

6. Modification of dendronized polystyrene

In the previous parts, a lot of efforts have been made to obtain dendronized polymers with higher generations, higher molar masses and functional groups at the periphery. Presently, we are focusing on converting these intriguing macromolecules into useful materials. The amine functionality at the resulting polymer surface allows us to conduct surface modifications both in organic solvents and water with a variety of interesting biological and non-biological building blocks, like alkyl chain, protein-targeting sugars, peptide sequences, catalytically active sites, or fluorescence labels.

From a broad point of view, the attach-to route is part of surface modification, in which the modifier is a dendron. Now we are interested in using some other simple modifiers to explore the feasibility of surface decorations and related properties of resulting polymers.

6.1. Modification of dendronized polystyrene with activated alkyl chains

In the orientated tests for the surface modifications, a main obstacle is the solubility of the polymer in the process of polymer reactions involving a dramatic change from water soluble to the organic-solvent soluble polymer. Alkyl chains have good solubility in common organic mediums and were used broadly in increasing the solubility of polymers and macrocycles. It has been reported that alkyl chains can self-assemble into spherical and cylindrical shapes. By introducing the alkyl chains, it was hoped to render the dendronized polymers a well-defined shape and dimension by the self-assembly of molecules.

As a model test, polymer **16c** with $P_n = 60$ was used as a starting polymer to test the modification reaction. It was noticed that during the first several hours, the reaction system was not homogeneous. Varying the polarity of the reaction medium by the addition of dichloromethylene did not improve much in this situation. After roughly one day, the resulting polymer can be totally dissolved. After similar work-up as above, the polymer

