

HYPERBRANCHED METHACRYLATES BY SELF-CONDENSING GROUP TRANSFER POLYMERIZATION

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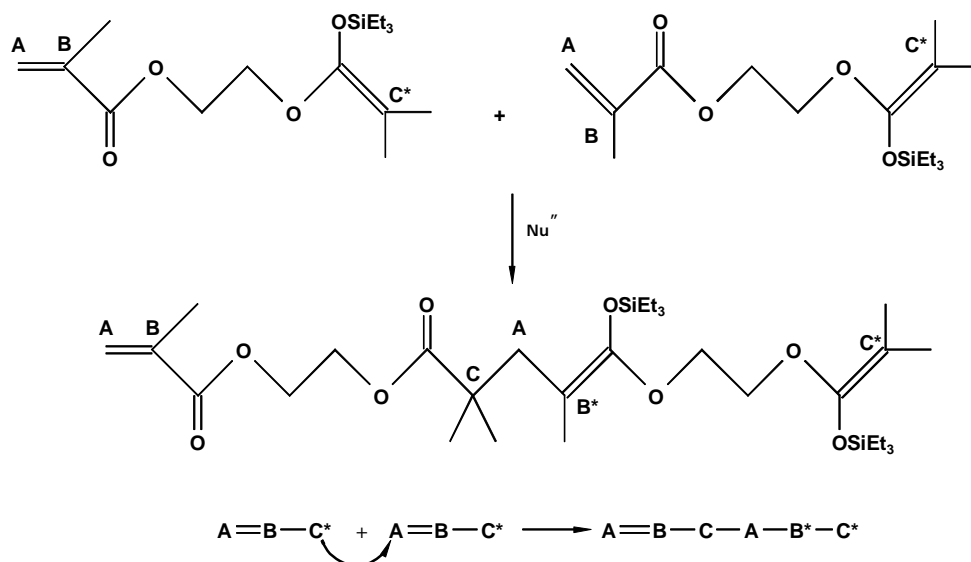
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Introduction

In the last decade, branched polymers have become a topic of scientific and industrial interest. Much has been achieved in the preparation of three-dimensional structures such as comb- and star-shaped polymers and dendrimers. The highly defined structure of the latter stimulated interest in the dendritic structures, although the preparation is rather sophisticated and time-consuming. A simple way to obtain highly branched structures is based on the ideas published by Flory¹ in 1953. He proposed that the condensation of monomers with AB₂ or AB_n functionality would lead to "highly branched" structures without the occurrence of gelation. The first synthesis of a "hyperbranched" polymer was reported in 1990 by Kim and Webster² using (3,5-dibromophenyl)boronic acid in a polycondensation reaction. Since then, the preparation of hyperbranched structures became a field of considerable interest.

Recently, Fréchet et al.^{3,4} reported a new way of forming hyperbranched polymers, i.e. the so-called self-condensing vinyl polymerization (SCVP). This reaction involves a monomer of the general structure A=B-C*, where C* is a group capable of initiating the polymerization of vinyl groups, A=B. The process is initiated by the addition of a C* group to the double bond of another monomer, leading to a dimer with two active sites, B* and C*, and one double bond, A=B (cf. Scheme 1). Both the initiating C* and the newly created B* groups can react with vinyl groups of other molecules in the same way. Theoretical calculations⁵ show that the molecular weight distributions of the polymers formed in this way are somewhat broader and the maximum degree of branching is slightly smaller than for an AB₂ system. SCVP has been applied to various kinds of living polymerization, i.e. cationic^{3,4}, radical⁶, and atom transfer radical polymerization.⁷ However, anionic or group transfer polymerization have not yet been applied for SCVP.

We here present a novel route to hyperbranched polymethacrylates using group transfer polymerization. 2-(2-methyl-1-triethylsiloxy-1-propenyl-oxy)ethyl methacrylate (MTSHEMA) was used as the monomer where A=B is a methacryloyl group and C* is a silylketene acetal which is activated by a nucleophilic catalyst.



Scheme 1: Initiation of Self-Condensing GTP of MTSHEMA. The dimer formed can react further with monomer or dimer to yield trimers and tetramers, etc.

