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Hyperbranched Aromatic Polyesters

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Summary: Having developed a theoretical model of hyperbranched polymerization involving AB_2 and B_2 monomers we present preliminary results of a test of its validity for the system consisting of 4,4-bis(4-hydroxyphenyl)pentanoic acid (AB_2 monomer) and bisphenol A (B_2 monomer). The monomers reacted at room temperature to yield the title hyperbranched polyesters. Diisopropylcarbodiimide (condensation water remover) along with an effective catalyst were used for that purpose. The total of AB_2 monomer was introduced at once to a reactor containing B_2 core monomer or it was divided into 3 or 5 equal portions and each of them introduced after the monomers previously present have reacted to a predetermined conversion. GPC measurements of the resulting molecular mass distribution gave inconclusive results because of poor reproducibility of polymer isolation/purification procedure and/or insufficient accuracy of GPC technique.

Keywords: AB2 monomer; molecular size distribution; monomer feeding; room-temperature polycondensation

Introduction

In the last twenty years, considerable effort of polymer chemists was devoted to preparation of nonlinear macromolecules having various, more or less regular, architectures. Among them were block copolymers, stars molecules, brushes, dendrimers, so called perfect networks, to name a few. Particularly interesting seemed to be regularly branched structures, such as dendrimers.[1] They were expected to become a kind of chemical nanomachines or nanocapsules capable of transporting certain active species, including drugs, to predetermined locations.[2] Most of these regular macromolecules were prepared using more or less tedious synthetic procedures making them rather expensive.

Highly branched polymers, in some aspects resembling the dendrimers, can be prepared following the procedure put forward more than half a century ago by Flory.[3] By condensation of a multifunctional monomer of AB_2 (or ARB_2) type, where A and B stand for functional groups capable of reacting with each other, one obtains a hyperbranched polymer[4] that share with dendrimers certain features, such as large number of terminal functional groups at the ends of macromolecules, good solubility, low solution and melt viscosity, and small hydrodynamic volume. These polymers are also particularly suitable multifunctional precursors of polymer networks.[5] On the other hand, the hyperbranched polymers have usually very broad size distribution as well and wide distribution of the topological structure of macromolecules. The size distribution of hyperbranched polymer prepared from AB_2 monomers can be controlled to some extent by:

- adding some proportion of a core monomer of B_g type, i.e. a monomer sharing the same B groups with AB_2 monomer ($g = 1, 2, \ldots$),[6,7]
- as above, but introducing AB_2 monomer to the reactor in portions or at a small rate,[8,9]

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– removing unreacted monomer and the smallest oligomers.[8]

In order to verify the methods of reducing the width of molecular size distribution in a condensation hyperbranched polymerization, we have developed a mathematical model that describes the time evolution of the polymerization system involving AB_2 and B_2 monomers.[10] We have also devised a model polymerization system yielding hyperbranched polyesters. The monomers and condensation promoting system was designed to carry on the reaction at room temperature. In this work we present preliminary results of the study, including the number- and weight-average molecular weights of hyperbranched polyesters prepared according to different reaction scenarios, as measured by GPC.

Theory

It is not difficult to see (cf. ref.[11]) that hyperbranched macromolecules formed in the system involving a mixture of AB_2 and B_2 monomers can be split into those containing a unit with exactly one unreacted A group (A-type molecules) and those containing exactly one core unit B_2 and, hence, no A group, anymore (B-type molecules). Let the entire degree-of-polymerization distribution of A-type molecules at a given moment of polymerization be described by the following counting function:

$$G(\tau, x) = \sum_{i=1}^{\infty} [i]_{\mathrm{A}} e^{ix}. \tag{1a}$$

Similarly, let the respective distribution of B-type molecules be:

$$G(\tau, x) = \sum_{i=1}^{\infty} [i]_{\mathrm{B}} e^{ix}. \tag{1b}$$

In Equation (1), the concentration of macromolecules of polymerization degree i, $[i]_{\mathrm{A}}$ or $[i]_{\mathrm{B}}$ is expressed as the number of molecules of the respective type, divided by the total number of units in the system and x is a dummy variable of no physical meaning ($|x| \leq 1$). The time τ is expressed in reduced units, so that the rate constant of the reaction between two monomers is taken as 1 or, in other words, $\tau = kt$, where t is the real time and k, the actual rate constant. The form of functions G and g makes it very easy to calculate the successive moments of distributions, simply by differentiation of (1) with respect to x, followed by setting $x = 0$. The zeroth moments (G_0 and g_0) are available by setting $x = 0$ directly into (1).

