

Self-Encapsulation, Acceleration and Control in the Radical Polymerization of Monodendritic Monomers via Self-Assembly

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Monodendritic building blocks are employed in the construction of supramolecular systems with complex architecture and shape via homopolymerization and copolymerization.¹ We reported the self-assembly of 12 second-generation conical monodendrons, 12G2-AG, into a spherical supramolecular dendrimer which self-organizes in a cubic Pm $\bar{3}$ n three-dimensional (3D) liquid crystalline (LC) lattice.² The attachment of methacrylate (12G2-AG-MA) and styrene (12G2-AG-S) to 12G2-AG followed by radical initiation yields, depending on the degree of polymerization (DP), spherical (DP < 20) and cylindrical (DP > 20) polymers (Scheme 1). The spherical polymers self-organize in the same cubic Pm $\bar{3}$ n 3D lattice while the cylindrical ones in a p6mm columnar hexagonal 2D LC lattice.³ Three laboratories reported that polymerization of monomeric monodendrons, which do not self-assemble in ordered structures, yield high DP polymers only when a spacer is inserted between the polymerizable and the monodendritic groups and after very long reaction times.⁴ Here we report a dramatic self-acceleration of the radical polymerization of 12G2-AG-S and 12G2-AG-MA containing no spacer in the self-assembled state and its application to their controlled polymerization both in the range of high (>20) and low (<20) DPs. A mechanism for this polymerization is proposed.

A sharp increase of the rate of polymerization (R_p) of 12G2-AG-S initiated with AIBN at 60 °C on increasing concentration, $[M]_0$, above 0.20 mol/L (i.e., 44.3 g/100 mL) is obtained (Figure 1a). This is consistent with a self-assembly which creates a supramolecular reactor of enhanced polymerizable groups concentration.^{2,3} Kinetics of polymerization below and above $[M]_0 = 0.20$ mol/L differs. We will discuss the kinetics above $[M]_0 = 0.20$ mol/L. Experiments for different $[M]_0/[AIBN]_0$ of 12G2-AG-S and 12G2-AG-MA (Figure 1b,c) carried out with $[M]_0 = 0.44$ mol/L (i.e., in bulk) at 90 °C showed a maximum conversion within about 10 min. The M_{peak} (GPC) of 12G2-AG-PS is in the range of 3.12×10^5 with $M_w/M_n = 2.40$, while that of 12G2-AG-PMA is 6.87×10^6 with $M_w/M_n = 3.30$. M_w by light scattering is from two, for 12G2-AG-PS, to six, for 12G2-AG-PMA, times larger. The orders of reaction of R_p in $[M]$ are in Table 1 and Figure 8 (Supporting Information). First

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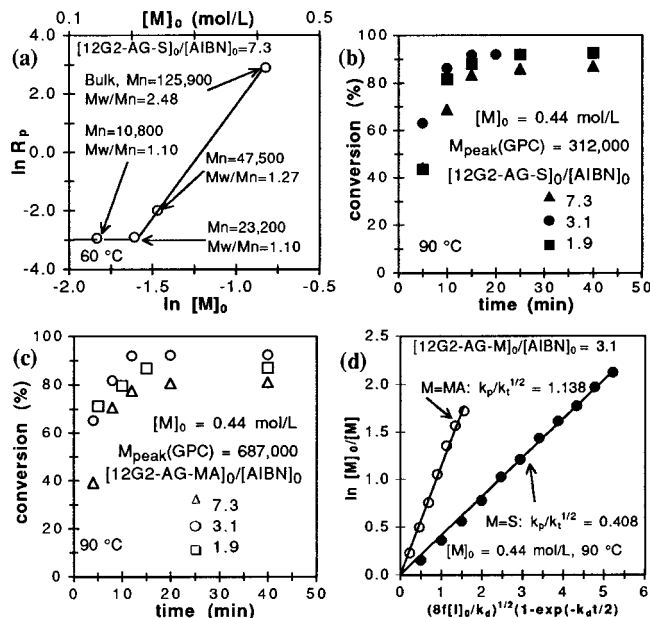


Figure 1. Dependence of $\ln R_p$ on $\ln [M]_0$ for the polymerization of 12G2-AG-S (in benzene and bulk) (a); conversion in time for the bulk ($[M]_0 = 0.44$ mol/L) polymerization of 12G2-AG-S (b) and of 12G2-AG-MA (c); and determination of the $k_p/k_t^{1/2}$ for the polymerization of 12G2-AG-S (●) and 12G2-AG-MA (○) (d).

