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3D Single Cyclized Polymer Chain Structure from Controlled Polymerization of Multi-Vinyl Monomers: Beyond Flory−Stockmayer Theory

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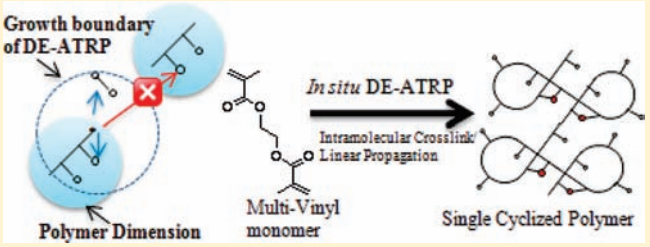
Supporting Information

ABSTRACT: Controlled/living radical polymerization (CRP) is a widely used technique that allows the synthesis of defined polymer architectures through precise control of molecular weights and distributions. However, the architectures of polymers prepared by the CRP techniques are limited to linear, cross-linked, and branched/dendritic structures. Here, we report the preparation of a new 3D single cyclized polymer chain structure from an in situ deactivation enhanced atom transfer radical polymerization of multivinyl monomers (MVMs), which are conventionally used for the production of branched/cross-linked polymeric materials as defined by P. Flory and W. Stockmayer nearly 70 years ago. We provide new evidence to demonstrate that it is possible to kinetically control both the macromolecular architecture and the critical gelling point in the polymerization of MVMs, suggesting the classical Flory−Stockmayer mean field theory should be supplemented with a new kinetic theory based on the space and instantaneous growth boundary concept.



INTRODUCTION

The introduction of living polymerization and controlled/living radical polymerization (CRP), now considered to have formed the foundation of modern polymer nanotechnology, led to a great advancement in both synthetic polymer chemistry and polymer physics.[1−4] CRP allowed such tight control over molecular weight and distribution that new well-defined polymer architectures and topologies can be produced.[5−7] Despite significant advances in CRP polymerization methods,[8−10] the architectures of polymers prepared by CRP techniques are still limited to linear, cross-linked, branched, or dendritic structures.[11−17] It is well-known that the polymerizations of multivinyl monomers (MVMs) have been commonly used to produce cross-linked polymeric materials as predicted by P. Flory and W. Stockmayer.[18−23] Recently, the rising interest in the polymerizations with MVMs has opened doors for wider applications, among these are the largely classical branched polymeric structures that have been reported from copolymerization using low proportion of MVMs as branching agents (part A of Figure 1).[24−30] Such kind of polymerizations are still claimed to obey the model and prediction of the Flory−Stockmayer mean field theory (F−S theory).[31]

In 1941, P. Flory had combined experimental observations with mathematical descriptions to construct a theoretical view — P. Flory's mean-field theory for determining gelation and critical extent of polycondensation reaction.[18−20] Two years later, it was extended and applied to homo- or (co)polymerization of MVMs by W. Stockmayer, termed as F−S theory.[21−23] The first assumption of F−S theory is that at any stage during the reaction, all vinyl groups are considered to be equally reactive in the reaction.[18] The second assumption is that the intramolecular reactions are neglected, in other words, the cyclization reactions are not considered[18,22] in F−S theory. W. Stockmayer thought that the fraction of pendant vinyl groups within the active growing chain is statistically negligible compared to the total amount of vinyl groups in other polymer chains and residual monomers.[23] Thus, the polymerization and gelation process of MVMs in F−S theory is, put simply, presumably a combination of linear polymer chains (part A of Figure 1). The F−S theory has been widely applied to the prediction of the gel point in addition polymerizations for example free radical polymerization (FRP) and CRP of MVMs.[32−34] However, soon after its introduction, some compromising data under certain reaction conditions showed critical gel points far higher than the F−S theory predicted.[35,36] On the basis of the F−S theory, it is believed from most recent studies that the intramolecular reactions can be suppressed when using CRP compared to FRP,[32] leading to the synthesis of polymers with various branched/cross-linked architectures from the polymerization of MVMs via CRP. However, herein, we report the generation of a new class of polymer structure — a 3D single cyclized polymer chain structure (part B of Figure 1) from a novel polymerization process