Synthesis of Hyperbranched Polymers

The monomer MTSHEMA was prepared by partial hydrosilylation of ethyleneglycol dimethacrylate⁸ using chlorotris(triphenylphosphine)-rhodium(I) as catalyst in 60 % yield (b. p. 85 °C / 3.5*10⁻² mbar).

The polymerization of MTSHEMA (0.5 M solution in THF) was initiated by addition of tetrabutylammonium bibenzoate (1 % with respect to monomer) at +20 °C. GC measurements showed a complete conversion of the monomer within 2 minutes. The polymerization at room temperature yielded oily substances with rather low molecular weights.

In order to test the stability of the active centers for prolonged reaction times, a PMTSHEMA solution was allowed to stand for two days under inert conditions. Addition of fresh methyl methacrylate (MMA) lead to a significant increase of the viscosity of the solution. After 20 minutes, no MMA was detectable by GC, indicating a complete conversion of the monomer used. The copolymer prepared by this manner showed a strongly increased molecular weight. This demonstrates that the propagating centers of PMTSHEMA can initiate the polymerization of suitable monomers, giving "hyperstar" polymers.⁶ Hyperbranched macromolecules can therefore be used as multifunctional initiating cores for the formation of multiarm star polymers.

In order to test the effect of sterical hindrance at the propagation sites, a bulk copolymerization of MTSHEMA with an equimolar amount of MMA was conducted at room temperature. Again, GC measurements indicate the complete conversion of the two monomers. The copolymerization with MMA showed no significant effect on the molecular weights obtained.

Running the reaction at lower temperatures, e.g. -50 °C, strongly increased the molecular weights of the hyperbranched polymers. In contrast to the rather low molecular species at room temperature, the molecular weights were considerably higher (see below). Surprisingly, kinetic meas-

measurements showed, that the degree of polymerization reaches a maximum at short reaction times (4 min) and then decreases rapidly (cf. Fig. 1)