As shown in our previous papers,[8,11] the time evolution of the entire degree-of-polymerization distribution of macromolecules prepared in a random condensation polymerization reads:

$$\frac{\partial G}{\partial \tau} = \left(\frac{\partial G}{\partial x} + G\right)(G - G_0) - [G_x + G_0 + g_x + g_0]G \tag{2a}$$

and

$$\frac{\partial g}{\partial \tau} = \left(\frac{\partial g}{\partial x} + g\right)(G - G_0) \tag{2b}$$

where, as described above:

$$G_x = G_x(\tau) \equiv \left.\frac{\partial G}{\partial x}\right|_{x=0} = \sum_{i=1}^{\infty} i[i]_{\mathrm{A}} \quad \text{and} \quad g_x \equiv \left.\frac{\partial g}{\partial x}\right|_{x=0} = \sum_{i=1}^{\infty} i[i]_{\mathrm{B}}. \tag{3}$$

Explicit formulas for zeroth through to second moments of distribution, as they change with time or conversion have been derived[11] from Equation (2) with the initial concentration (fraction) of B_2 monomer being g_0 (the value of g_0 do not change with conversion since at most one B_2 unit per molecule may occur).

These formulas were used to examine how the synthetic procedure of carrying out the polymerization may affect the width of molecular size distribution.

One example of the results of such calculations is presented in Figure 1, where the calculated dispersity $D_m \equiv P_w/P_n = M_w/M_n$ (P being the average polymerization degree and M, average molecular weight) versus conversion of the minority A groups

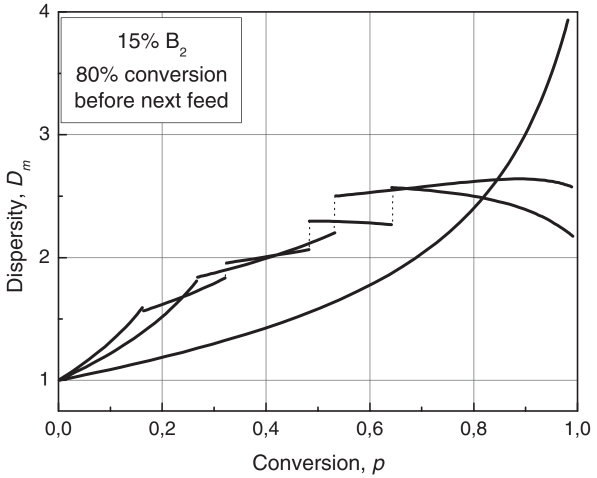


Figure 1.
The calculated dispersity of the macromolecules obtained by polymerization of 85 mol. % of AB_2 monomer and 15 mol. % of B_2 monomer versus conversion of A groups. The lowest curve corresponds to one-batch system. The other two curves were calculated for the semi-batch system with the whole amount of B_2 introduced at the start and with monomer AB_2 introduced in three or five portions, each next portion after 80% of the previously introduced A groups had reacted. The branches of curves are connected with dotted tie lines to facilitate keeping eye on the relationships.

is shown. Three procedures are compared each with the same fraction of B_2 monomer equal to 0.15.

In the simplest case, the calculations were made for polymerization carried out straight after mixing all monomers at once (the lowest curve). The other two calculation procedures were the following. Monomer AB_2 (85 mol. %) was divided into three or five portions. The first portion was introduced to the reactor with the total of B_2 monomer. The reaction of that mixture was carried out to 80 % conversion of A groups present, and then the new portion of AB_2 monomer was added. Again, the system was allowed in calculations to reach 80% conversion until the next feed of fresh monomer. The curve fragments in Figure 1 representing the semi-batch systems illustrate the jumps in dispersity after introducing the next portions of the monomer. The important finding, however, is that the final dispersity of the hyperbranched polymer is lower for the semi-batch system than for the single run system, where the dispersity of the resulting polymers quickly increases as the conversion degree approaches unity. The reason is that, in the former system, the molecules containing B_2 units are, on average, bigger than those with an A group that 'start anew' after each portion of AB_2 monomer has been introduced. As hyperbranched molecules that have a large number of B groups, B-type species grow faster in the semi-batch system than A-type ones. In the one run procedure, both A-type and B-type molecules grow simultaneously.[8]

