

# KINETICS OF FORMATION OF MANY ARMED STARS WITH DENDRIMER CORES AS A MODEL OF CROSSLINKING

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## Introduction

A variety of model networks made from end functionalized low polydispersity linear polymers have been studied<sup>1</sup> since linking of "living" anionic polymers was first described<sup>2</sup>. The functionality of the crosslinks is either a 3 or 4 functional small molecule or a polydisperse, multifunctional gel such as divinyl benzene<sup>3</sup>. The use of dendrimers as a multifunctional branch point should give high functionality since dendrimers have up to several thousand attachment sites and low polydispersity. Initial studies of this approach are reported elsewhere<sup>4</sup>.

The efficiency of the reaction is difficult to measure in networks, analytical methods that measure end group conversion are difficult and subject to uncertainties at high conversions. Extraction experiments are also inexact at high conversions. Studies of the reactions of polymers with a single end functionality are simpler since they form stars rather than networks which are soluble and can be more easily characterized.

Reactions of end functionalized PEG with dendrimers have been reported for amino terminated dendrimers and succinimide terminated PEG<sup>5</sup>. High conversions have been reported forming stars with large numbers of arms. Only the high conversion results were studied, however. No measures of the kinetics were made. This work reports the use of gel permeation chromatography to follow the conversion of arms to stars.

## Experimental

**Materials.**<sup>6</sup> Poly(propylene imine) (PPI) and poly(amido amine) (PAMAM) dendrimers were purchased from Aldrich. Monofunctional vinyl sulfone poly(ethylene glycol) (VS-PEG) of molecular mass 5000 g/mol and Mw/Mn < 1.1 was purchased from Shearwater Polymers.

**Gel permeation chromatography (GPC).** Volume fraction 0.1 % triethylamine in H<sub>2</sub>O was used as a mobile phase with a Phenomenex Polysep-GFC-P column. Appropriate amounts of VS-PEG and dendrimer at total mass fraction 10 % in the mobile phase solvent were mixed and 10 ul quantities were repeatedly injected. Detection was by an evaporative light scattering detector (Varex, model Mark IIa).

## Results and Discussion

Figure 1 shows GPC results of the curing study of a PAMAM G4 dendrimer with the VS-PEG at a total solids mass fraction of 10 %. The ultimate number of arms was 31 out of a possible 64 (designated PAMAM 31/64). The initial sample injection was taken 1 min after mixing of the components and is virtually identical to that of the VS-PEG itself. A mass fraction of ca. 7.5 % of the VS-PEG elutes earlier than the main peak. This peak is present in the chromatograms taken at later times and is probably a PEG dimer formed during the functionalization step. It is unchanged during the reaction and its contribution to the reaction is subtracted out. It is evident that the stars formed by the linking reaction to the dendrimers can be separated from the unreacted arms.

The VS-PEG peak lowers in intensity during the reaction and the star peak increases, and integration of the peaks gives the extent of the reaction. There are also subtle changes in the peak positions and shapes during the reaction. The VS-PEG peak shifts slightly to higher molecular mass. There is a reduction of the amount of low molecular mass component in the reacting VS-PEG suggesting that low molecular mass polymer can more easily find its way to the dendrimer. The high molecular mass star component peak shifts to lower elution volume with time and becomes narrower showing that the stars formed increase in size and that the polydispersity, as measured by hydrodynamic volume, becomes lower.

Figure 2 shows the conversion of arms with time for the PAMAM 31/64 sample. The kinetics of the reaction can be modeled by kinetics that are first order in VS-PEG and first order in dendrimer end groups as in equation 1.

$$\partial[PEG]/\partial t = -k[PEG][NH_2] \quad (1)$$

The solid line in figure 2 is a fit of equation 1 to the first order kinetics. The fit is quite poor, underestimating the rates at low conversion and

overestimating the rates at high conversion. The reaction seems to be slowing down considerably with conversion due to the crowding that occurs when a large number of arms are placed on the star. The error bars give the range of values typical of GPC results of this instrument.

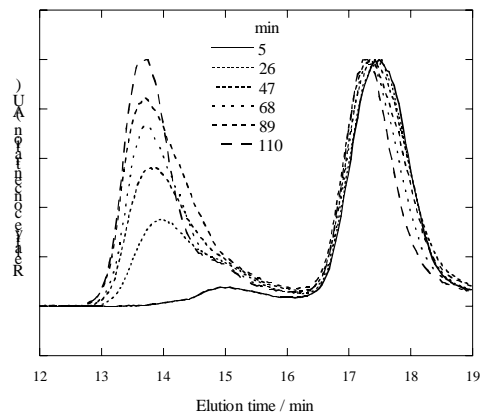


Figure 1. GPC chromatograms for PAMAM 31/64.

If the crowding that occurs when a large number of arms are on the dendrimer, the reaction may not obey first order kinetics in the concentration of available dendrimer terminal groups. The kinetics was refit to equation 2, which allows the order of the reaction with respect to dendrimer end groups to float.

$$\partial[PEG]/\partial t = -k[PEG][NH_2]^\alpha \quad (2)$$

Equation 2 assumes that the reaction is first order in PEG concentration. Assumption of a floating value of the PEG order causes the fits to become unstable since the order of the two reactions is highly correlated for any given sample. Equation 2 is used to fit the consumption of PEG with time in a semi-empirical way. The fit of equation 2 is quite good, giving an exponent  $\alpha = 9.2$  with a standard deviation of  $\pm 1.0$ .