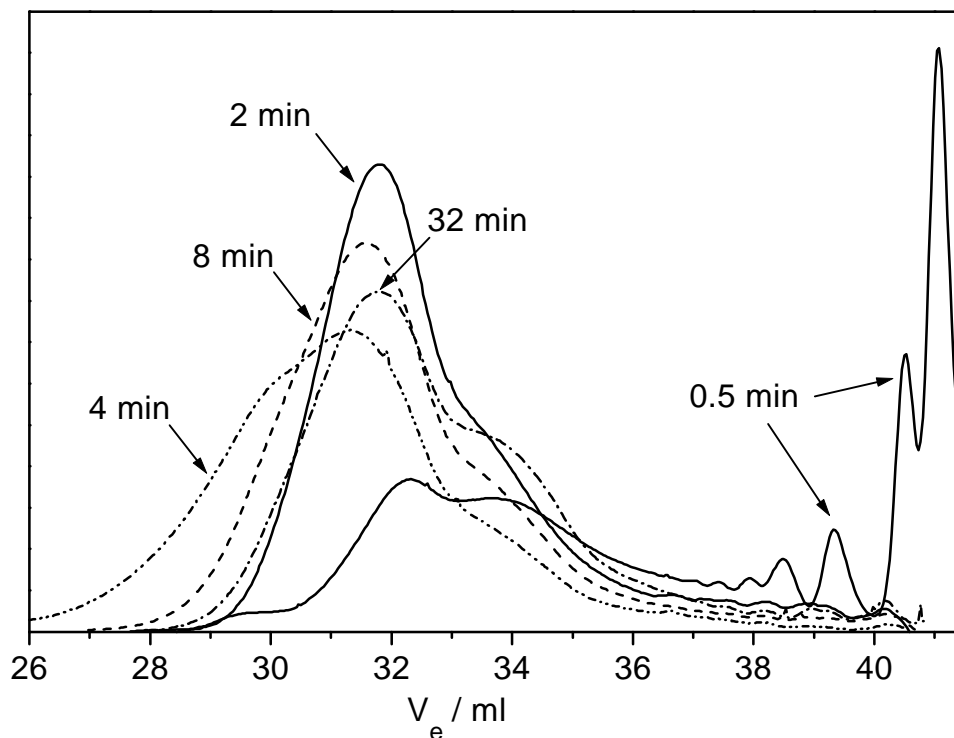
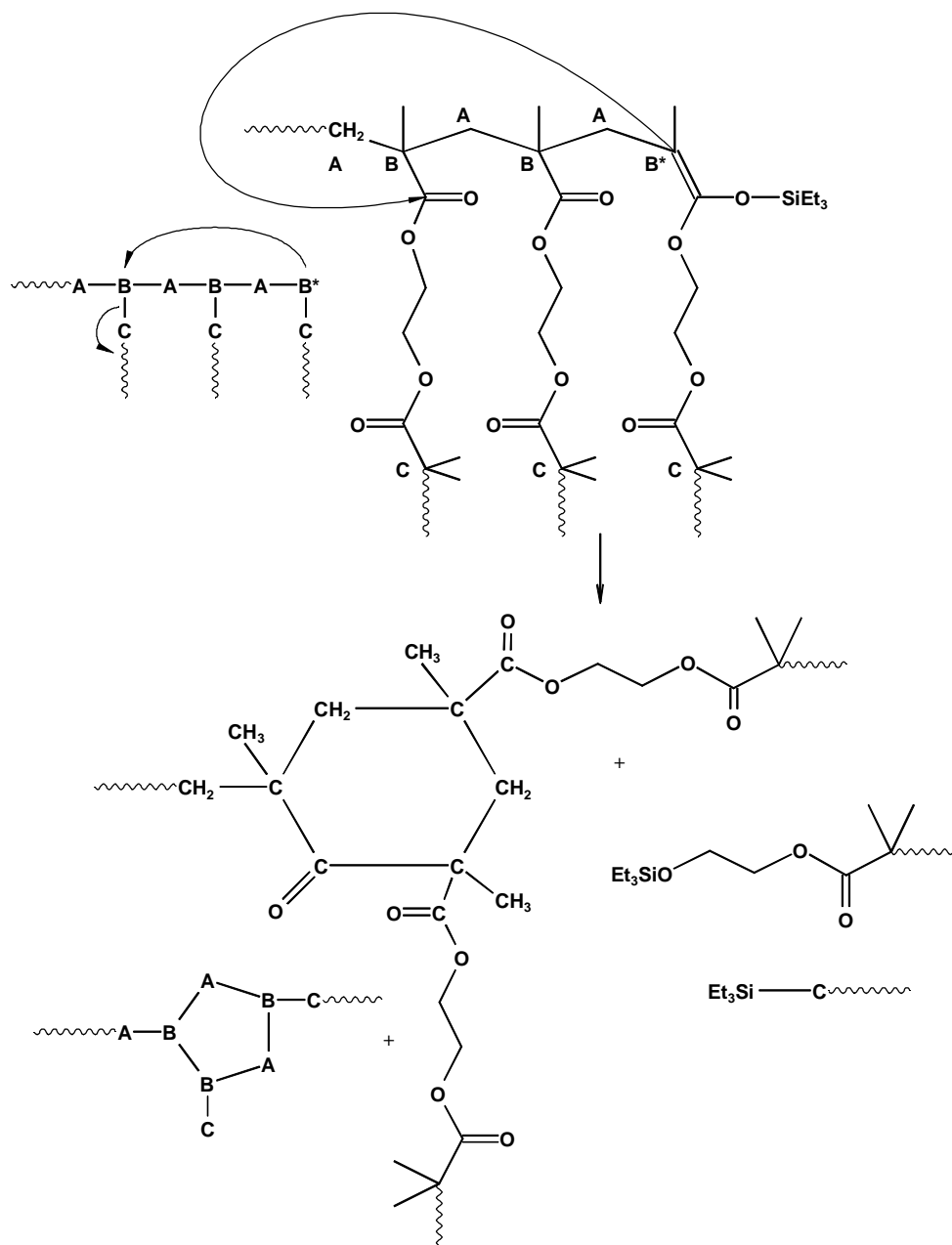


Fig. 1: Eluograms of polymers formed in the self-condensing GTP of MTSHEMA at -50 °C