Experimental Part

The system used in the experimental verification of the theory consisted of 4,4-bis(4-hydroxyphenyl)pentanoic acid (AB_2 monomer) and bisphenol A, i.e., 2,2-bis(4-hydroxyphenyl)propane (B_2 monomer). The polycondensation was carried out in solution at room temperature in the presence of 4-(N,N-dimethylamino) pyridine-4-toluenesulphonate (DPTS) catalyst and with N,N′-diisopropylcarbodiimide (DIC) as a condensation water remover. The solvent was freshly dried DMF. The catalyst DPTS and DIC were used in the amounts of 0.15 and 1.5 moles per mole of AB_2, respectively. DIC was introduced in several portions after all components had dissolved. The reaction mixture was continuously stirred for up to 4 days. Meanwhile, precipitation of N,N′-diisopropylurea (DPU) was observed. The polymer was isolated by filtering off DPU and pouring the filtrate into ice-cold water while vigorously stirring. The white precipitate was left until the next day and then filtered out and washed with ice-cold water. The polymer was dried and the averages of molecular weight and dispersity determined by GPC.

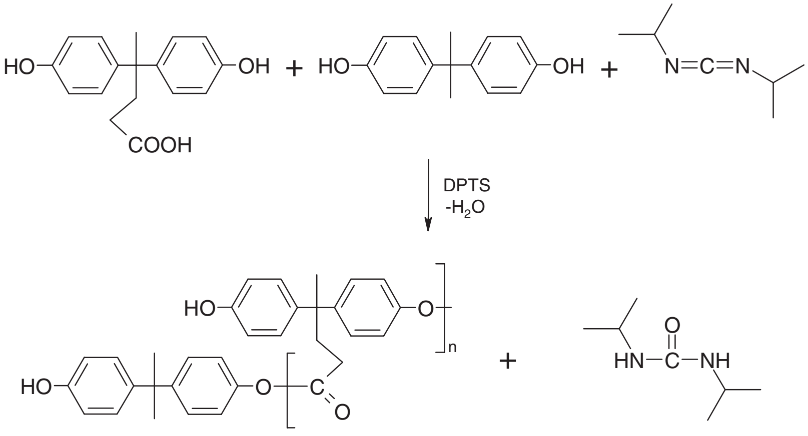
In the semi-batch experiments with monomer AB_2 divided into portions, the total amount of B_2 monomer was introduced at once together with the first portion of AB_2 monomer. At predetermined times (1, 24, or 96 hrs), small samples of reaction mixture were withdrawn, diluted with acetone and the content of unreacted carboxylic groups determined by titration to establish the conversion degree. Meanwhile, the next portion of AB_2 monomer along with the appropriate amounts of DMF, DPTS, and DIC were introduced into reactor. The polymer was isolated only after completing all the steps of a polycondensation.

The averages of molecular weight, M_n and M_w were determined using a GPC machine equipped with a PSS SDV 100 Å + 1000 Å + Guard column set (bead diameter 5 μm) and a Viscotec RI/RALLS/viscometer triple detector in THF. The data were processed with TriSEC v. 3.0 software.

The rate of polycondensation in the system used in this work was determined by ^{1}H NMR (Brucker 500 MHz). A sample of the composition corresponding to that used in typical polycondensation runs was placed in an NMR tube and immediately placed into the apparatus. Spectra were recorded every 15 min. and, later, every 30 min. The conversion of DIC was calculated using integrated signals of protons from CH_3 (1.20 ppm) or CH (3.57 ppm) in the isopropyl groups of DIC.

Results and Discussion

The polycondensation system used in this work is presented in Scheme 1. The system seems very convenient for studying the effect of feeding procedures, as analyzed in the theoretical model, on the molecular weight and width of size distribution of the resulting hyperbranched polymers. However, it should be pointed out that the use of

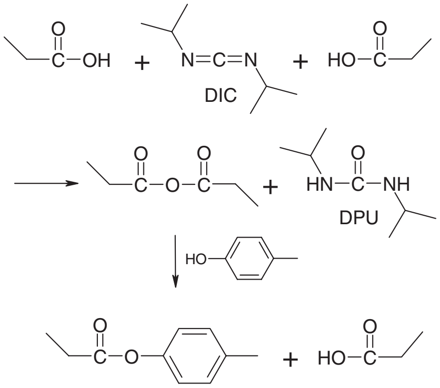


Scheme 1.
Polyesterification reaction with diisopropylcarbodiimide as water remover.