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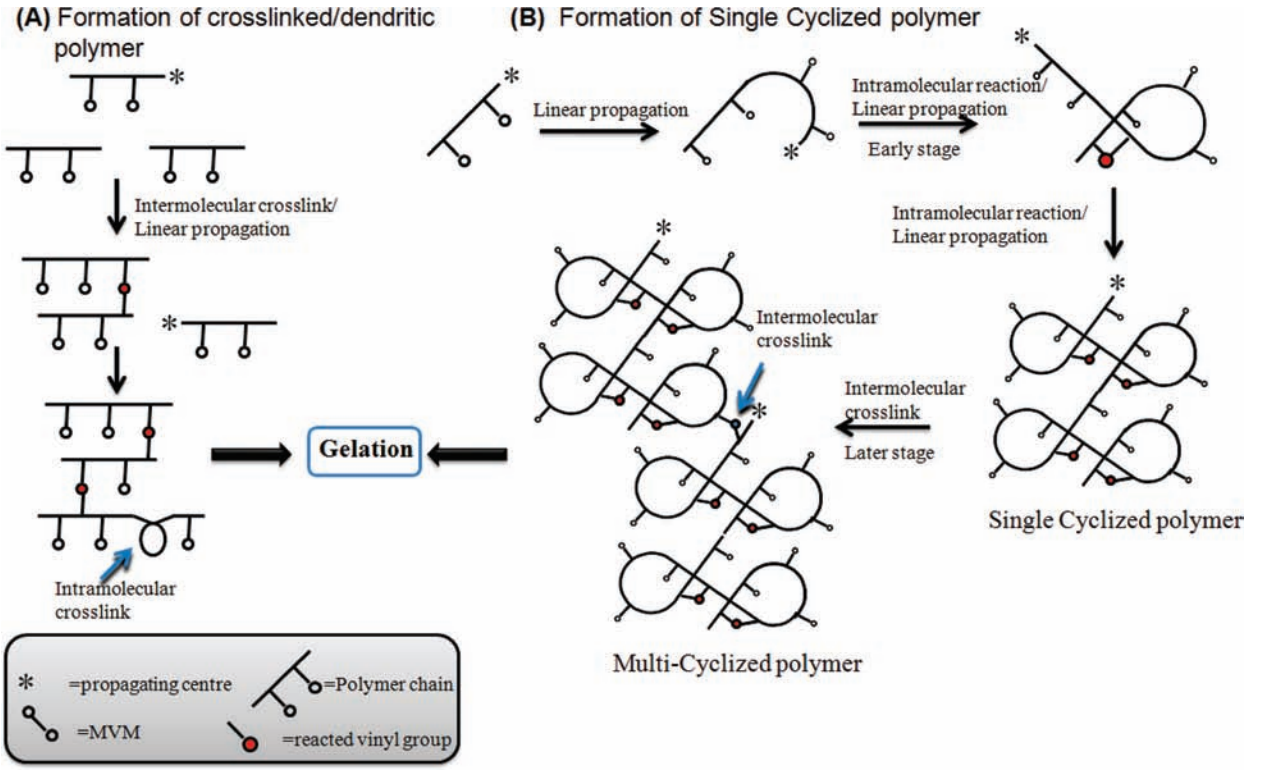

Figure 1. (A) Traditional formation of branched materials, with accompanying cyclizations defined by F−S theory; (B) formation of a 3D single cyclized chain via in situ DE-ATRP. The intermolecular cross-linking only occurs at later stages when the free monomers decrease and the macromolecule concentration rises up to the point where the neighboring polymer chains start to come into the scope of the maximum growth boundary, leading to the combination of different single cyclized molecules and the formation of a multiple single cyclized polymer.

