

Non-linear Radical Additions-Coupling Polymerization of Monovinyl Monomers towards Polymer Networks: Theory, Tunability and Heritable Architecture

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Electronic Supplementary Information

Abstract Exploring new polymerization strategy for current available monomers is a big challenge in polymer science. Here we re-investigate radical polymerization of monovinyl monomer (MVM) initiated by uniform branched polyfunctional initiator (PFI), which is termed non-linear radical additions-coupling polymerization (NLRAsCP). In NLRAsCP, both addition and coupling reactions of radical contribute to the construction of the polymer chains, which leads to continuous growth of branch topology. Theoretical analysis of NLRAsCP predicts that the gelation is determined by the functionality of PFI (a), the extent of initiation of the PFI (q) and the termination factor of radical (ϕ). NLRAsCPs of styrene and methyl methacrylate promoted by Cu(0)/Me₆TREN or Mn₂(CO)₁₀/visible light were conducted. After the cleavage of incorporated PFI fragment or junctions in the network, the network was transformed to linear chains having almost the same structure as segmental chains in the precursor network. This allows the reverse deducing the network structure from its cleaved products. It has been proven that NLRAsCP includes stepwise initiation of PFI, chain-growth of segmental chains and successive endlinking of macroradicals derived from PFI. The three parameters related to the gelation process, a , q and ϕ , were adjusted via binary PFI, the feed ratio of [Mn₂(CO)₁₀]/[PFI] and addition of non-homopolymerizable comonomer respectively. The minimum values of a and q , and the minimum amount of comonomer required for gelation were determined, which can be applied to estimate ϕ of various macroradicals. NLRAsCP opens a general and facile strategy for synthesis of a variety of polymer networks with heritable architecture by one-pot polymerization of various MVMs.

Keywords Non-linear radical additions-coupling polymerization; Monovinyl monomer; Polyfunctional initiator; Polymer network; Theory

Citation: Ren, L. M.; Li, C. L.; Wang, Q. Non-linear radical additions-coupling polymerization of monovinyl monomers towards polymer networks: theory, tunability and heritable architecture. *Chinese J. Polym. Sci.* 2022, 40, 1623–1630.

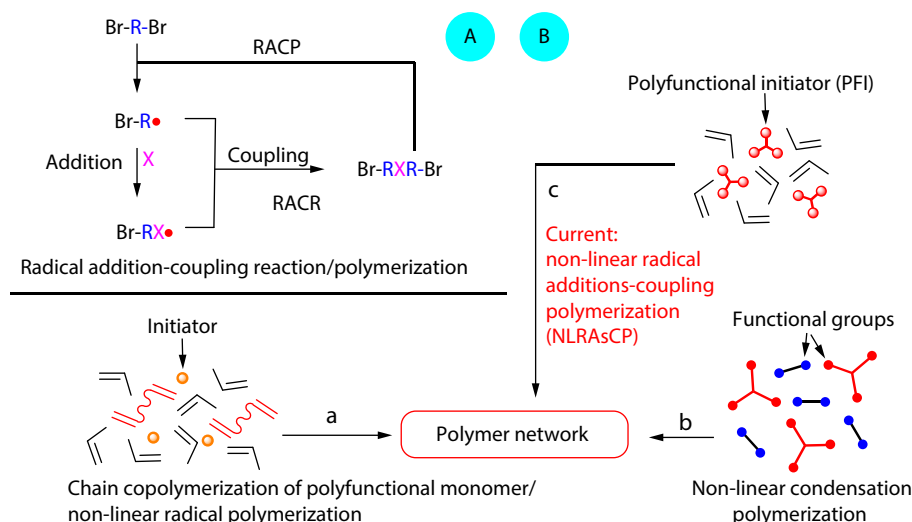
INTRODUCTION

Polymers with different segmental and topological structures can be prepared from the same monomer via different polymerization methods. For example, polypropylene with different stereoregularities (atactic, isotactic and syndiotactic) or polyethylene with different topologies (linear and branched) can be synthesized from propylene or ethylene by different mechanisms. Manufacture of various polymers from one monomer not only makes full use of available resources and meets practical applications, but also facilitates the recovery and reuse of polymers. Therefore, exploring new polymerization strategy for current available monomers is a big challenge in polymer science.

