrow 2$ dendritic polyacetylene using more precise B3LYP/3-21G//PM3 model chemistry[15]. The results imply that at least up to 6th generation, which corresponds to a molecular weight of 22 848, the hyperbranched polymer is not excessively strained. In Tab. 1 the results of calculations for various isodesmic reactions to estimate the effect of the presence of the support molecule on the relative stability of the dendritic molecule are given. The first important observation that can be made from the results is that in most of the cases ΔE is positive or to put it differently there is some kind of the attractive interaction between the support and the dendrimer even for very bulky 5th and 6th generations for all supports except **14S′3**. In the case of **7S1** support, ΔE becomes slightly negative for most bulky 5th and 6th generation, however, according to the results obtained for the **14S1** molecule, which differs from **7S1** only by the number of repeating units, all ΔE's are positive. This phenomenon should be due to the attractive van-der-Waals interactions between the support and bound dendrimer molecule. The larger **14S1** molecule provides better intermolecular interactions with dendrimers thus contributing to a higher ΔE. It follows that the steric hindrance between the support and the dendrimer up to at least 6th generation do not contribute much to the instability of the system dendrimer-support. On the contrary, there is an attractive interaction between the dendrimer molecule and the support.

While the steric hindrance between the bound dendrimer molecule and the support is negligible even for the 6th generation dendrimer as follows from the obtained results, there could be significant steric hindrances
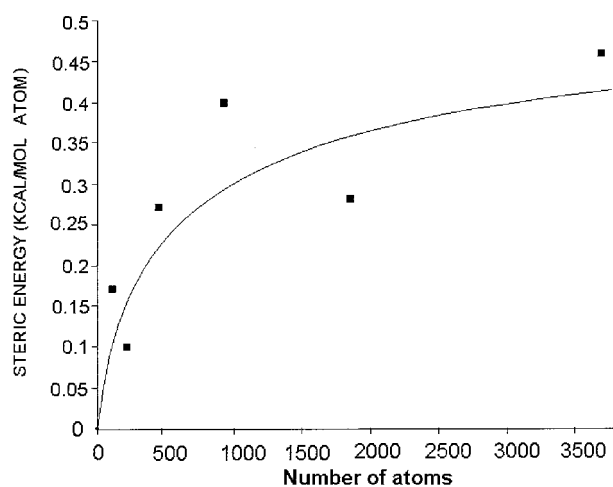
Tab. 1. Calculated energies of studied molecules and isodesmic reactions

n	D_n[a]-7S1[b] + MeOH = D_n + 7S1				ΔE[c]/ (kcal/mol)
	E[d]/ (kcal/mol)	E/ (kcal/mol)	E/ (kcal/mol)	E/ (kcal/mol)	
1	−113	1	18	−94	36
2	−118	1	21	−94	44
3	−19	1	122	−94	10
4	204	1	369	−94	70
5	550	1	510	−94	−134
6	1 697	1	1 698	−94	−94
	D_n-7S2 + MeOH = D_n + 7S2				
1	−152	1	18	−78	91
2	−167	1	21	−78	109
3	526	1	122	−78	−482
4	160	1	369	−78	131
5	367	1	510	−78	65
	$2(D_n)$-7S′1 + 2 MeOH = 2 D_n+ 2 7S′1				
1	−96	2	36	−97	33
2	−161	2	42	−97	104
3	9	2	244	−97	136
4	379	2	738	−97	260
5	1 045	2	1 020	−97	124
6	118	2	3 396	−97	2 281
	D_n-14S1 + MeOH = D_n + 14S1				
1	−249	1	18	−234	33
2	0	1	21	−234	−212
3	−215	1	122	−234	−102
4	−4	1	369	−234	132
5	184	1	510	−234	91
	$2(D_n)$-14S′3 + 2 MeOH = 2 D_n + 14S1				
1	−20	2	36	−15	3
2	−103	2	42	−15	74
3	43	2	244	−15	184
4	483	2	738	−15	238
5	2 003	2	1 020	−15	−998

[a] D_n = dendrimer of generation n
[b] See Fig. 1 for structure.
[c] Change in energy of the reaction.
[d] E = steric energy.