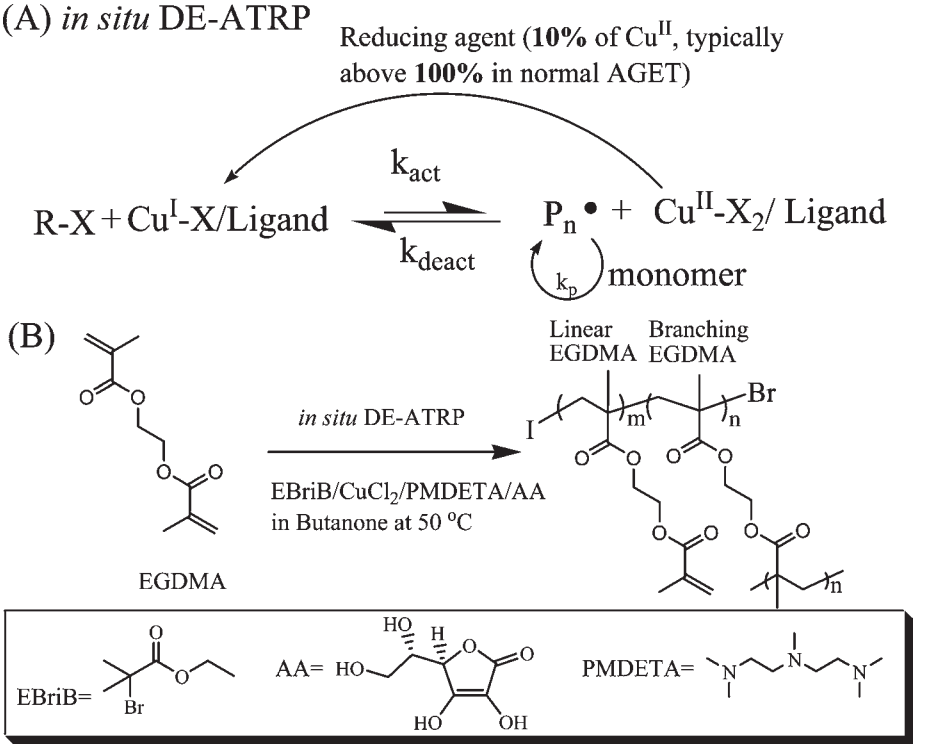

Figure 2. In situ deactivation enhanced ATRP of EGDMA: (A) deactivation enhanced strategy is achieved by adding a low level of reducing agent (10% ratio to Cu^{II}, as opposed to typically above 100% in normal AGET ATRP); (B) Homopolymerization of EGDMA via in situ DE-ATRP. EBriB/EGDMA/$CuCl_2$/PMDETA/AA = 1:100:0.125:0.125:0.0125, [EGDMA] = 1.45 M in butanone, T = 50 °C (for further reaction details, see Supporting Information).

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so-called in situ deactivation enhanced atom transfer radical homopolymerization (in situ DE-ATRP) of MVMs. The 3D cyclized structure that we achieve from the homopolymerization of MVMs consists of single knotted chains cyclized upon themselves specifically via intramolecular reactions. This new class of polymer structure termed as the single cyclized structure (part B of Figure 1) is fundamentally distinct from the definition of conventional dendritic/hyperbranched and cross-linked polymeric materials. We provide firm evidence that shows it is possible to kinetically control both the macromolecular architecture and the critical gelling point in the homopolymerization of MVMs without the need of dilution. Our experimental results significantly contradict the classical F−S theory. These cracks, beginning to appear in the foundations of F−S theory, have led us to rethink F−S theory. We proposed a new kinetic model that serves to acknowledge F−S theory but has the advantage of allowing greater applicability.

RESULTS AND DISCUSSION

We had previously reported deactivation-enhanced atom transfer radical polymerization (DE-ATRP).[37] Here, we report a new, well controlled reaction: in situ DE-ATRP homopolymerization of MVM. In situ DE-ATRP, like the activators generated by electron transfer (AGET) process, uses a reducing agent (e.g., ascorbic acid, AA) to reduce the catalyst from the higher oxidation state (Cu^{II}) to the active state (Cu^{I}) for the activation of alkyl halide initiators, hence leading to free radical formation and chain propagation (part A of Figure 2). However, the important difference is that we used extremely low proportions of reducing agent for in situ DE-ATRP, compared to the high amount used for AGET-ATRP.[38,39] While previously, large conversion of Cu^{II} to Cu^{I} was desired for conventional ATRP, in situ DE-ATRP retains a large proportion of deactivated species (via Cu^{II}). The in situ DE-ATRP of ethylene glycol dimethacrylate (EGDMA) (part B of Figure 2) allows us to significantly delay the onset of gelation in the concentrated reaction condition ([EGDMA] = 1.45 M or 28% w/v), which opposes the present understanding of cross-linking reactions for the polymerization of MVMs. Now, once more, our experimental data are in accordance with the contradiction to F−S theory (Table 1): the gel point with in situ DE-ATRP of EGDMA (over 50% monomer conversion) is far higher than the value predicted by F−S theory. FRP of EGDMA shows fast gelation at low yield (7%) with high molecular weight (M_w) and high polydispersity (PDI) as defined by F−S theory. However, in comparison, in situ DE-ATRP of EGDMA demonstrates a much delayed onset of gelation shown by the profile of molecular weight dependence on yield (part A of Figure 3). This in situ DE-ATRP of EGDMA reveals a reaction process significantly different from that of FRP, which occurs in two distinct phases. First, the polymer chains display an initial linear-like growth, that is the increase of molecular weight is linear with monomer conversion and PDI remains low with unimodal molecular distribution (part B of Figure 3, up to 9 h, 19% yield). This differs from the molecular weight characteristics typically encountered in the classic hyperbranched polymerization systems for example polycondensation or self-condensation vinyl polymerization (SCVP).[40−42] Then second, the combination of chains typically accompanied by greater increase in M_w and PDI, seemed to appear only at the later stages of DE-ATRP, marking the second of a two-phase process. Monitoring the structure of polymer samples via ^{1}H NMR (Figure S1 of the Supporting Information) indicated a high proportion of branched EGDMA units (21%) are formed even at the beginning of the reaction (6 h, even at 3% yield).