Monovinyl monomers (MVM) can be polymerized to linear polymers via various chain polymerizations. Chain polymerization includes several steps, such as initiation, propagation, termination, chain transfer, etc. Radical addition reactions contribute to the chain propagation in radical polymerization, while radical coupling reaction or disproportionation/chain transfer leads to termination when the polymerization is initiated by monoradicals. When polymerization of MVM is initiated by biradical, radical coupling reaction will contribute to the construction of polymer chains in addition to the addition reaction. Direct coupling of biradicals generates linear polymer chains,^[1–5] while polymer network has been produced when three-armed macroradical is used.^[6] Radical addition-coupling reaction/polymerization (RACR/RACP) shown in Scheme 1(A) between biradicals and various non-homopolymerized double bonds results in multi-segmental or multiblock linear polymers.^[7–15] Branched polymer and network can be obtained when branched polyradical and nitroso compound are employed via RACP.^[16,17]

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Received March 24, 2022; Accepted May 12, 2022; Published online August 17, 2022



Scheme 1 (A) Radical addition-coupling reaction/polymerization (RACR/RACP), (B) Different one-pot polymerizations for synthesis of polymer network.

When the polymerization of MVM is initiated by branched polyradicals, the coupling reaction generates a continuous branch topology leading to the formation of the network. Gelation of grafting copolymerization of various monomers initiated by poly(vinyl trichloroacetate)/ $\text{Mn}_2(\text{CO})_{10}/h\nu$ was previously reported by Bamford *et al.*, which was aimed to determine the fraction of termination by coupling ($\delta = k_{tc}/(k_{td} + k_{tc})$) of various radical polymerizations.^[18,19] This is an example of a polymer network produced by the polymerization of MVM initiated by nonuniform polyfunctional initiator (PFI), in which the radical coupling reaction contributes to the growth of branch topology. We name this polymerization nonlinear radical additions-coupling polymerization (NLRAsCP), which is similar to but different from RACP. The plural forms in “additions” and “NLRAsCP” represent the repeated addition reactions occurring before one coupling reaction, which is different from previous linear and nonlinear RACP including only one addition reaction before one coupling reaction. The gel time, weight-average degree of polymerization and molar concentration of poly(vinyl trichloroacetate), and the rate of formation of radical were required for calculating δ according to Flory’s theory of crosslinking between linear chains.^[20] In fact, Flory’s theory cannot be applied to NLRAsCP initiated by nonuniform PFI. The analysis of gelation criterion had obvious drawbacks and was incorrect. Comments on Bamford’s analysis were given in Section 1.4 of the electronic supplementary information (ESI). During the synthesis of miktoarm star copolymers by the secondary atom transfer radical polymerization (ATRP) of styrene, both inter-star and intra-star couplings were reported,^[21] but no careful study on their role in non-linear polymerization was reported.

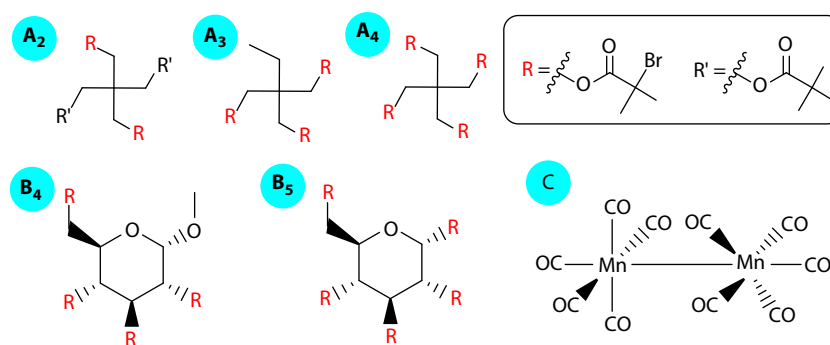
Copolymerization of MVM with polyvinyl comonomer (PVM) initiated by the monoradical is the traditional method to produce branched and crosslinked polymers (Route a in Scheme 1B), which has been termed non-linear radical polymerization (NLRP). Controlled radical polymerizations, such as ATRP, have been applied in NLRP^[22–33] for the synthesis of polymer networks, and the control on the length and its distribution of primary chains has been reported.^[27] Non-linear condensation polymerization produces polymer networks

with various functional moieties uniformly distributed throughout the network (Route b in Scheme 1B). This strategy is extended to endlinking polymerization of precursors of known masses and chemical structures.^[34–37] Endlinking of one or two kinds of star-polymer directly or by crosslinkers produces polymer networks with specific variable length of network-chain and uniform distribution of junctions. The control on the network structure is achieved through convenient control on the structure of the star polymer *via* current living polymerization techniques and chain-end transformation. The above two kinds of polymerization involving monomers are based on polyfunctional monomers (PFM), if one vinyl group is considered as a bifunctional group.

