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Control of Macromolecular Architecture of Polyamides by Poly-functional Agents. 2. Use of Oligomerization in Polycondensation Study

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Summary: In the first paper of the series, a statistical model for star-branched polycondenzation of AB type monomers in the presence of a polyfunctional agent RA_f was completely developed. The analytical expressions obtained for the number-average ($\overline{DP}_n$) and weight-average ($\overline{DP}_w$) degree of polymerization, and the dispersion index (D) for whole polymer species, linear and star macromolecular chains, are now derived as function of the feed and of end-group analysis. Also the important molecular parameter, mole fraction of star-branched polymer, can be evaluated. Some numerical examples are presented. It is illustrated that the molecular weight properties of the linear and star-branched polymers in the mixture of the products, very important factors for the application of this kind of polymeric materials, can be determined starting from the feed and terminal group analysis.
Polymerization and oligomerization of 6-aminocaproic acid were carried out in the presence of trimesic (T3) acid and 2,2,6,6-tetra(β-carboxyethyl)cyclohexanone (T4) and EDTA as tri- and tetra-functional agents. The molecular weights calculated are in good agreement with those obtained by Size Exclusion Chromatography (SEC), end group analysis and NMR spectra.

Keywords: molecular weight distribution, polycondensation, size exclusion chromatography (SEC), star polymers

Introduction

Star-branched polymers are characterised by a branch point from which emanate a number of polymer chains or "arms". Star-branched polymers have been actively studied since the first star-shaped polystyrene was prepared by linking living anionic polystyrene with silicon tetrachloride.[1] The interest in star-branched polymers increased rapidly over past decades due

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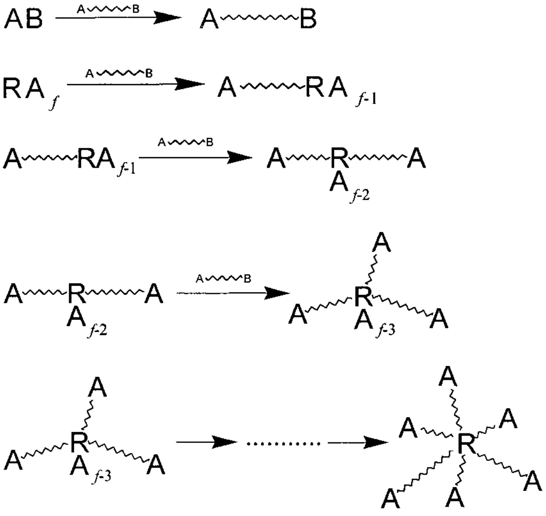
to their unique physical and chemical properties as compared to their linear analogues. It is known that star branching chain decreases the molecular dimensions of polymers and results in a decrease in viscosity. This reduction of melt viscosity allows for processing at lower temperatures and pressures as well as the ability to process higher molecular weight polymers. Additionally, reduced viscosity allows also for improved extrudability as well as injection moulding.[2-4] Both the physical properties of polymeric materials and their processing behaviour at elevated temperatures depend essentially on the average molecular weight and the molecular weight distribution (MWD). It is therefore essential to give a precise description of the molecular weight distribution.

The synthesis of macromolecules with star architecture is produced with almost all polymerisation methods by two general approaches: 1) by terminating reaction of linear polymers with a multisited reagent; 2) by initiating polymerisation from a polyfunctional agent. For star–branched polyamides very few paper are present in the literature; Wilkes presented a paper devoted to a crystallisation behaviour[5] of star nylon-6 prepared by using as a comonomer the second-generation starburst polyethyleneimine described by Tomalia.[6] Anionic polymerisation of caprolactame to give six-arms nylon-6 was studied by Mathias and Sikes.[7,8] In our experience both these method cannot be used in hydrolytic polymerisation conditions due to the low thermal stability of comonomer used or to the not well determined molecular mass distribution in caprolactame anionic polymerisation.

In the previous paper we discussed some experimental results which confirm our theoretical model.[9] In the paper we illustrated that the molecular weight properties of the linear and star-branched polymers in the mixture of the products are very important factors for the application of this kind of polymeric materials.