DIC condensation water remover changes the mechanism of polycondensation as compared with the classical polyesterification. According to Moore and Stupp[12], the esterification reaction in the presence of aliphatic or cycloaliphatic carbodiimide proceeds as described by Scheme 2.

Hence, anhydride groups are formed first. Then, they react with phenol OH to the final ester. The polyesterifacation cannot be regarded anymore as a series of the second order elementary reaction steps, implicitly assumed by the theoretical model based on the Smoluchowski coagulation equation. However, as shown long ago by Stockmayer[13], the statistical analysis based on the conversion of functional groups as the independent variable leads to the size distribution in the random polycondensation system exactly the same as that obtained by solving the Smoluchowski coagulation equation. In the present system, whatever the mechanism of individual reaction steps, the overall polycondensation reaction proceeds randomly and, hence, the distribution obtained from the Smoluchowski equation has to be correct, if expressed as the function of conversion degree rather than as a function of time.

The rate of conversion of carboxylic groups in the polycondensation deduced from the rate of disappearance of the signal from methyl or methine protons in isopropyl groups of DIC is shown in Figure 2. The signals from respective protons in DPU appear in different parts of spectra. Very rapid conversion takes place in the first hour of polycondensation. It exceeds 40%. Then, the conversion grows slightly slower and, finally, the rate curve levels at a conversion approaching ca. 80%.



Scheme 2.
The reaction between carboxylic and phenolic groups in the presence of DIC.

Typical GPC chromatograms of the hyperbranched polyesters obtained in this work are shown in Figure 3 and 4. The first figure shows how the monomer and individual oligomers disappear after each next portion of AB_2 monomer is added to the polymerization system.

It is interesting, though, that the high molecular fraction seen at the small retention volume side has a shoulder suggesting a bimodal distribution of molecular sizes. This has to be confirmed by some other method. A similar, although much less pronounced shoulder can be seen in Figure 4, at the retention volume of around 15 mL.

Figure 4 illustrates reproducibility of the whole polycondensation and characterization procedure including polymer isolation. The chromatograms presented there were recorded for three samples of hyperbranched polymers prepared in different, but identical polycondensation runs. Only the differential refraction index signal is shown.

It is seen that the three curves in Figure 4 are not identical. Also the molecular parameters shown in the insert that were calculated using the TriSEC® software which processes also the results from viscometric and RALLS detectors differ among themselves quite significantly.

Collected results of dispersity measurements in the system with 10% of B_2 monomer, but prepared according to different procedures: in one step (for 96 hrs.) and with AB_2 monomer divided into three or five portions, each next introduced 1, 24, or 96 hrs. after the previous one.

Theoretical predictions like those shown in Figure 1 suggest that the larger number of portions that is used and the higher the conversion of functional groups before the

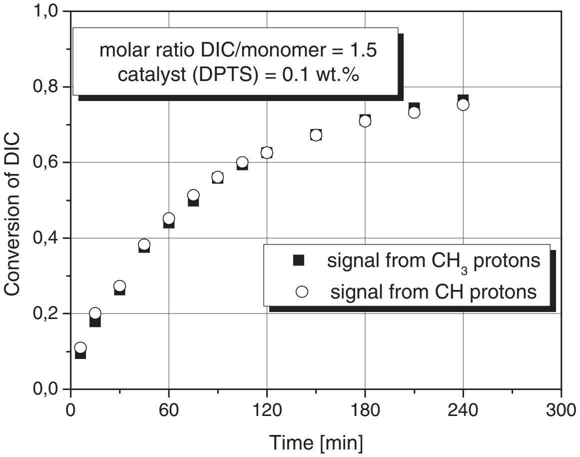


Figure 2.
Conversion of diisopropylcarbodiimide (DIC) vs. time in the room-temperature polycondensation of 4,4-bis(4-hydroxyphenyl)pentanoic acid as measured by ^{1}H NMR.

next monomer portion, the more reduced is the final dispersity of molecular weight that would be expected. The results presented in Figure 5 do not confirm these predictions, but in view of the attainable precision of the present measurements, the dispersity figure bears too large an error to confirm or disprove the theory. The dispersity has been shown[8] to be very sensitive to the amount of unreacted monomer left in the polymer. This smallest component of the polymer is most likely to be lost in an uncontrolled way