Table 1. Polymerization Conditions and Molecular Weight Characteristics of the Polymers from FRP and in Situ DE-ATRP, Respectively; Solvent: 2-Butanone, [EGDMA] = 1.45 mol L^{-1} or 28% w/v, $CuCl_2$/Ligand = 1:1, AA: L-Ascorbic Acid; Further Details Are Given in Table S1 of the Supporting Information

	time (hrs)	M_n[c] (x10^3)	M_w[c] (x10^3)	PDI[c]	yield[d] (%)	branch[e] ratio
FRP[a]	0.33	56	114	2	7	3%
in situ DE-ATRP[b]	8	5.7	8.2	1.4	10	26%
	9	6.9	10.6	1.5	19	24%
	12	11	22.1	2	26	24%
	13	20	42	2.1	35	26%
	15	32	280	8.7	54.2	27.5%

[a] I/EGDMA = 1:100, I: 1,1′-azobis-cyclohexane carbonitrile (ACBN), T = 70 °C. [b] I/EGDMA/$CuCl_2$/PMDETA/AA = 1:100:0.25:0.25:0.025, I: ethyl 2-bromoisobutyrate (EBriB), L: 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), T = 50 °C; [c] M_n, M_w, and PDI are determined by GPC equipped with a refractive index (RI) detector, the results from the light scattering (LS) detectors are given in Table S1 of the Supporting Information. [d] Polymer yield was calculated gravimetrically. [e] Calculated by ^{1}H NMR, as seen in Figure S1 and eq S1 of the Supporting Information.

To further prove our findings, we designed and prepared a cleavable polymer via in situ DE-ATRP from an acid cleavable divinyl (ACD) monomer, within which is an acetal linkage, that can cleave quickly under acidic conditions (Figure 4).[43−45] It can be expected that, according to F−S theory, the polymer would degrade and separate into much lower molecular weight chains as the intermolecular cross-linked points are broken (part B of Figure 5), which was indeed demonstrated recently by Armes et al., with branched polymers from the conventional ATRP copolymerization of MVMs.[29,46] However, we show that with the polymer formed at the early stages of in situ DE-ATRP of cleavable MVM (18% conv., M_w = 5.7KDa, PDI = 1.3) despite having 24% branch ratio (Figure 4 and eq S4 of the Supporting Information), shows little reduction in the hydrodynamic volume and the molecular weight as determined by GPC-RI (part D of Figure 5). In contrast, although it has a low branch ratio 5% (15% conv, M_w = 195 KDa, PDI = 4.9), the polymer obtained from FRP of cleavable MVM has a far different degradation profile. The high molecular weight polymer chains were degraded into small chains and the molecular weight shows a very large reduction after degradation (part E of Figure 5). The degradation studies of cleavable MVM homopolymers clearly proved that the structure of polymer formed at the early stages of in situ DE-ATRP of MVM is very different from one from FRP of MVMs. We believe that an intramolecular linked knot structure is formed by in situ DE-ATRP (part C of Figure 5) rather than a branched structure. These puzzling and conflicting results and their deviation from classical F−S theory led us to apply a new kinetic model (a supplement to classic models) to in situ DE-ATRP.