Theoretical Aspects

Theoretical studies and some experimental approach to produce star-branched polyamides are present in the literature from the beginning of polyamides industrial production. More than 50 years ago, the molecular weight distribution of the resulting polymer by the polycondensation of AB type monomers with a polyfunctional agent RA_f (f is the functionality of active group A), at completion of the reaction, were studied by Flory[10,11] and Schulz.[12] The molecular weight distribution becomes narrower with increasing functionality of the agent RA_f. Dispersion index D depends only on the functionality f and equals to $1 + 1/f$. However, Farina[13] proposed that a) the final product of AB monomer polymerisation in the presence of a polyfunctional agent RA_f is a mixture composed solely of linear chains and of star-branched macromolecules with f-arm; b) the length of the linear chains is equal to that of a branch of the star polymer. According to these hypotheses, Farina observed that during the polymerization for $f>2$ the dispersion index first increases, reaches a maximum and decreases until to the limiting value equal to $(1 + 1/f)$.



Scheme 1. Reaction scheme between the RA_f and AB monomer.

In our recent paper,[9] we assume (Scheme 1) that all the kinetic constants, in the polycondensation of AB type monomer with a polyfunctional agent RA_f, are independent of chain length and the same reactivity for all the functional groups in both polyfunctional compounds and macromolecular ones; a complete statistical and kinetic model was developed for the star-branched polycondensation of AB type monomers in the presence of a polyfunctional agent RA_f. The analytical expressions, as function of conversion of the functional group of RA_f, for the number-average ($\overline{DP_w}$) and weight-average ($\overline{DP_w}$) degree of polymerization, and the dispersion index for various polymer species were derived through independent methods: both kinetic and statistical ones. In order to easily use the theoretical results, in this work, we have derived the analytical expressions for the molecular parameters as function of the concentrations of terminal groups (for example: A=-COOH and B= -NH_2). In the next, we will refer to a multifuntional RA_f where A is a -COOH function.

The concentrations of the linear primary chain having r monomeric units (P_r) and the branched polymer having r monomeric units on i branches (P_r^i) are given by

$$P_r = [NH_2]\frac{[COOH]}{N_0 + fC_0}\left\{\frac{N_0 - [NH_2]}{N_0 + fC_0}\right\}^{r-1} \tag{1}$$

$$P_r^i = C_0\binom{f}{i}\binom{r-1}{i-1}\left\{\frac{[COOH]}{N_0 + fC_0}\right\}^{f}\left\{\frac{N_0 - [NH_2]}{N_0 + fC_0}\right\}^{r} \tag{2}$$

All the molecular weight properties can be derived from Equation (1) and (2).

The mole fraction of the total star polymer (f_S) and linear polymer in the (f_L)is given by

$$f_S = 1 - f_L \tag{3}$$

$$f_L = \left\{[NH_2] + \frac{fC_0(N_0 - [NH_2])}{[COOH]}\left(\frac{[COOH]}{N_0 + fC_0}\right)^{f}\right\} \Big/ \left\{[NH_2] + C_0\left(1 - \left(\frac{[COOH]}{N_0 + fC_0}\right)^{f}\right)\right\} \tag{4}$$

where C_0 and N_0 are the initial concentrations of polyfunctional agent RA_f (with f functionality) and monomer AB, [NH_2] and [COOH] are the mole concentrations of terminal groups.

The number- and weight-average degree of polymerization and dispersion index are as follows:

$$\overline{DP_n} = \frac{N_0}{[NH_2] + C_0\left(1 - \left(\frac{[COOH]}{N_0 + fC_0}\right)^f\right)} \tag{5}$$

$$\overline{DP_w} = \frac{2N_0 + fC_0 - [NH_2]}{[COOH]} + \frac{C_0}{N_0} f(f-1)\left(\frac{N_0 - [NH_2]}{[COOH]}\right)^2 \tag{6}$$

$$D = \frac{\overline{DP_w}}{\overline{DP_n}} \tag{7}$$

When the reaction goes to completion, i.e. $[NH_2] = 0$, the limiting values of number- and weight-average degree of polymerization and dispersion index were be obtained.

$$\overline{DP_n}(\lim) = \frac{1}{a(1 - (\frac{fa}{1+fa})^f)} \tag{8}$$

$$\overline{DP_w}(\lim) = 1 + \frac{1}{a}\left(1 + \frac{1}{f}\right) \tag{9}$$

$$D(\lim) = \left(a + 1 + \frac{1}{f}\right)\left(1 - \left(\frac{fa}{1+fa}\right)^f\right) \tag{10}$$

where a is the initial ratio of C_0 to N_0.