Scheme 1

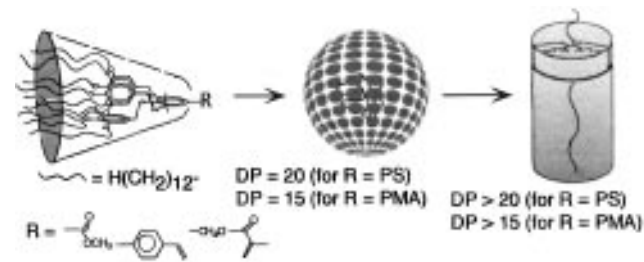


Table 1. Order of R_p in $[M]$ (x) for the Radical Polymerization of 12G2-AG-S and 12G2-AG-MA ($R_p = k_p[M]^x[I]^{1-x}$)

monomer	initiator	T (°C)	$[M]_0$ (mol/L)	$[M]_0/[I]_0$ (mol/mol)	$t_{1/2}$	x	mechanism ^a
12G2-AG-MA	AIBN	60	0.15	1.9	22 h	2	PRT
12G2-AG-S	AIBN	60	0.15	1.9	22 h	2	PRT
12G2-AG-MA	AIBN	90	0.44	7.3	25 min	3	DC
12G2-AG-MA	AIBN	90	0.44	3.1	25 min	1	TC
12G2-AG-MA	AIBN	90	0.44	1.9	25 min	2.7	DC
12G2-AG-S	AIBN	90	0.44	7.3	25 min	1.6	PRT
12G2-AG-S	AIBN	90	0.44	1.9	25 min	2	PRT
12G2-AG-MA	BPO	90	0.44	13, 25	100 min	1	TC
12G2-AG-S	BPO	90	0.44	13, 25	100 min	1	TC
12G2-AG-MA	tBuPO	90	0.44	7, 13, 25	35 days	0	SI

^a Key: PRT, primary radicals termination; DC, diffusion controlled polymerization; TC, termination by combination; SI, slow initiation.

order ($x = 1$) demonstrates termination by combination.⁵ Termination by primary radicals⁶ is indicated by $x = 2$. Zero order ($x = 0$) and $x > 2$ are of no interest for this discussion.⁷ When $x = 1$ we determine $k_p/k_t^{1/2}$ (Figure 1d) from eq 1.⁵

$$a = \ln \frac{[M]_0}{[M]} = k_p \left(\frac{8f}{k_d k_t} [I]_0 \right)^{1/2} (1 - \exp(-k_d/2)) = b \frac{k_p}{(k_t)^{1/2}} \quad (1)$$

Table 1 summarizes x values for different conditions and shows that x depends on the nature of I, the ratio $[M]_0/[I]_0$ and $[M]_0$. Table 2 compares $k_p/k_t^{1/2}$ for the polymerization of 12G2-AG-S, of 12G2-AG-MA, and of their low molar mass models,

Table 2. Kinetic Data for the Radical Polymerization of 12G2-AG-S, 12G2-AG-MA, S, and MMA^a

monomer	$k_p/k_t^{1/2}$ (s ^{-1/2} mol ⁻¹ L)	f	DP _{th} ^b	DP	MW GPC ^c or LS-SEC ^d
MMA	0.049	0.99	4	4	401 ^c
12G2-AG-MA	1.132	0.11	1208	1270	2 735 100 ^d
S	0.033	0.8	4	4	416 ^c
12G2-AG-S	0.408	0.55	214	236	522 900 ^d

^a [M]₀ = 0.44 mol/L, [AIBN]₀ = 0.14 mol/L, 90 °C, solvent for S, cyclohexanone and for MMA, *p*-xylene. ^b Calculated using eq 2 with $t = 1$ min and $k_d = 4.8 \times 10^{-4}$ s⁻¹ mol⁻¹ L.

styrene (S) and methyl methacrylate (MMA). Under identical conditions, $k_p/k_t^{1/2}$ for 12G2-AG-S and 12G2-AG-MA are more than 1 order of magnitude higher than the values for S and MMA. DPs of the polymers derived from monodendrons are between 50 and 300 times and the corresponding molecular weights 10^3 and 5×10^4 times larger than those of PS and PMMA. The large DPs obtained above critical [M]₀ with low [M]₀/[I]₀ ratios imply a low initiator efficiency (f). Below critical [M]₀ and at low [M]₀/[I]₀ ratios, in ideal solution, the high f is reestablished. Therefore, as expected only low DP poly(monodendron)s (Figure 1a) are obtained, even at high conversion. The difference between $k_p/k_t^{1/2}$ and DP values of the two series of monomers, at [M]₀ and [I]₀ corresponding to bulk concentrations of monodendrons (Table 2), demonstrates much lower f values (calculated⁵ by eq 2) for 12G2-AG-S and 12G2-AG-MA than for S and MMA. These results support the

$$v(t) = \frac{DP}{2} = \frac{k_p}{\sqrt{k_t}} \frac{[M]_0(1-p)}{[2fk_d[I]_0(1-\exp(-k_d t))]^{1/2}} \quad (2)$$