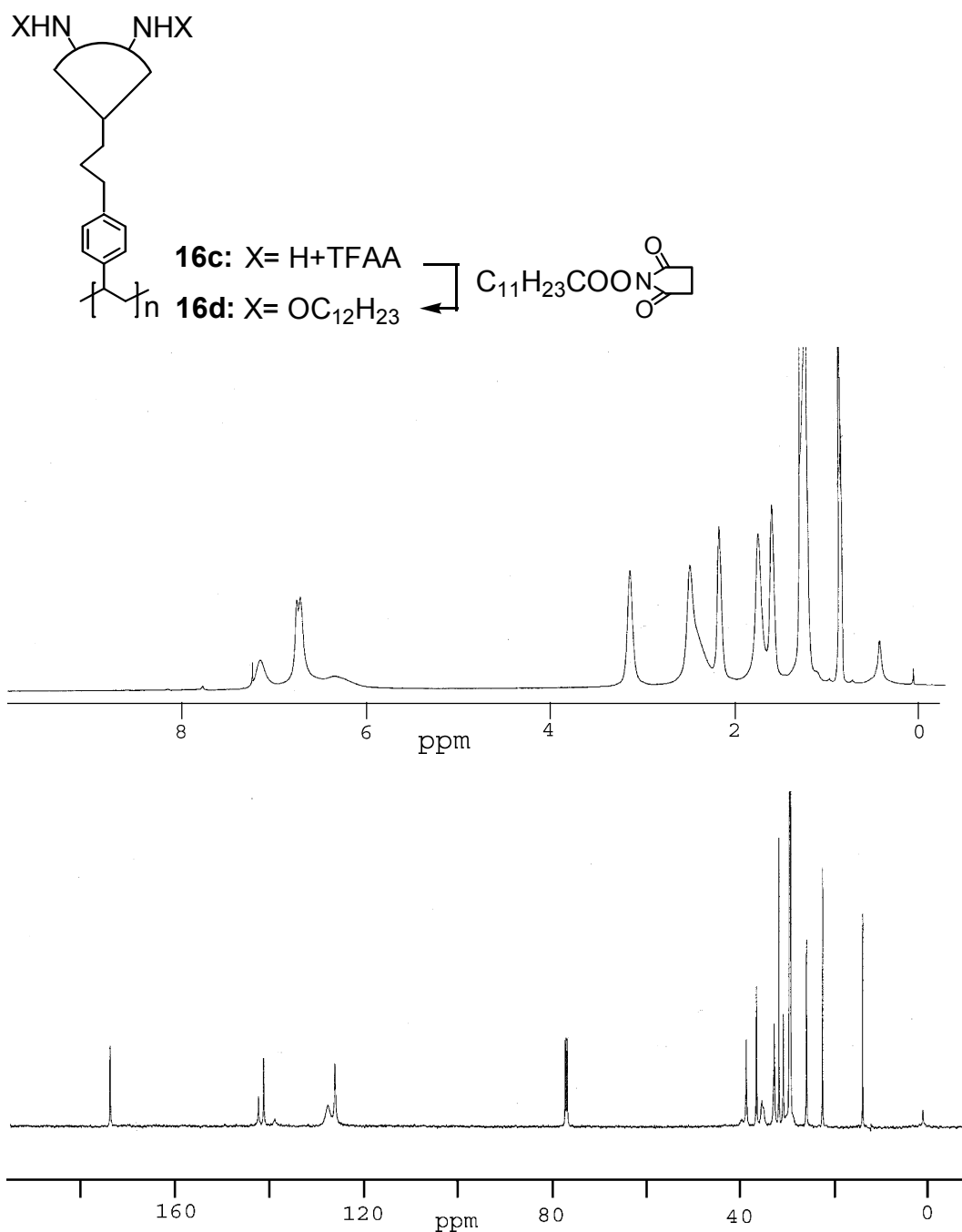
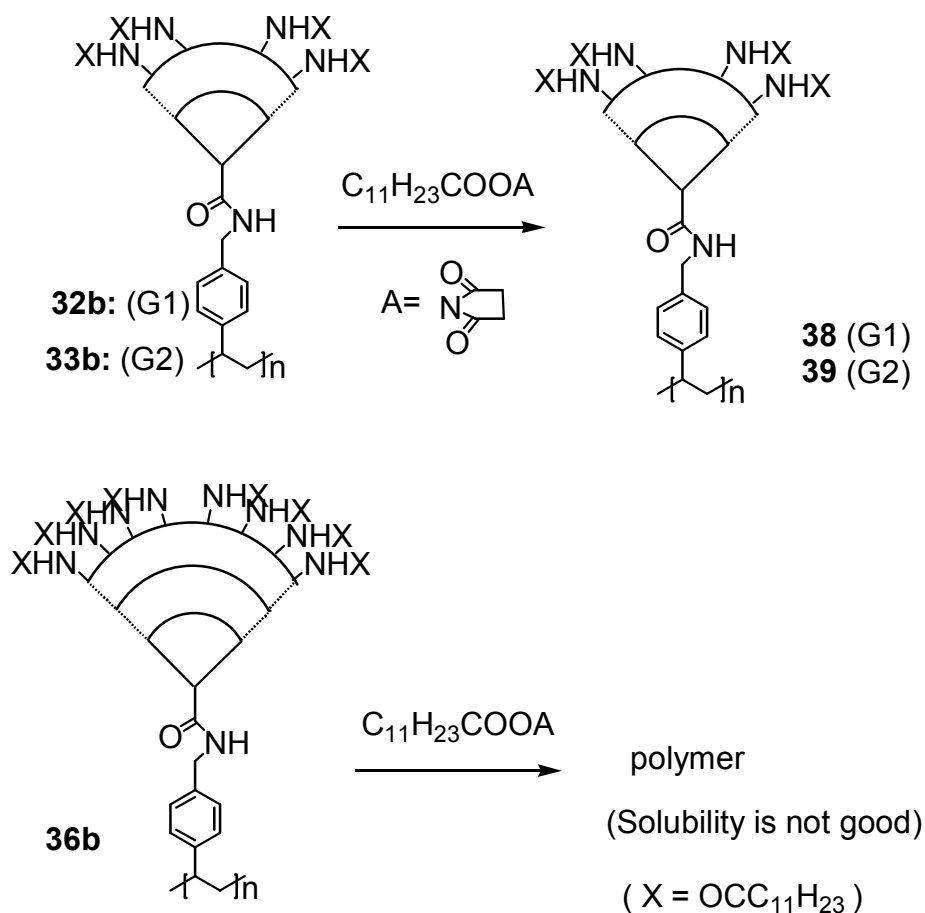