Experimental

2,2,6,6-tetra(β-carboxyethyl)cyclohexanone (T4) was synthesized according to literature.[14] 6-aminocaproic acid (AB), trimesic (T3) acids, EDTA and octadecylamine (n-C18-NH2) (Fluka) were used without further purification.

The mixture of monomer and agent (total 200 g) was poured into a glass reactor beforehand dried by heating above 100°C under 1 Torr pressure. Reactions were carried out in a glass reactor at 275°C with mechanical stirring under the flow of N_2 (5 l/h) for 6 hours.

The SEC analyses were performed in anhydrous CH_2Cl_2 at 20°C by using a six Ultrastyragel column set (10^5, $2*10^4$, $2*10^3$ and 500 Å). The molecular mass of relative polyamides were determined through N-trifluroacetylation.[15] Column calibration was performed by polystryrene standards; the linear polyamide calibration curve was calculated according to the universal calibration principle.[16,17]

The titration of functional groups of $-NH_2$ and $-COOH$ in the polyamides was carried out by potentiometer Metrohm 716 DMS in a solution of 0.7 – 2% polyamide dissolved in 85% trifluoroethanol and H_2O. The solution of polyamide was titrated by HCl N/50 for the determination of the concentration of $-NH_2$. The concentration of $-COOH$ was titrated by NaOH N/50. NMR spectra were carried out in CF3COOD solution with a Bruker 400 MHz spectrometer.

Results and Discussion

In order to visualise the relationship between the molecular parameters and reaction conditions, some numerical examples are given. For a tri- and tetra-agent and initial ratio of RA_f to monomer 6-aminocaproic acid of 0.003, the molecular weight distributions of linear and star species are reported vs. degree of polymerization (r) in Figs. 1-4.

Figures 1,2 and 3,4 report in the case of a tri- and tetra-functional agent respectively, the molecular weight distribution of linear and star polymers at different state of polymerization passing from 0.99 to 0.999 of the complete reaction ($[NH_2]= 0$). It is evident from the figures that the molecular weight of the relative polymer and the star-branched fraction increase with increasing the conversion and f ($f \geq 3$). Final properties of the polymeric material will depend on the balance between linear and star macromolecules as on their molecular mass.

Equation (5) gives us the general relationship between the dispersion index D and the polymerization conditions, i.e. f value and initial ratio ($a=C_0/N_0$) of RA_f vs end group titration which is shown in Figure 5. Dispersion index increases with decreasing concentration of $[NH_2]$, reaches a maximum and then goes to its limiting value (Eq. 8). In the Figure 5 only the D value at high conversion is reported.

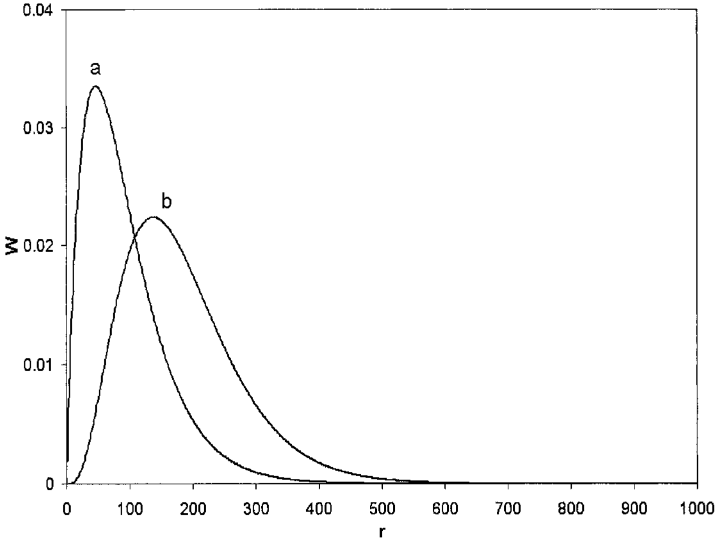


Fig. 1. Molecular weight distribution of linear and star-branched polymer. T3/No = 0.004 at 99% of the limiting conversion. a: Linear; b: 3 arm branched polymer.