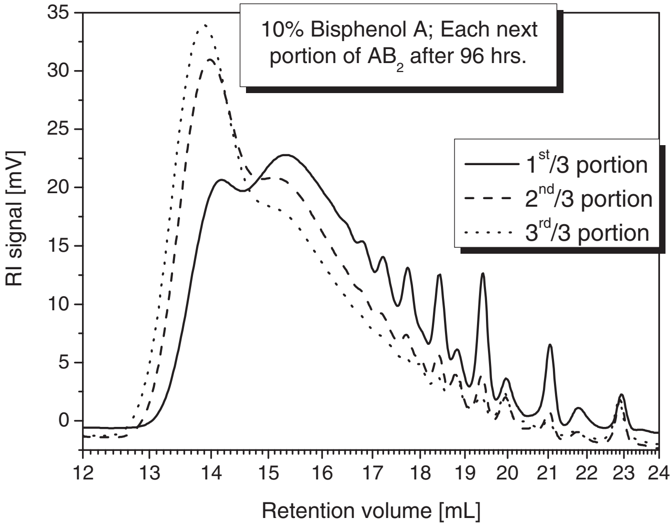


Figure 3.
GPC chromatograms of hyperbranched polymers of 4,4-bis(4-hydroxyphenyl)pentanoic acid with bisphenol A as a core monomer. The chromatograms were recorded after completing the reaction for each of 3 equal portions of monomer.

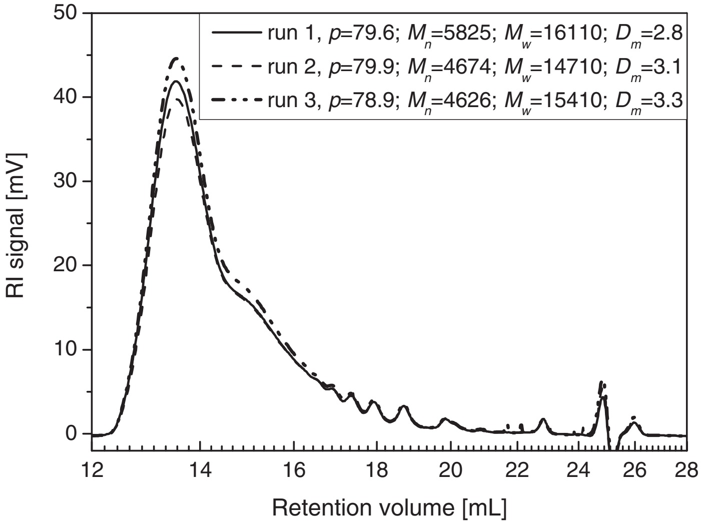


Figure 4.
The chromatograms recorded for three identical runs with almost the same final conversion of 4,4-bis(4-hydroxyphenyl)pentanoic acid (no core monomer). The reproducibility of dispersity D_m is not better than 15%.

during post polymerization processing of the product. Future experiments will be carried out with particular attention paid to this problem, i.e. a standardized procedure of polymer isolation will be applied. Other techniques for verification of the molecular masses will also be applied to confirm the data produced by GPC.

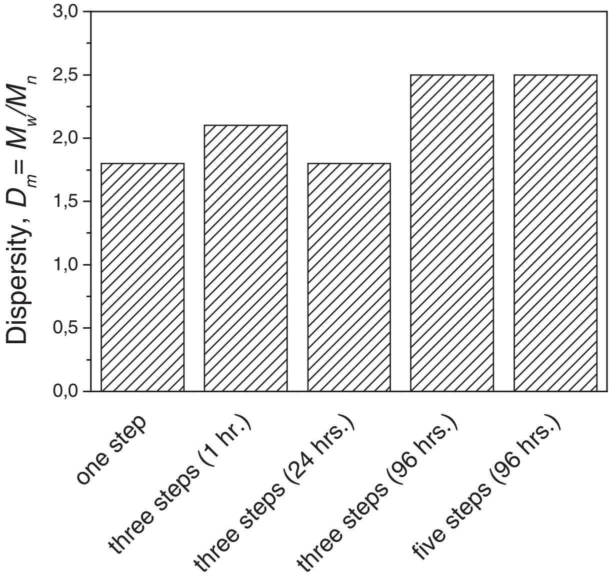


Figure 5.
Dispersities of hyperbranched polymers prepared at different feeding schedules. The molar fraction of core B_2 monomer: $g_0 = 0.10$.

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