Fig. 21. ^1H and ^{13}C NMR spectra of alkyl modified polymer **16d**.

was dissolved in benzene and lyophilised to give solid material. The ^1H and ^{13}C NMR spectra are presented in Figure 21. From the ^1H NMR spectrum, all peaks appear as expected. Because of the shift of base line, it is difficult to measure the coverage by integration of the corresponding protons. All the resonances of carbons appear as

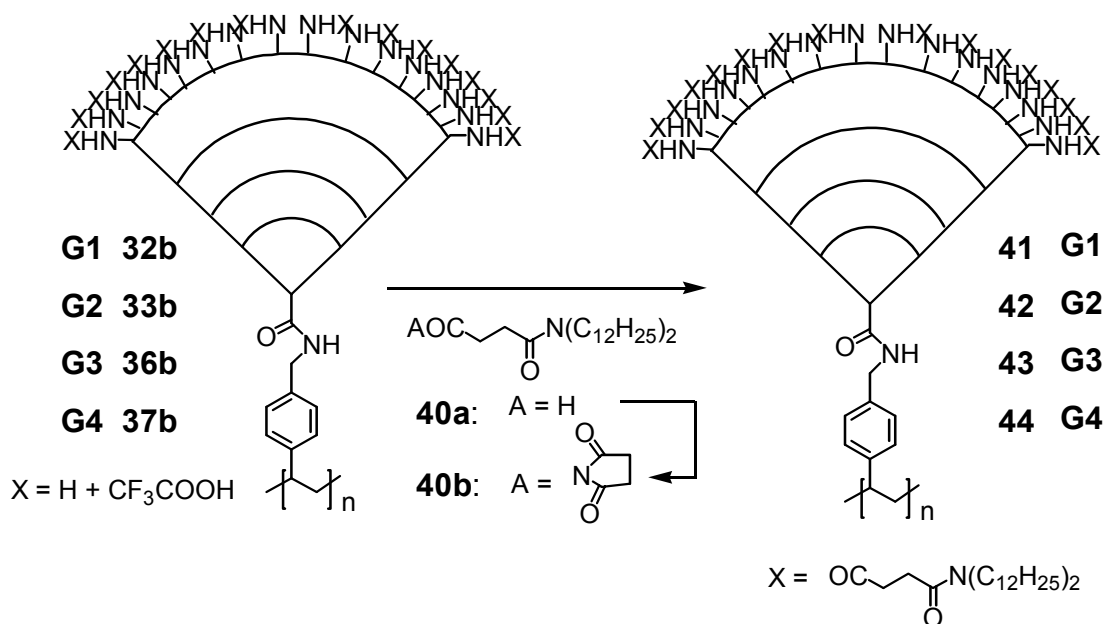
expected, from the above investigation, it is clear that the coverage is virtually 100 percent (no absorption was observed at $\delta = 42$ ppm).

The modifications of charged polymers **32b**, **33b**, and **36b** are displayed in Scheme 22. The starting polymers were first dissolved in methanol and deprotonated by addition of triethylamine (as a base). The surface modification reactions were brought about by slow addition of alkyl activated Ester to the polymer solution. After some minutes, methylene dichloride was added to account for precipitation of the polymer from the solution due to change of polymer polarity. The crude polymer was dissolved in THF and purified by precipitating that four times into methanol / water and lyophilised from benzene.