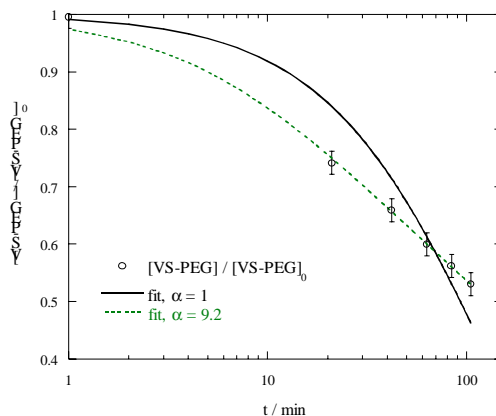
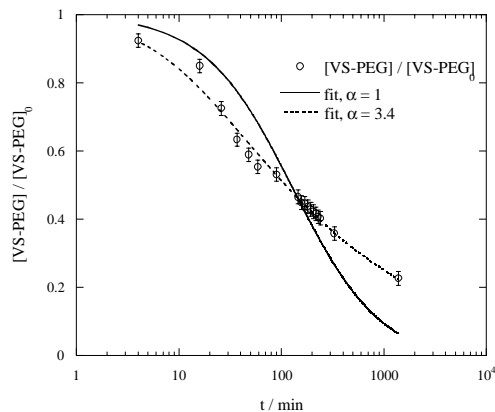
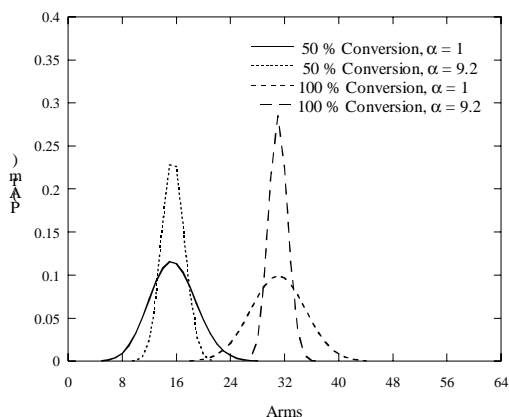


Figure 2. Conversion of arm to star,  $[VS-PEG] / [VS-PEG]_0$ , fits of first order kinetics, and higher order kinetics for sample PAMAM 31/64.

The kinetic experiment was repeated with a G4 PPI dendrimer having 32 terminal amines with an amount of VS-PEG that would give 30 arms at complete conversion. GPC data were taken between 4 min and 1383 min and are plotted in figure 3. The conversion of arms to star is approximately 80 % complete after one day. If the kinetics are followed to high conversion, it may take several days of reaction time to achieve the ultimate star formation, or ultimate gel formation when applied to a bifunctional polymer reacting with a dendrimer.



**Figure 3.** Conversion of arm to star,  $[VS-PEG] / [VS-PEG]_0$ , fits of first order kinetics, and higher order kinetics for sample PPI 30/32.



**Figure 4.** Probability distribution of stars formed from PAMAM 31/64 at 50 % and 100 % conversion from kinetic fits of random,  $\alpha = 1$ , and retarded,  $\alpha = 9.2$ .

The polydispersity in the number of arms per star can be calculated from the kinetics of the reaction. If the  $[-NH_2]$  concentration can be separated into terms of the total dendrimer concentration,  $[D]$ , and the probability that  $n$  arms have been attached,  $P[n]$ , so that

$$[-NH_2] = [D] \sum_{n=0}^N (1 - n/N) P(n) \quad (3)$$

The reaction kinetics can be expressed in terms of the reaction of an  $(n-1)$ -arm star to form a  $n$ -arm star.

$$\frac{\partial P(n)}{\partial t} = -k' [PEG] \times ((N - n + 1) P(n-1)^\alpha - (N - n) P(n)^\alpha) \quad (4)$$

where  $k'$  is a constant. Therefore, for any data fit from equation 2, the arm number distribution can be calculated as a function of conversion. If  $\alpha = 1$ , the probability of any individual terminal  $-NH_2$  group being reacted is equal, and the resulting probability distribution is a binomial distribution. If  $\alpha > 1$ , however, stars with a low number of arms will react faster than ones with a high number of arms. The result is a narrowing of the distribution of arms and hence molecular mass.

Equation 4 can be solved numerically to produce arm distributions as a function of conversion. Figure 4 shows the distribution of arms of a star for

the case of PAMAM 31/64 at relative conversion of 50 % and 100 % arms, both for the case of  $\alpha = 1$  and  $\alpha = 9.2$ .

The polydispersity of the stars formed by these kinetics is extremely narrow. The  $M_w/M_n$  of the random case is 1.017 and for the retarded case is 1.002 for the case of linking monodisperse arms. It is obvious that the stars formed are very narrow in their molecular mass distribution so that any networks formed by the same kinetic scheme will also be very narrow. While some of the linear chains may be connected at only one end at lower conversions, the number of connections to any dendrimer is highly uniform. It is not necessary to consume all of the functional groups on a dendrimer to produce uniform crosslinking.

### Conclusions

GPC can be used to follow the kinetics of star formation from end functionalized PEG and dendrimers. The rate of linking is inhibited at high conversions probably due to the crowding that occurs when a large number of arms have been attached. This causes the distribution of arms to be very narrow. Any networks that would be formed from PEG functionalized at both ends will also have a narrow polydispersity. Even if excess dendrimer is used and the terminal functional group are not completely consumed, the polydispersity of the network functionality is still very low.

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- (6) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or method is necessarily best suited for the application.