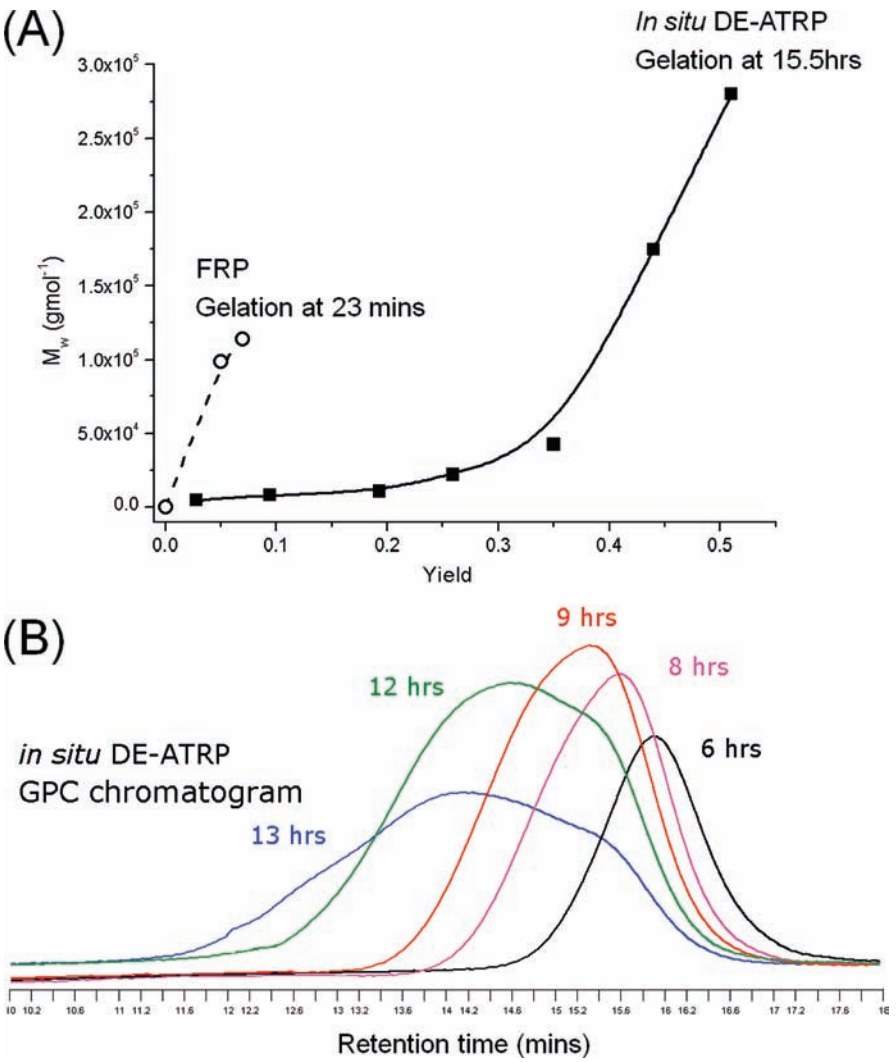

Figure 3. (A) Dependence of the weight-average molecular weight (M_w) of the polymers formed by FRP and in situ DE-ATRP on the polymer yield; (B) time dependence of the composition of the polymerization mixtures monitored by GPC equipped with a RI detector, showing the unimodal peaks at initial stages (<9 h) and multimodal peaks appearing later (>9 h) in the in situ DE-ATRP of EGDMA.

To unveil the Achilles heel of F−S theory, we realize that a crucial intrinsic feature of FRP was neglected when P. Flory's mean-field theory was first applied to the addition polymerization by W. Stockmayer.[18] This feature is the much faster propagation of FRP, in comparison to the polycondensation reaction with which Flory initially introduced his statistical model (part A of Figure 6). Bearing this important difference in mind, we introduce a new kinetics model, which is in agreement with one of the assumptions of F−S theory: the reactivity of all vinyl groups is considered to be the same throughout the reaction mixture. However, we think there is a limiting distance from the propagating center to its boundary, termed as the maximum growth boundary (dependent on the kinetics chain length), which should now be introduced (part B of Figure 6).

Our new kinetics model serves to acknowledge F−S theory, but has the advantage of allowing greater applicability. In our kinetic model, there are two parameters that are used to determine the reaction type (propagation, intramolecular reactions, and/or intermolecular cross-linking). The first parameter is the growth boundary, which depends on the kinetics chain length of the polymerization. The second parameter is the polymer chain dimensions (shaded parts in parts B and C of Figure 6), which is related to the polymer chain length (or degree of polymerization) and the concentration of polymer chains in the reaction system according to the chain end diffusion theory. The predominant example of agreement of this new model with F−S theory emerges when we consider the conventional FRP of MVMs. In this case, with a large growth boundary (part B of Figure 6 and eq S2 of the Supporting Information), the intermolecular reactions become unavoidable because the region becomes so large that the vinyl groups from other polymer chains are inside the growth boundary even at very low conversion (growth boundary overlaps with the other polymer chain dimensions). Thus, insoluble gels inevitably form even at low monomer conversion (part A of Figure 1) from the combination of polymer chains via the intermolecular cross-linking reactions. However, the effect of the kinetics model becomes apparent when considering polymerizations where the instantaneous kinetics chain length is very small. During in situ DE-ATRP, the maximum growth boundary is extremely small due to the