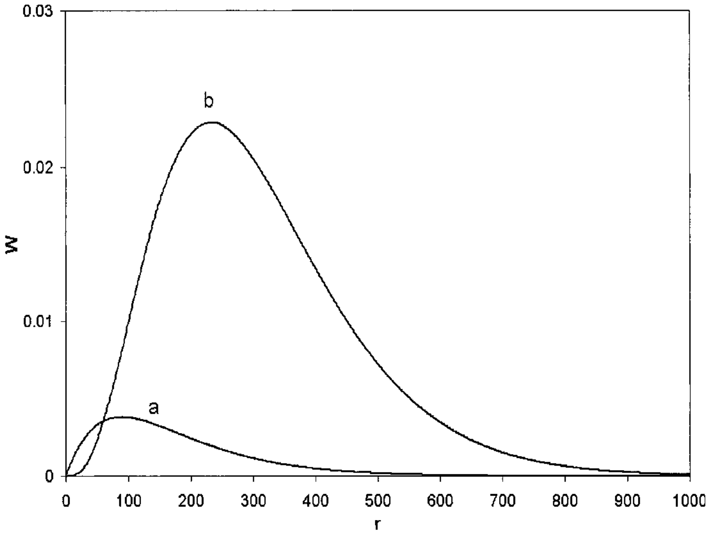


Fig. 2. Molecular weight distribution of linear and star-branched polymer. T3/No = 0.004 at 99.9 % of the limiting conversion. a: linear; b: 3 arm branched polymer.

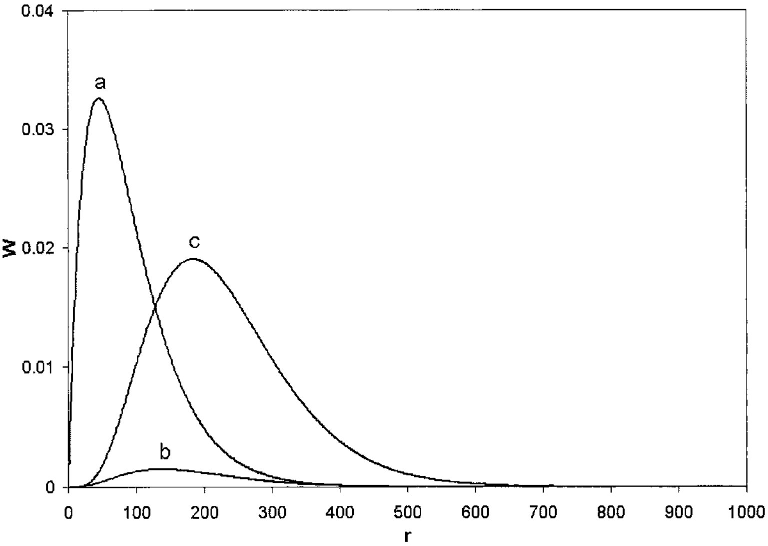


Fig. 3. Molecular weight distribution of linear and star-branched polymer: T4/No = 0.003; at 99 % of the limiting conversion. a: linear; b: 3 arm star polymer; c: 4 arm star polymer.

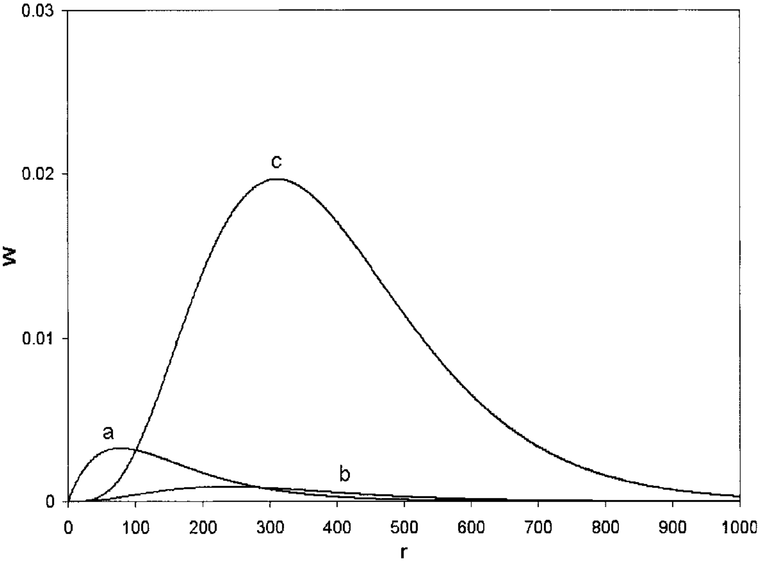


Fig. 4. Molecular weight distribution of linear and star-branched polymer. T4/No = 0.003, at 99.9 % of the limiting conversion; a: linear; b: 3 arm star polymer ; c: 4 arm star polymer.