The key issue for network synthesis is the construction of branch topology. Although radical coupling reaction has been applied in different polymerizations for synthesis of linear and branched polymers, no detailed investigation on its role in building branch topology was reported except for Bamford’s study.^[18,19] In this article, we re-investigate NLRAsCP of MVM initiated by uniform PFI both theoretically and experimentally. The results prove that NLRAsCP is a facile polymerization strategy for the synthesis of polymer networks with heritable architecture from various MVMs (Route c in Scheme 1B).

EXPERIMENTAL

Various PFIs shown in Scheme 2 were prepared by reactions between polyols and 2-bromoisobutryl bromide. Polyfunctional initiators (PFI), 1,1,1-tris(2-bromo isobutyryloxymethyl)propane (**A**₃)^[38] and pentaerythritol tetrakis(2-bromoisobutyrate) (**A**₄)^[39] and 1,2,3,4,6-penta-*O*-isobutyryl bromide- α -D-glucose (**B**₅)^[40] were prepared by published method. NLRAsCP of styrene and methyl methacrylate promoted by $\text{Cu}(0)/\text{Me}_6\text{TREN}$ or $\text{Mn}_2(\text{CO})_{10}/\text{visible light}$ were conducted. Polymers were cleaved by hydrolysis. Soluble polymers were characterized by GPC. Full descriptions of the methods and analytical data for the compounds and polymer used and generated in the study are given in ESI.



Scheme 2 Polyfunctional initiators (PFI) and dimanganese decacarbonyl (Mn₂(CO)₁₀).

RESULTS AND DISCUSSION

Theoretical Analysis of NLRAsCP

The course of NLRAsCP initiated by trifunctional initiator I₃ has been proposed in Scheme 3 as an example, which includes initiation, chain propagation, coupling/endlinking of macroradical, and termination (disproportionation/chain transfer) steps. Upon initiation, three kinds of radicals R₁–R₃ can be generated from I₃ and three kinds of macroradicals P₁–P₃ can be formed *via* addition reactions. In current course, macroradicals are terminated by two ways: the coupling reaction and disproportionation/chain transfer reactions. One coupling reaction of two macroradicals generates one segmental chain and builds up linkages between two PFIs at the same time. Disproportionation/chain transfer reactions of macroradicals terminates radical propagation as well and generates one pendant chain linked to the PFI. The incorporated PFI is transformed into a junction (such as P₃) within the network once more than two functional groups of PFI have been initiated. Scheme 3 presents just one possible way of building polymer network. In fact, chain growth *via* radical addition and the growth of branch topology *via* endlinking of macroradicals may occur simultaneously.

To discuss the gelation condition of NLRAsCP, the following assumptions should be accepted. (1) The reactivities of all radicals are equivalent, (2) the intramolecular cycling reaction

is ignored, (3) all rate constants keep constant before gelation, (4) the contribution of additional monoradical generated by chain transfer is neglected.

Because the continuous branch topology is constructed by coupling reaction of branched polyradicals in NLRAsCP, the network is proposed to be generated from various macromonomers having different numbers of radicals with identical reactivity, such as P₁, P₂ and P₃ shown in Scheme 3. According to the gelation criterion for non-linear condensation polymerization of monomers having different functionalities proposed by Durand and Bruneau,^[41,42] the critical condition in NLRAsCP is given by Eq. (1):

$$(a_w - 1)q\phi = 1 \quad (1)$$

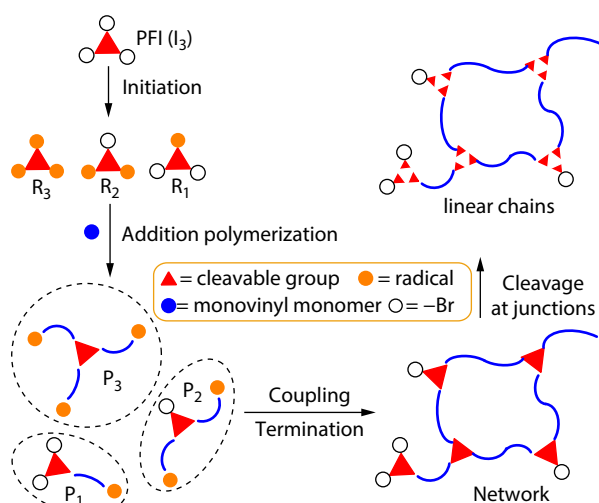
where a_w is the weight-average functionality of all PFIs, q is the extent of initiation of the functional group of PFI, and ϕ is the ratio of the coupling reaction rate (R_{tc}) to the sum of the rates of all termination reactions (R_t), which is termed the termination factor.