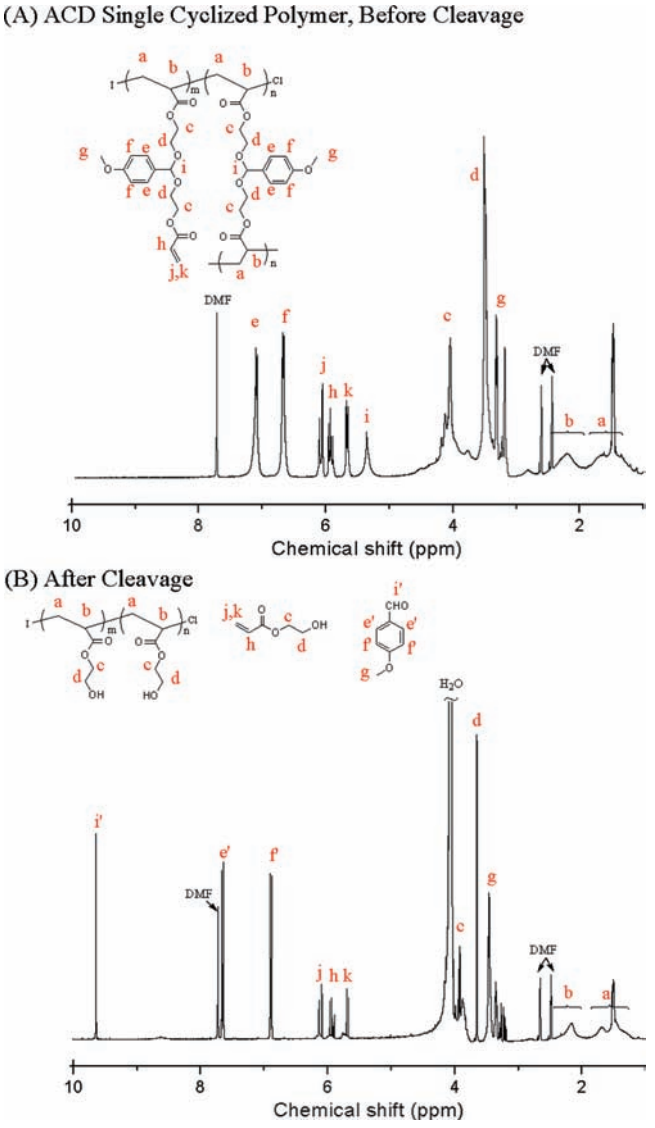

Figure 4. ^{1}H NMR spectrum of the ACD single cyclized polymer (A) prepared via in situ DE-ATRP and after cleavage (B) in acid conditions (pH = 3, 2 hrs) in Dimethylformamide-d_7 at 300 MHz (Entry 4, Table S2 of the Supporting Information). The ACD polymer was completely cleaved after 2 h since resonance of proton i (5.3 ppm) is completely disappeared and shifted to i' (9.7 ppm).

high ratio of Cu^{II} (part C of Figure 6 and eq S3 of the Supporting Information), thus the propagation center is limited to the few nearest vinyl groups during the limited time that the propagating chain is active. Furthermore, the polymer chain dimension is small at the beginning of the reaction, and thus cannot overlap with the small growth boundary. Taken together, because the nearest vinyl groups to the propagating center are those vinyl groups within the same polymer chain or belonging to the free monomers, it can be expected that the intramolecular cyclization and free monomer addition into the chain dominate during the early stages of the reaction. At the later stages, since the polymer chain length and polymer concentration increases with conversion (the critical overlap conversion of in situ DE-ATRP EGDMA is 58% according to the calculation via eq S5 and Figure S3 of the Supporting Information),[47] the polymer dimension grows and finally overlaps within the growth boundary from other propagating centers, hence intermolecular reactions occur. Thus, the intramolecular reaction is not only impossible to ignore, but actually enhanced by in situ DE-ATRP to produce polymer chains that effectively link to themselves in a knot structure that we term as the single cyclized polymer (part B of Figure 1). The produced 3D knotted polymeric materials differ from cross-linked and/or hyperbranched polymers as they are no longer a combination of different polymer chains but are indeed a structure of cyclization within a single polymer chain. It is worth noting that the knotted polymer structure from the polymerization of MVM, although resembling the single-molecule nanoparticles[48−50] made from the intramolecular collapse of linear polymer chains, has the distinct difference not only based on the preparation method but also the topology structure. We believe that the facile nature of the controlled MVMs polymerization will significantly permit wide variation in monomer selection and functional group incorporation, enabling a new generation of nanosize 3D macromolecular architectures to be designed and prepared.

■ CONCLUSIONS

In conclusion, we demonstrate that it is possible to kinetically control both the macromolecular architecture and the critical gel point in the polymerization of MVMs, which is beyond the scope of F−S theory. This new kinetically controlled approach allows the preparation of a new 3D single cyclized polymeric material which is distinct from the definition of conventional dendritic/hyperbranched and cross-linked materials. It can be expected that the ability and understanding to control intramolecular cyclization within polymer structures for the polymerization of MVMs will be proved to be a revolutionary concept in the field of polymer science. The broad range of novel nanosize 3D polymeric materials that can be designed and produced from the numerous available multivinyl monomers will have significant applications in a wide range of different fields.

■ EXPERIMENTAL SECTION

■ SYNTHESIS OF MONOMER AND POLYMERS

In Situ DE-ATRP of EGDMA. The polymers were prepared in a two-necked round-bottom flask. EBriB (390 mg, 2 mmol, 1 equiv), EGDMA (39.6 g, 0.2 mol, 100 equiv), 2-Butanone (100 mL, [EGDMA] = 1.45 M or 28% w/v), $CuCl_2$, (66 mg, 0.5 mmol, 0.25 equiv) and PMDETA (86 mg, 0.5 mmol, 0.25 equiv) were added into the flask and oxygen was removed by bubbling argon through the solutions for 30 min. AA solution (0.088 mL of 100 mg/mL AA/deionized water solution, 0.05 mmol, 0.025 equiv) was added into the flask with a microliter syringe under positive pressure of argon before the flask was immersed in a preheated oil bath at 50 °C. The solution was stirred at 800 rpm and the polymerization was conducted at 50 °C in an oil bath for the desired reaction time.