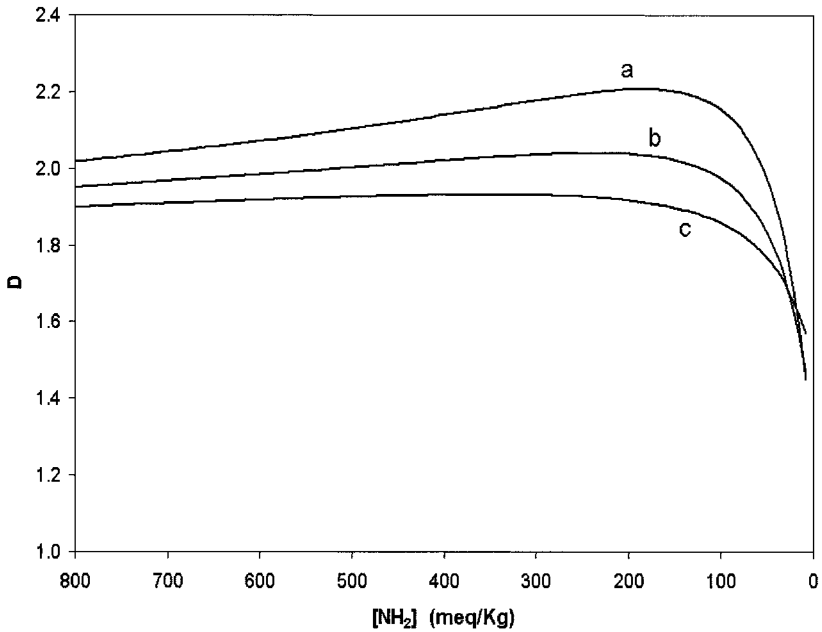


Fig. 5. Evaluated D values vs end group analysis [NH$_2$]: a: T4/No = 0.003; b: T3/No = 0.004; c: T2 /No = 0.006.

Therefore, some important conclusions can be obtained from the proposed model.

The molecular weight of the reaction system depends essentially on the ratio $a = C_0 / N_0$: the smaller value of a, the larger molecular weight can be obtained when the reaction goes to completion.

The molecular weight distribution becomes narrower with increasing functionality of the agent RA_f.

Dispersion index D depends not only on the functionality f but also on the mole ratio a.

When $f \geq 2$ and $a \leq 0.01$, the limiting values of number-average degree of polymerization and dispersion index are about equal to $1/a$ and $1/a + 1 + 1/f$ which is close to the value obtained by Flory.[2]

At the beginning of polymerization most of the polymers are linear, and the star-branched polymer will form only at very high conversion.

Polymerization Results

Polymerizations of 6-aminocaproic acid were carried out in the presence of tri- and tetra-functional acids. The theoretical and experimental data, as obtained by Size Exclusion Chromatography (Figure 6), for linear, tri- and tetra-branched polyamide are reported in table 1.

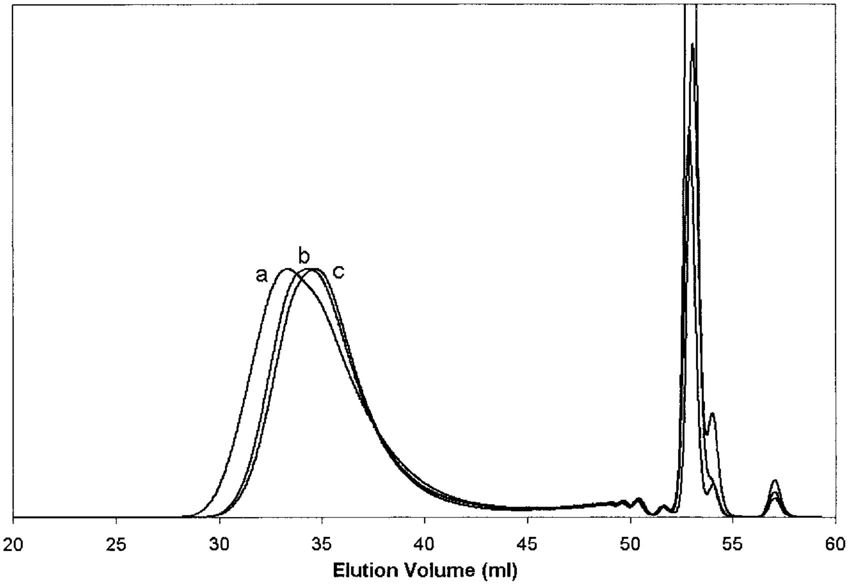


Fig. 6. Examples of SEC curves of PA6. a: linear; b: star polymer (T3 = 0.3% in mole); c: star polymer (T4 = 0.3% in mole).