$$\phi \equiv \frac{R_{tc}}{R_t} \leq \frac{k_{tc}}{k_{tc} + k_{td}} \equiv \delta \quad (2)$$

When only coupling and disproportionation reactions are considered in the termination step, ϕ can be derived from k_{tc} and k_{td} as shown in Eq. (2) and is equivalent to δ in radical polymerization, which are available in literatures.^[43,44]

Eq. (1) describes a quantitative relationship among a_w , q and ϕ under critical condition and suggests that gelation is not affected by the propagation step, which does not change the concentration and the functionality of the radicals. Because the maximum value of q or ϕ is unity, the minimum value of $\phi_{c,min}$ or $q_{c,min}$ required for gelation is $(a_w - 1)^{-1}$. Details of theoretical analysis of NLRAsCP can be found in ESI.

If chain transfer reaction is considered, chain transfer to PFI is predominant before the PFI is exhausted, because α -bromoester-based PFI used in the following investigation is an active chain transfer agent. Chain transfer to PFI is equivalent to one disproportionation of macroradicals and one initiation of a functional group of PFI, which does not generate additional monoradicals. Chain transfer to other compounds in the reaction media might occur after PFI is exhausted, which produces additional monoradicals irrelevant to PFI. The weight-average functionality of radicals estimated by Eq. (S6) in ESI will change if additional monoradical is generated, which affects the gelation. Therefore, if the chain transfer is negligible or only chain transfer to PFI occurs, the gelation criterion described by Eq. (1) is applicable. If chain transfer ex-



Scheme 3 Proposed formation of the network topology in NLRAsCP of MVM initiated by PFI.

ists, ϕ is lower than δ according to Eq. (2).

Polymer Networks Synthesized by NLRAsCP

Poly(α -bromoester) is one kind of PFI that can be easily prepared and widely used for the synthesis of star polymers via ATRP upon the coupling reaction is negligible.^[21,39,45–54] It is also a cleavable initiator due to the ester group. The cleavage of incorporated PFIs or junctions in the network results in linear chains, which can be characterized by normal methods. Several poly(α -bromoester)s shown in Scheme 2 have been prepared from polyols and glucose according to published procedures.^[38–40] The subscript of the symbol represents its functionality (in ESI).

NLRAsCP of styrene was initiated by pentaerythritol tetraakis(2-bromoisobutyrate) (**A**₄) and Cu(0)/Me₆TREN in anisole. The radical is produced by single-electron-transfer redox reaction between α -bromoester and Cu(0)/ligand, which had been previously applied in RACP reported by us.^[9] Although *in situ* formed complex CuBr/ligand may generate radical through the interaction with α -bromoester as well, its rate is much slower than that by Cu(0)/ligand and can be neglected.^[8,9] Therefore, the initiation in RACP and NLRAsCP is different from that in ATRP, which is confirmed by the successful NLRAsCP promoted by Mn₂(CO)₁₀/visible light in the following cases. The polymerization was monitored by the camera. The gelation occurred at 84 min (Run 1 in Table 1) when the rapid change in the fluidity of the reaction medium can be observed (see Video in ESI). The product was extracted with ethanol/THF to remove sol and metal complex. Gel fraction was obtained after drying. When 1,1,1-tris(2-bromo isobutyryloxymethyl)propane (**A**₃) was used as PFI, gelation occurred as well (Run 2 in Table 1). Polystyryl radical prefers the termination by coupling which suggests its δ is more than 0.5. It is reasonable that gelation occurs when **A**₃ and **A**₄ are used according to Eq. (1). NLRAsCP of methyl methacrylate (MMA) initiated by **B**₄ was conducted, no gelation occurred (Run 4 in Table 1). If q is supposed to be close to unity, then $\phi < 1/(a_w - 1) = 1/3$ in this case. Eq. (1) predicts that gelation in NLRAsCP of the monomer having low ϕ might occur by using PFIs with larger a_w . When **B**₅ was tried, the gelation occurred at 157 min (Run 5 in Table 1). Since $q \leq 1$, $\phi \geq 1/(a_w - 1) = 1/4$ in this case. This suggests that MMA's $q\phi$ is between 1/4 and 1/3. PNIPA gel was prepared by one-pot polymerization of *N*-

isopropylacrylamide (NIPA) initiated by pentaerythritol tetra(2-chloropropionate) in the presence of 1,3,4,6-tetraallylglycoluril as polyfunctional crosslinking agent,^[55] which is different from NLRAsCP in mechanism. According to above results, it is possible to synthesize polymer networks by using suitable PFI and various commercial MVMs instead of special double bonds in previous RACP.^[16]