Synthesis of ACD Homopolymer via in Situ DE-ATRP. The polymers were prepared in a two-necked round-bottom flask. EBriB (19.5 mg, 0.1 mmol, 1 equiv), acid cleavable divinyl monomer (3.5 g, 10 mmol, 100 equiv), 2-butanone (5 mL, [ACD monomer] = 1.45 M), $CuCl_2$, (33 mg, 0.25 mmol,

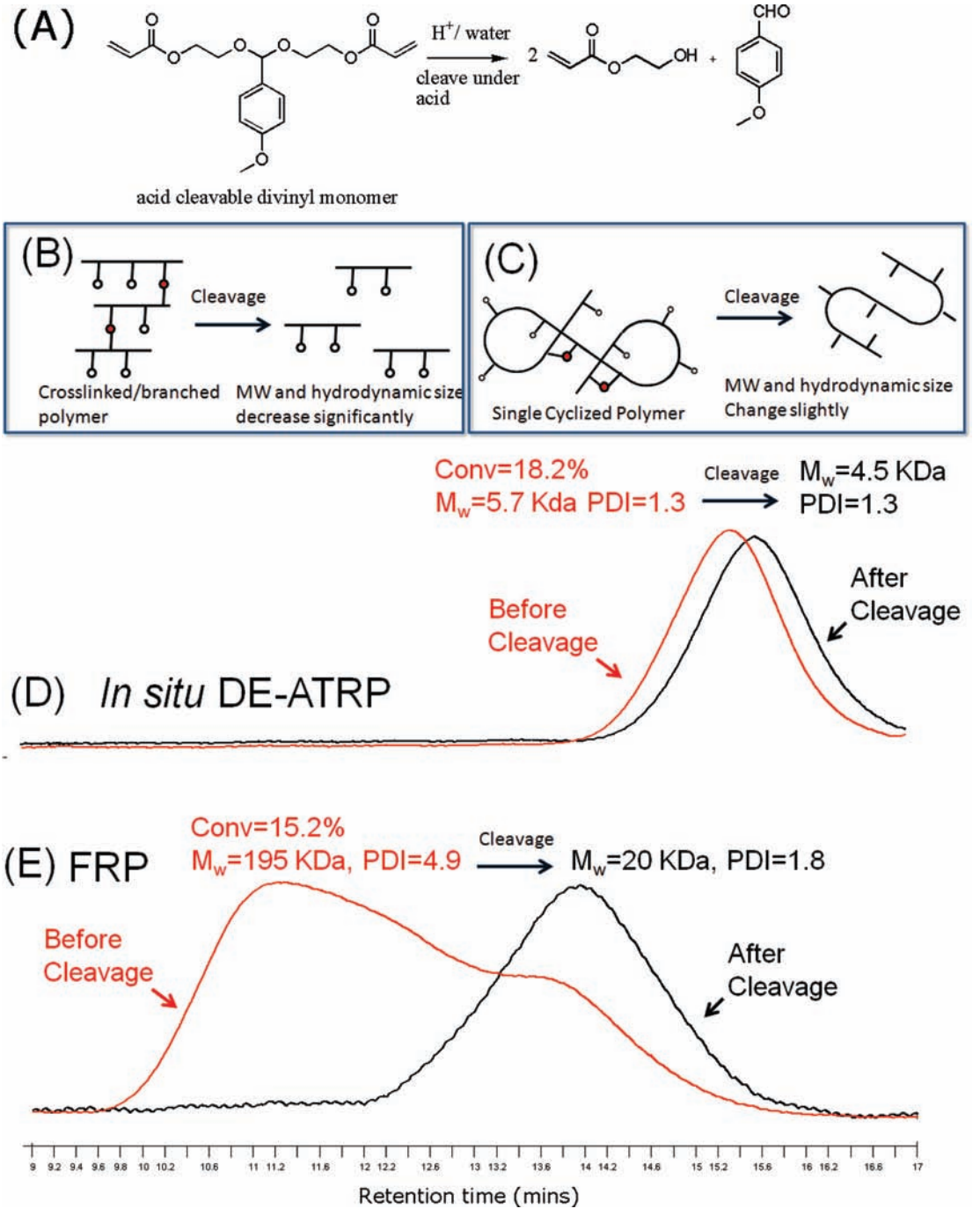

Figure 5. (A) Cleavage reaction of acid cleavable divinyl (ACD) monomer, (B) MW and hydrodynamic size of polymer chains will decrease significantly in cross-linked/branched polymers, (C) but will only change slightly in single cyclized polymer, (D) the GPC trace before and after cleavage of ACD polymer at 18.2% yield with in situ DE-ATRP, proves the single cyclized structure because the MW and hydrodynamic size only slightly decreased after cleavage (from 5.7 kDa to 4.5 kDa), in contrast, (E) the polymer synthesized by FRP demonstrates a substantial reduction (from 195 kDa to 20 kDa). The vastly different degradation behaviors confirm the large variance between the polymer chain structures from in situ DE-ATRP and FRP. For detailed results and MW obtained by LS detector, see Table S3 of theSupporting Information.