Table 1. Feed, end group analyses and a comparison between evaluated and experimental molecular mass data (SEC).

Sample	NH2 (meq/Kg)	COOH (meq/Kg)	Mn		Mw		D	
			model	SEC	model	SEC	Model	SEC
Nylon 6	45.50	41.97	21978	20832	43956	41576	2	1.996
T3 0,3%	20.07	102.17	21066	20534	35011	33733	1.662	1.643
T4 0,3%	14.11	133.25	22211	19118	34852	31840	1.569	1.665

We note that the SEC calibration was performed with linear PA6 and so the agreement between experimental data and the evaluated ones confirms the validity of the proposed reaction scheme.

We note also that all the SEC curves in figure 6 present the plateau due to cyclic oligomeric species; this is a further proof of the presence of linear chains in the obtained polymer.

Therefore, we can conclude that the optimisation of mechanical properties of material can, really, be obtained by a proper choice of the functionality and initial concentration of RA_f and of final conversion of amino group; the fraction of star-branched and linear polymer, and their molecular weights are very important for application of this kind of polymeric materials, because the first one offers reduction in melt viscosity and the linear ones gives good mechanical behaviours.

The key point in the synthesis of star-branched polycondensates is the choice of the multifunctional agent; the selected molecules must be stable in the polymerization and final processing conditions. In the case of polyamides polymerization and processing temperatures are very high (up to 300 °C). We discuss now an approach to solve this crucial problem.

Oligomerization Results

The first method generally used for a test of thermal stability is a DSC or a TG analysis; it should be noted that polymerization conditions differ from DSC analysis. In the thermal analysis the tested molecule is pure, solid or liquid according its phase; as a consequence, parasite reactions occurring in the thermal treatment cannot be the same as in the polymerization process. In the last case, the added reagent is in a dilute and reactive condition. At contrary, during oligomerization condition the substance can react with the monomer and parasite reactions can be better observed by the usual analytical methods.

By oligomerization, we tested several possible compounds as multifunctional molecules both polyamino or polyacid. Figure 7 reports SEC curves of 6–aminocaproic acid oligomerization in the presence of T4 and EDTA. The effect of parasite reactions in polymerization conditions is evident and agrees with the observed thermal decomposition of EDTA.

Oligomerization at different feeds can confirm the thermal stability of a multifunctional reagent; figure 8 reports SEC curves of PA6 oligomers obtained at T4 different feeds.

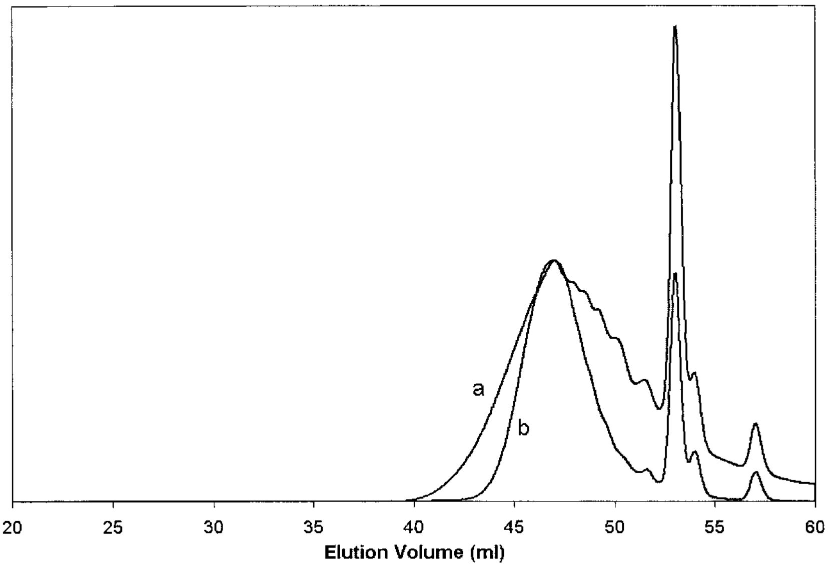


Fig. 7. SEC curves: a: AB /EDTA = 6; b: AB/T4 =6.