Scheme 22: Decoration of dendronized polymers **32b**, **33b** and **36b** with activated fatty acid.

The resulting polymers **38** and **39** are soluble in THF and chloroform, allowing characterization possible. It was found that alkyl-modified G3 polymer could not be totally dissolved in THF, chloroform and hexane et..



Scheme 23: Modifications of charged G1-G4 polymers **32b**, **33b**, **36b**, and **37b** with **40b**.

Table 8. Results of the measurement of the coverage of G1-G4 polymers(41, 42, 43 and 44) by the attach-to route.

polymer	W×10 ³ (g)	V×10 ³ (L)	A	Y(%)
41	7.1	3.0	0.21	99.67
42	12.9	3.0	0.27	99.76
43	13.1	3.0	0.64	99.43
44	11.4	3.0	0.70	99.27

Note: (V) is used volume of labelled polymer solution in 1,1,2,2-tetrachloroethane, absorption (A), and coverage (Y), weight of labelled polymer (w).

In order to improve the solubility of modified polymers, compound **40a** was converted to **40b** (Scheme 23). **40b** has two alkyl chains in comparison with the fat acid used in Scheme 21. The modification reactions were brought about as for polymer **32b** or **33b**. The resulting polymers are all soluble in THF and chloroform, and could be purified by precipitation procedures. GPC measurements were carried out by using THF as eluent

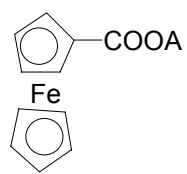
The coverage of polymers **41**, **42**, **43** and **44** were measured by the same method as before. The results are presented in Table 8. It was found that the coverage of all the polymers investigated are beyond 99 %.

6.2. Modification of dendronized polystyrene with other activated Esters

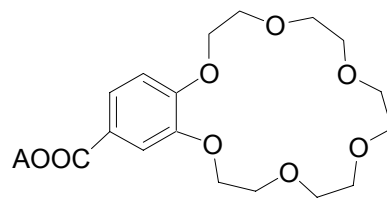
The rich chemistry of amino functional groups allows us to do surface modifications with a broad choice.

Attachments of a charged G1 polymer **16c** with other activated Esters were carried out under the same conditions described above. The structures of them are depicted in Scheme 24, in which compounds **45**, **46** and **47** were obtained by DCC method using the corresponding acid. Compound **48** is commercially available. The results of the modifications are as follows: For compound **47**, the resulting polymer is soluble in chloroform and THF with virtually 100 % coverage (according to NMR spectra); for compound **46**, the resulting polymer can be dissolved in THF/methanol (v:v / 1:1).

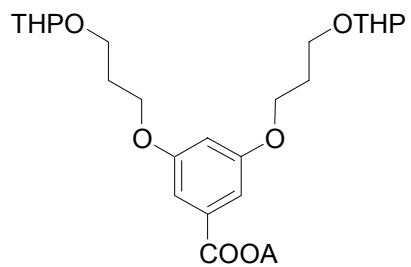
Unfortunately, the remained reagent could not be totally removed by precipitation method. This makes characterization of the resulting polymer impossible. As to compound **45** and **48**, after polymeric reaction, the obtained crude polymer were not soluble in THF, chloroform, methanol and hexane or their corresponding mixture. These surface modification results indicate that the structure and polarity of the attached compounds play an important role for the solubility of the resulting dendronized polymers.



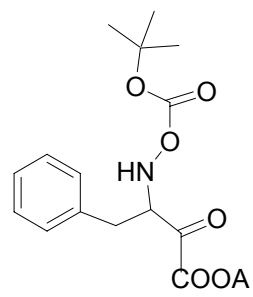
45



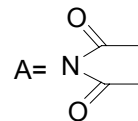
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47



48



Scheme 24. Some of activated acid tested for the attachment of G1 polymer **16c**.