Considerations about the major termination pathway in GTP – the "back-biting" process in which a living chain end, i.e. nucleophilic moiety, attacks a carbonyl carbon atom yielding a cyclic β -ketoester and silylether – showed that this mechanism could explain the unexpected decrease of the molecular weight with reaction time. Contrary to a linear polymer which contains one living chain end per molecule, the mechanism of SCVP leads to one active center, B* or C*, per monomer unit; cf. Scheme 1. Moreover, the polymer PMTSHEMA contains two different kinds of carbonyl groups, each of which can be attacked by a B* or C* group in the back-biting process. Taking into account that this reaction can occur not only at the end of a chain but also somewhere inside the molecule, a "back-biting" reaction of this type would not only lead to the usual low molecular weight silylethers – as obtained by normal GTP – but to polymeric silylethers as shown in Scheme 2, causing whole branches of the polymer to be detached. This decreases the molecular weight of the polymer considerably. On-line SEC-UV, MALDI-TOF and FT-IR measurements of the obtained polymers give strong evidence for the existence of β -ketoesters.



Scheme 2: Example of the "back-biting" reaction for PMTSEMA. The letters denote different types of active centers

Synthesis of a Linear Analogue

In order to compare the properties of the hyperbranched methacrylate with those of a linear polymer one needs a suitable linear analogue. In principle, two linear analogues of PMTSEMA are conceivable, resulting from different possibilities of active centers to add to the vinyl groups. One limiting case would result from consecutive B* additions and yield a vinyl polymer, i.e. poly(2-[isobutyryl]ethyl methacrylate) (PIBHEMA), the other one would arise from consecutive C* additions and give a polyester like-polymer (cf. Scheme 1).

IBHEMA was prepared from 2-hydroxyethyl methacrylate and isobutyric acid chloride in the presence of triethylamine⁹ in a yield of 82 % (b. p. 45 C / 0.55 mbar). In order to obtain PIBHEMA with a broad molecu-

lar weight distribution which is favorable for establishing a calibration curve by universal calibration and SEC-light scattering, IBHEMA was polymerized radically (1 M solution in toluene, 1 % dibenzoylperoxide, 36 h). The resulting polymer had a molecular weight of $M_w = 185,000$ and a polydispersity index, $M_w/M_n = 10$ (SEC with universal calibration).

Characterization

For both polymers, the determination of the molecular weight distributions by SEC of is complicated by the lack of suitable standards. Universal calibration¹⁰ presents a possibility to determine molecular weights even without standards. Using an on-line viscosity detector,¹¹ absolute molecular weights and the Mark-Houwink coefficients of PMTSEMA and PIBHEMA were determined. In addition, on-line light-scattering measurements were performed to cross-check the viscosity results.

Absolute calibration curves for both polymers were constructed using SEC-viscometry and SEC-light scattering, respectively (Fig. 2). The calibration curve for PIBHEMA shows for lower elution volumes a slight difference to the PMMA calibration curve. In comparison to PIBHEMA, the calibration curve for PMTSEMA is strongly shifted to higher molecular weights, due to the lower hydrodynamic volume of the branched structure.