following mechanism. Above a critical [M]₀, the dendritic monomers self-assemble in spherical supermolecules providing a *reactor* of enhanced polymerizable groups concentration. At DP > 20, this *reactor* becomes cylindrical.^{2b} In both cases, it resembles a capsule or a cagelike environment in which the polymerizable groups are jacketed by their own dendritic coat.^{2,3} Due to the high mass of the dendritic monomers (MW = 2215.6 for 12G2-AG-S and 2153.6 for 12G2-AG-MA) their molar concentration for the same weight percent concentration as of S and MMA is 20.0 and respectively 21.4 times lower. The increased concentration at the polymerization place increases dramatically R_p and decreases f since the polymerizable groups are located in a very small volume fraction while the radical initiator is distributed uniformly in the reaction mixture. The high mass of monodendrons and their self-assembly forces slow their diffusion. Slow diffusion is supported by the plateau of conversion in time (Figure 1b,c) which demonstrates the inability of the monodendrons to migrate from their assembly to the reactive growing chain. The high DPs of the poly(monodendron)s require not only low f values but also a decreased k_t , which assumes that polymerization experiments initiated with higher half-life time initiators than AIBN should produce a living-like dependence of DP on conversion. The low k_t is demonstrated by the conversion in time and molecular weight conversion plots from Figure 2. Depending on reaction conditions, a linear dependence of M_{peak} on conversion is observed. These plots support a controlled polymerization⁸ with slow initiation. The low k_t is supported by the low DP (5–11) and very narrow polydispersity ($M_w/M_n = 1.10$ for 12G2-AG-PS, Figure 1a, and 1.06 for 12G2-AG-PMA)³ of the poly(monodendron)s obtained at [M]₀ < 0.20 mol/L.

Increased $k_p/k_t^{1/2}$ was previously observed in radical polymerization of monomers with bulky substituents.⁹ This was explained by a decrease of k_p and an even larger decrease of k_t .

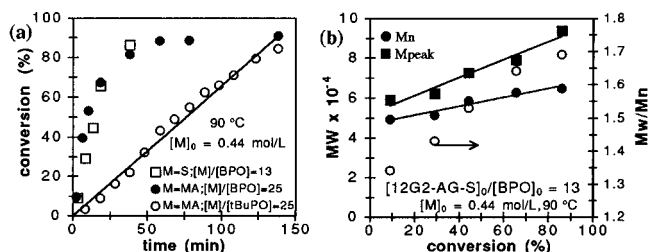


Figure 2. Conversion in time for the bulk polymerization of 12G2-AG-S and 12G2-AG-MA (a) and dependence of M_n , M_{peak} , and M_w/M_n on conversion for the bulk polymerization of 12G2-AG-S and 12G2-AG-MA (experimental conditions are on the figure) (b). Conversion in time plots for the experiments b are in a.

However, these monomers can diffuse, f is high and high DP were obtained only with low [I]₀ and at very long reaction time. An increased R_p was reported for the radical polymerization of LC or isotropic monomers in a LC solvent.¹⁰ Slow diffusion of monomer, orientation and spatial aggregation increased its concentration and decreased k_t while k_p was less affected. Diffusion controlled polymerization with low f , primary radical termination, low R_p and conversion, was observed for macromonomers¹¹ and lipids.⁶

The polymerization process reported here borrows features from all nonclassic radical polymerizations. Self-assembly and self-organization with slow monomer diffusion produce an increased concentration of polymerizable groups, a low f , and steric hindrance around the rigid³ and crowded growing chain generates a low k_t . This combination of effects yields high DP poly(monodendron)s in very high conversion and short reaction time (3 to 5 min) (Table 2) by using short half-life time initiators (AIBN at 90 °C, $t_{1/2} = 25$ min) and [M]₀ > 0.20 mol/L. Alternatively, long half-life time initiators (BPO, $t_{1/2} = 100$ min, and tBuPO $t_{1/2} = 35$ days) yield a controlled polymerization. When this polymerization is carried out in dilute ideal solution (i.e., [M]₀ < 0.20 mol/L) the diffusion of the monomer and f increase. Nevertheless, the high concentration of radicals and low k_t produce almost monodisperse polymers (i.e., $M_w/M_n = 1.06$ –1.10) of low DP (Figure 1a).³

Previous radical polymerizations of monodendrons are divided into two classes. The first class is marked by the inability to polymerize in ideal solution due to steric hindrance.⁴ These monodendrons do not self-assemble. Second class is noted by accomplishing high DP polymers in ideal solution^{1d,f} or in melt^{4c} from monomers containing a flexible spacer. Both monodendrons which do^{1d,f} and do not^{4c} self-assemble were polymerized in this case. This polymerization follows a conventional mechanism requiring very long reaction time and low [I]₀. High DP polymers were also obtained by metal-catalyzed and living metathesis polymerization of phenylacetylene^{1e} and oxanorborene monodendrons.^{1f} The unusual combination of kinetics reported here accesses the control of radical polymerization of large but self-assembling monodendrons in the range of low and high DPs without the need of spacer between the polymerizable and dendritic groups. In the present case, a *reactor* is generated by jacketing the polymerizable groups with their own dendritic coat. Therefore, we refer to this unprecedented polymerization^{7,8} as being *self-encapsulated*, *self-accelerated* and *self-controlled*.

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Supporting Information Available: Synthesis of monomers and kinetic plots (14 pages). See any current masthead page for ordering and Internet access instructions.

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