0.25 equiv), and PMDETA (4.3 mg, 0.025 mmol, 0.25 equiv) were added into the flask and oxygen was removed by bubbling argon through the solutions for 30 min. AA solution (0.0044 mL of 100 mg/mL AA/deionized water solution, 0.0025 mmol, 0.025 equiv) was added into the flask with a microliter syringe under positive pressure of argon before the flask was immersed in a preheated oil bath at 50 °C. The solution was stirred at 800 rpm and the polymerization was conducted at 50 °C in an oil bath for the desired reaction time. Samples taken from the reaction at different reaction time points were diluted with acetone and dialyzed for 48 h in excess amount of acetone with TEA to remove ACD monomer and copper catalyst. The ACD polymer was cleaved in acid condition (add 0.5 M HCl into solution to pH = 3). The

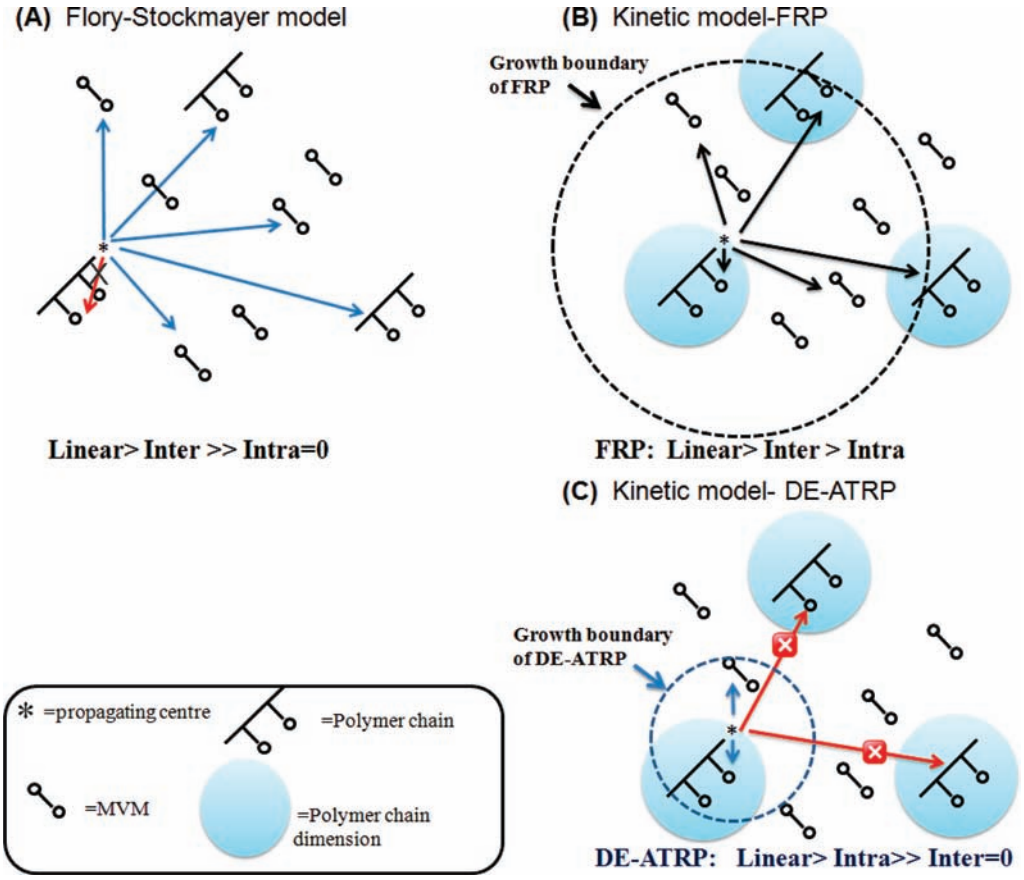

Figure 6. (A) Model based on F−S theory, where intramolecular cross-linking is ignored; (B) model of FRP; and (C) model of in situ DE-ATRP based on the kinetics model. The kinetic model considered two parameters: the growth boundary which depends on the kinetics chain length of the polymerization (dotted circle) and polymer dimension depends on the polymer chain length and concentration (shaded part). The maximum growth of a polymer chain (defined as the instantaneous kinetics chain length), which depends on the possible number of vinyl groups reacted during its active lifetime during the propagation process. The probability of monomer addition to the chain decreases with distance from the active propagation center up to the maximum growth boundary, moreover, past which the probability of monomers adding tends to zero.

polymer was completely cleaved after 2 h, which confirmed by both the GPC and ^{1}H NMR.

■ ASSOCIATED CONTENT

Supporting Information. Full kinetic results of FRP and in situ DE-ATRP of EGDMA and ACD monomer; ^{1}H NMR spectrum of polyEGDMA produced from in situ DE-ATRP and monitored GPC traces of polyACD produced from in situ DE-ATRP with full legends; supplementary eqs and additional references; calculation of critical overlap concentration; measurement of initiation efficiency of in situ DE-ATRP. This material is available free of charge via the Internet at http://pubs.acs.org.

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