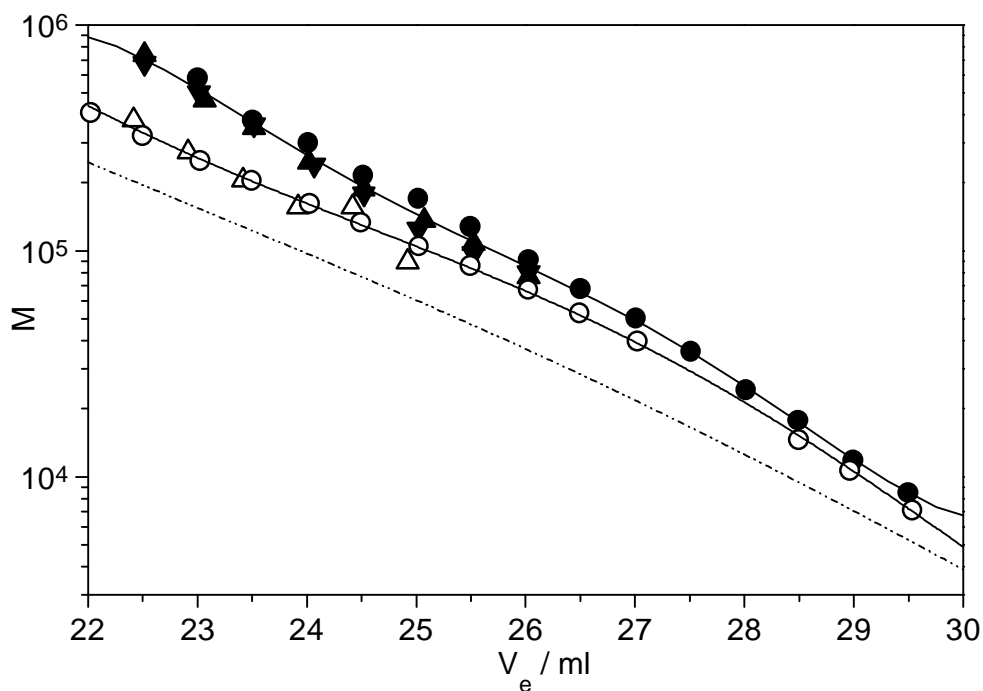


Fig. 2: SEC calibration curves of PIBHEMA (∇) and PMTSEMA (\circ) compared to that for linear PMMA (---); (\bullet) SEC-viscosity data (\blacklozenge) SEC-LS data: A different column set than in Fig. 1 was used.

From the measured intrinsic viscosities and the molecular weights obtained from universal calibration, Mark-Houwink plots were established for both polymers, cf. Fig. 3.

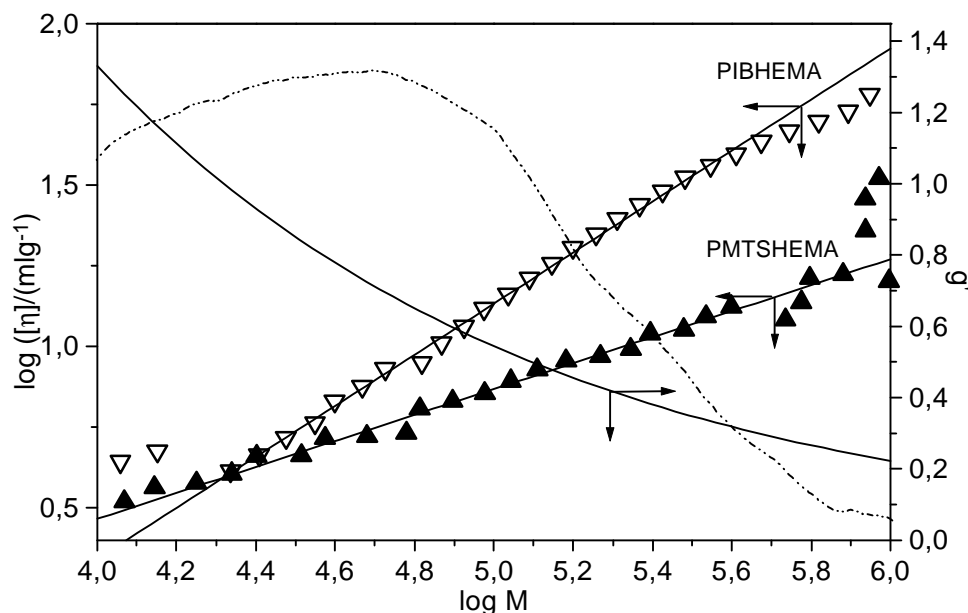


Fig. 3: Mark-Houwink plots for PMTSHEMA (\blacktriangle) and PIBHEMA (∇) and contraction factors (—): $g' = [\eta]_{br}/[\eta]_{lin}$; (·····): RI signal of PMTSHEMA prepared at $-50\text{ }^{\circ}\text{C}$ (32 min; $M_w = 87,000$; $M_w/M_n = 4.4$).

The low value of the Mark-Houwink exponent found for PMTSHEMA ($\alpha = 0.40$) compared to PIBHEMA ($\alpha = 0.79$) shows undoubtedly a densely packed three-dimensional structure resulting from the hyperbranched topology.

Contraction factors¹¹ $g' = [\eta]_{br}/[\eta]_{lin}$ were calculated from the Mark-Houwink plots and are given in Fig. 3. It becomes clear, that the density of the hyperbranched polymer increases with molecular weight. This is a consequence of the fact that the degree of branching increases with increasing conversion of vinyl groups.⁵ However, it should be mentioned that PIBHEMA is a poor linear analogue for low molecular weights, since a polyester-like polymer (cf. Scheme 1) would better describe a linear structure.

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