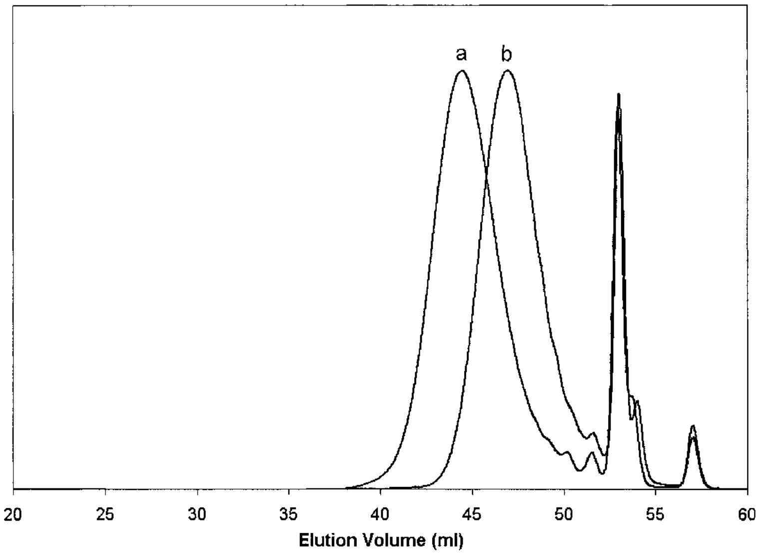


Fig. 8. SEC curves of 6–aminocaproic acid in the presence of T4: a: AB/T4 = 12; b: AB/T4 = 6.

In principle, the presence of the multifunctional agent can be observed in a NMR spectrum of oligomers. Figure 9 reports an example of a ^{1}H NMR spectrum of oligomer mixture obtained in the presence of T4. In this case, no clear signals are present for a correct determination of degree of reaction and or of anomalous reaction pathway. In particular, we searched for the presence of imidation reaction between amino group of the monomer and two different acid function of two different arms. However, degree of polymerization agrees with SEC results. Work is in progress on these mixtures by MALDI-TOF.

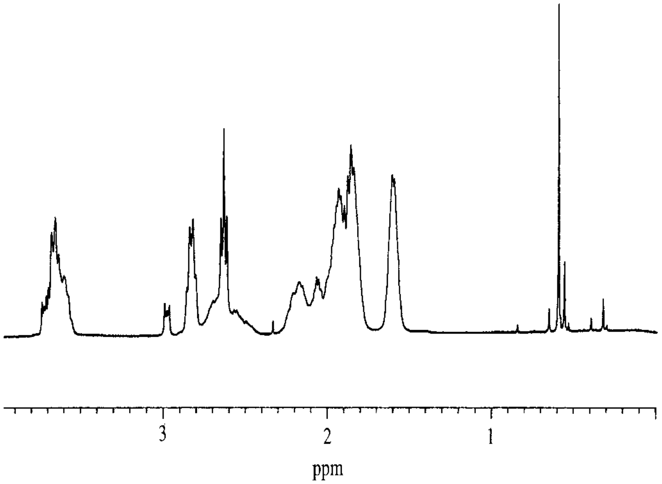


Fig. 9. ^{1}H NMR spectrum of oligomers. AB/T4 = 6.

The so far discussed difficulties in T4 oligomerization can be attributed to the absence of NMR signals far from those of the macromolecular chain. Assuredly to this hypothesis, we select trimesic acid as multifunctional reagent.

In order to have qualitative and quantitative results from NMR spectra we reacted T3 with n-C18-NH2 in different ratios. MS-, proton and carbon NMR spectra confirm the structure of products.

Figure 10 reports formulas and assignment of the aromatic region of 1H NMR spectrum of a mixture; from this spectrum quantitative results about product distribution vs feed can be obtained.