Fig. 4. Steric energy per atom for dendrimers from the 1 to 6 generation

between two growing hyperbranched molecules attached to the adjacent active sites of polymeric support. The modelling of this partricular case is represented by supports **7S′1** and **14S′3**. As seen from Tab. 1, the chemical structure and the architecture of the support seems to hardly affect the steric interactions of the dendrimer-support which is followed from qualitatively similar ΔE for all types of support presented in Tab. 1 when a single dendritic molecule is bound to the support. As can be seen from Tab. 1 in the case of supports **7S′1** and **14S′3** when to dendritic molecules are attached to adjacent active sites, for low generation dendrimers ΔE is positive indicative of the attractive interaction between dendrimer and the support, moreover for the **7S′1** support even for 6th generation ΔE is highly positive showing that there is no important steric hindrance between two dendritic molecules bound to the support. The situation is different,

however, for the **14S′3** molecule. As seen from the Tab. 1 for relatively small dendritic molecules (from first to forth generation) ΔE is positive and increases with generation number. For two fifth generation dendrimers bound to adjacent active sites of the support, ΔE becomes highly positive reaching 998 kcal/mol which implies a significant steric hindrance between the two dendritic molecules. To ensure that the above mentioned negative ΔE is due to the steric hindrance between adjacent dendritic molecules, the Connolly's solvent excluded volumes of **D₅**, **D₆**, **7S′1**, **14S′3**, **2D₅-14S′3** and **2D₆-7S′1** were calculated using the equilibrated conformation after the molecular dynamic run. The Connolly's solvent excluded volume represents the volume contained within the contact molecular surface created when a probe sphere (representing the solvent molecule) is rolled over the molecular shape[16]. A probe radius of 1.4 Å was chosen to fit the van-der-Waals radius of elements composing the molecule to ensure the correct estimation of the molecular volume. The sum of the volumes of two **D₆** and one **7S′1** molecules was found to be 74860 Å³, while the volume of **2D₆-7S′1** fragment was 76340 Å³. This means that the **2D₆-7S′1** molecule has a relatively loose structure without any steric hindrance which is confirmed by the high and positive ΔE. On the other hand, similar calculations carried out for **2D₅** + **14S′3** and **2D₅-14S′3** molecules gave 39910 and 38210 Å³. These results show that there should be significant steric hindrance between adjacent **D5** molecules in the case of the use of **14S′3** support, thus explaining a large negative ΔE in this case.

This is due to the structural difference between **7S′1** and **14S′3** solid supports as seen from the Fig. 5. The
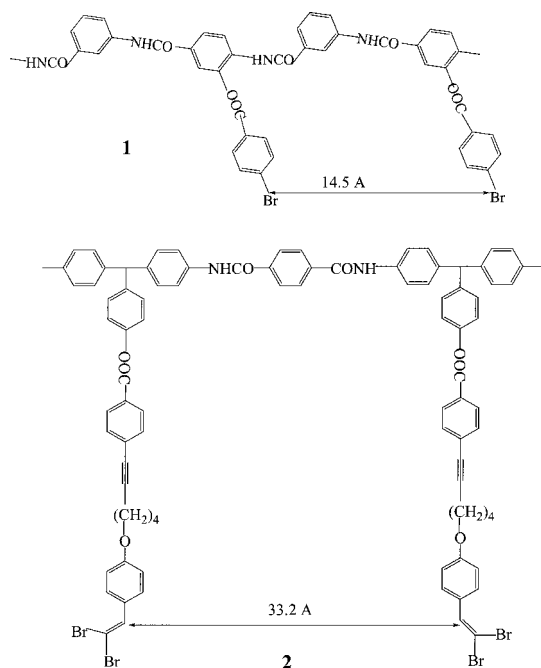

Fig. 5. Equilibrium distances between active sites of **7S′1** (**1**) and **14S′3** (**2**) supports

minimisation of the geometry of the dimers corresponding to **7S′1** (**1**) and **14S′3** (**2**) supports with MM2 force field showed that while the equilibrium distance between halogen atoms in **1** is 14.5 Å, the distance between adjacent dibromovinyl groups in **2** is more then twice that value. Thus, all other things being equal, when two hyperbranched polymer chains grow attached to adjacent functionalities, **7S′1** provides more space for growing hyperbranched molecules allowing them to reach higher molecular weight compared to **14S′1** support. It seems that in the case of a solid-supported hyperbranched polymer synthesis it is possible to regulate the molecular weight of the hyperbranched polymers by changing the distance between active sites on the support. These conclusions are confirmed by the experimental data. Thus the solid supported polymerisation of 4-(5-hexynyloxy)-β,β-dibromostyrene using an **S1** type of support produces hyperbranched polymer with $\overline{M}_n$ of 7300 while when using **S3** type support $\overline{M}_n$ was only 4200–4300 according to GPC[16].

Conclusions

The results of the molecular modelling show that at least up to the 6th generation of hyperbranched poly[4-(5-hexynyloxy)-β,β-dibromostyrene], which corresponds to a molecular weight of 22848, no excessive strain due to the steric hindrances in the molecule exist. Moreover it seems that steric energy per atom tends to a limit with the number of generation, which agrees with the results obtained for $1 \rightarrow 2$ hyperbranched polyacetylene using more precise B3LYP/3-21G//PM3 model chemistry.

Steric hindrance between a single bounded hyperbranched molecule and the support is far less than the attractive van-der-Waals interactions, independent of the nature of the polymeric support and generation number.

The only important steric hindrance was found between two bounded hyperbranched molecules attached to adjacent active sites on the polymeric support. In this particular case the distance separating two attached hyperbranched molecules is strongly affected by the steric interactions thus allowing the control of molecular weight of the hyperbranched polymers by changing the distance between active sites of the support.

It seems that the most important restriction imposed by the solid-supported hyperbranched polymerisation on the molecular weight of the polymer arises from the steric hindrance between adjacent dendritic molecules.

[1] L. Mathias, T. Carothers, *J. Am. Chem. Soc.* **113**, 4043 (1991)

[2] Y. Kim, O. Webster, *Macromolecules* **25**, 5561 (1992)

[3] K. Uhrich, C. Hawker, J. Frechet, S. Turner, *Macromolecules* **25**, 4583 (1992)

[4] F. Chu, C. Hawker, *Polym. Bull. (Berlin)* **30**, 265 (1993)

[5] R. Spindler, J. Frechet, *Macromolecules* **26**, 4809 (1993)

[6] C. Hawker, R. Lee, J. Frechet, *J. Am. Chem. Soc.* **113**, 4583 (1991)

[7] P. Bharathi, J. Moore, *J. Am. Chem. Soc.* **119**, 3391 (1997)

[8] P. Guadarrama, L. Fomina, V. Pankov, W. Matus, S. Fomine, *Polymer J.* **31**, 423 (1999)

[9] M. L. Connolly, *"The Molecular Surface Package", J. Mol. Graphics* 1993, Vol. 11

[10] U. Burkert, N. L. Allinger, *"Molecular Mechanics"*, ACS Monograph 177, American Chemical Society, Washington DC 1982

[11] (a) D. H. Lo, M. A. Whitehead, *Can. J. Chem.* **46**, 2027 (1968); (b) Heterocycle parameter according to G. D. Zeiss, M. A. Whitehead, *J. Chem. Soc.* (**A**), 1727 (1971)

[12] M. J. S. Dewar, C. H. Reynolds, *J. Comp. Chem.* **2**, 140 (1986)

[13] J. J. P. Stewart, *J. Comp. Chem.* **10**, 221 (1989)

[14] J. Foresman, A. Frisch, *"Exploring Chemistry with Electronic Structure Methods"*, 2nd Ed., Gaussian, Pittsburg, PA 1996

[15] S. Fomine, L. Fomina, P. Guadarrama, *Macromol. Theory Simul.* **8**, 54 (1999)

[16] P. Guadarrama, L. Fomina, S. Fomine, *Macromol. Chem. Phys.* submitted