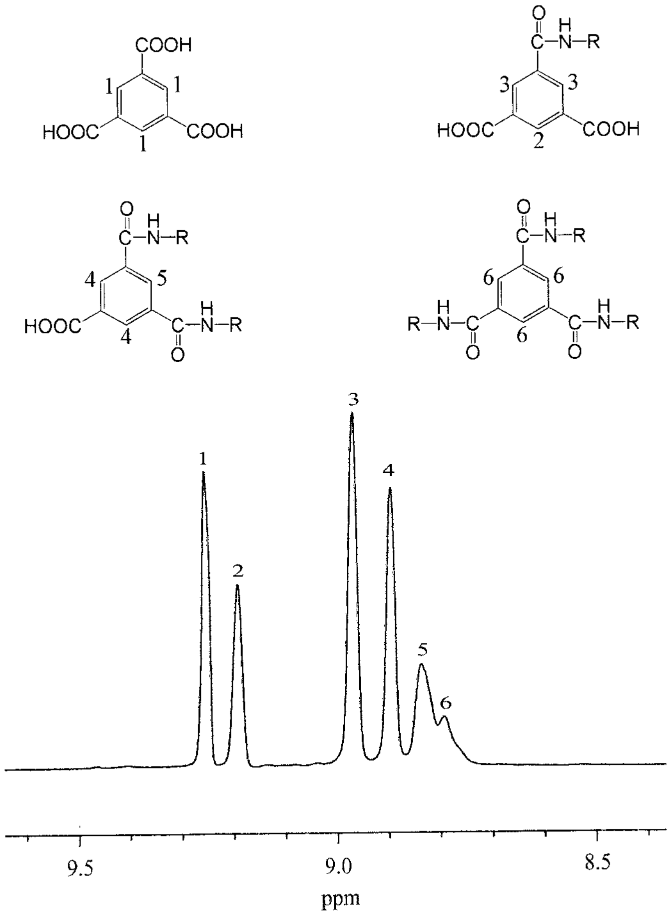


Fig. 10. Formulas and aromatic region of ^{1}H NMR spectrum of T3/6–aminocaproic oligomers.

Several oligomerization reaction were performed between ε–aminocaproic and trimesic acid in different ratios; as in T4 case, SEC data confirm thermal stability of the comonomer (two example are in Figure 11).

NMR spectra confirm the absence of parasite reaction and allow a quantitative determination of oligomeric species. Also in this case, no evidences of imide group is present in NMR and MS spectra. A more detailed study of these mixture by ^{1}H, ^{13}C NMR and MALDI-TOF is in progress.

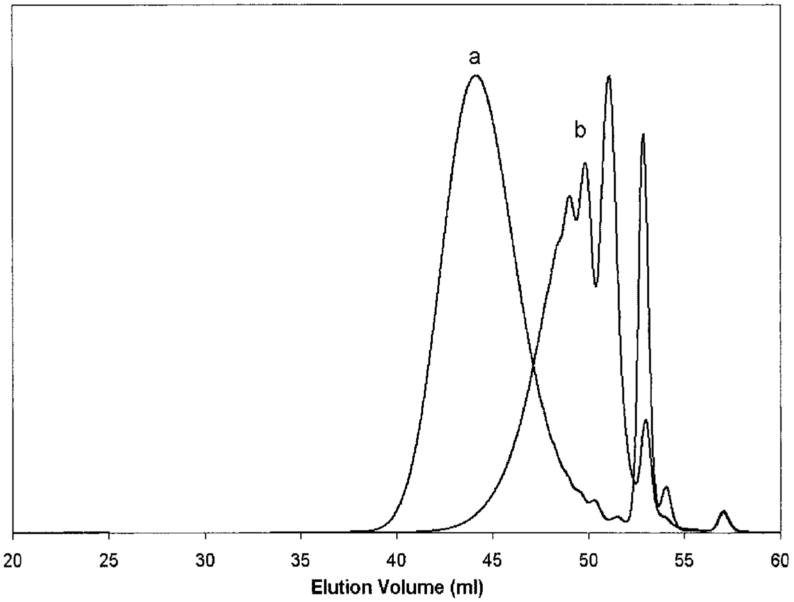


Fig. 11. SEC curve of T3/6–aminocaproic oligomers. a: AB/T3 = 18; b: AB/T3 = 4,5.

Two examples of oligomer distribution as obtained from end group analysis and ^{1}H NMR spectra are presented in table 2 for two different feed.

Table 2. Oligomer distribution from NMR data and end group analysis according to the model.

Sample	COOH (meq/Kg)	*T3*		*T3(NHR)*		$T3(NHR)_2$		$T3(NHR)_3$	
		NMR	model	NMR	model	NMR	model	NMR	model
AB/T3=4.5	5931.12	0.1869	0.1804	0.4094	0.4166	0.3140	0.3207	0.0897	0.823
AB/T3=18	1617.28	0	0.0051	0.0736	0.0738	0.3515	0.3542	0.5749	0.5669

The agreement between these data is excellent and confirm the assumption of equal reactivity of functional groups since the beginning of macromolecular chain growth independently of the chain length.

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