Network Formation

Either thermolysis or photolysis of the relatively weak Mn-Mn bond of Mn₂(CO)₁₀ (C in Scheme 2) can be used to generate carbon-centered radicals from organohalides, which is a homogenous initiation system.^[56,57] Homogenous NLRAsCPs of styrene initiated by **A**₃/Mn₂(CO)₁₀/visible light at different times before gelation were conducted to examine network formation and the results were given in Table S2 (in ESI). According to previous procedure,^[6] the soluble products were treated by NaOH/MeOH in THF to cleave ester moieties via transesterification process. The linear segmental chains were obtained and characterized by ¹H-NMR (Figs. S11 and S12 in ESI). The gel fractions can be cleaved by the same method. GPC measurement of the samples before and after the cleavage provided the number-averaged degree of polymerization of macromolecule (X_n) and its segmental chains ($X_{n,seg}$). The molar concentrations of macromolecule ($[M]_p$) and segmental chain ($[M]_{seg}$), and the number of segmental chains per macromolecule (N) can be evaluated by following equations.

$$[N]_p = \frac{[M]_0 Y}{X_n}; [N]_{seg} = \frac{[M]_0 Y}{X_{n,seg}}; N = \frac{[N]_{seg}}{[N]_p} = \frac{X_n}{X_{n,seg}} \quad (3)$$

where $[M]_0$ is the initial molar concentration of monomer, Y is the conversion of monomer.

As shown in Fig. 1, $X_{n,seg}$ slightly changed with polymerization time, which clearly indicates that the growth of linear chain follows the chain-growth mechanism. $[N]_{seg}$ increased with polymerization time, while $[N]_p$ increased at the beginning of the polymerization and gradually decreased before the gelation. This suggests the gradual initiation of functional groups of PFI and stepwise coupling of macroradicals with the polymerization time. The increment of N accelerates before the gelation, which clearly demonstrates that the network is constructed via stepwise radical coupling reaction. Because the molar mass of branched polymer is underestimated by GPC, the true value of X_n is greater than the mea-

Table 1 Non-linear radical additions-coupling polymerization (NLRAsCP) of various monovinyl monomers (MVM) initiated by different PFIs.

Run	MVM	Condition	a_w ^d	$\Sigma[PFI]$ (mmol/L)	t_{gel} ^e (min)	Y_{gel} ^f (wt%)	$M_{n,seg}$ ^g / $\bar{D}$ ^g (kDa)/–	ϕ ^h
1 ^a	St	A ₄	4	25.0	84	50	2.7/1.4	$\geq 1/3$
2 ^a	St	A ₃	3	33.3	104	54	4.5/1.8	$\geq 1/2$
3 ^a	St	[A ₂]: [A ₄]=98.2:1.8	2.07	49.1	19	15	4.3/2.3	0.93
4 ^a	MMA	B ₄	4	25.0	NG ⁱ	–	–	$< 1/3$
5 ^a	MMA	B ₅	5	20.0	157	34	5.0/1.9	$\geq 1/4$
6 ^a	MMA	[B ₄]: [B ₅]=97.6:2.4	4.03	24.8	41	30	5.0/2.0	0.33
7 ^b	MMA	[C] : [B ₅]=1.94 ^b	5	20.0	468	20	4.5/2.0	0.32
8 ^c	MMA	4 [B ₄]: [AMS] =10 ^c	4	25.0	247	19	5.3/1.5	$\geq 1/3$

^a Polymerization conditions: $[F]_0 = 0.1$ mol/L, $[M]_0$: $[F]_0$: $[Cu]_0$: $[Me_6TREN]_0 = 30:1:1.2:1.2$, anisole, 90 °C, total volume is 2 mL, further reacted 20 min after gelation; ^b C=Mn₂(CO)₁₀, $[F]_0 = 0.1$ mol/L, $[M]_0$: $[F]_0 = 30:1$, THF, 30 °C, total volume is 2 mL, further reacted 20 min after gelation; ^c AMS is α -methyl styrene; **[C]**:**[B**₄]=4, $[F]_0 = 0.1$ mol/L, $[M]_0$: $[F]_0 = 30:1$, THF, 30 °C, total volume is 2 mL, further reacted 20 min after gelation; ^d Weight-average functionality of PFI; ^e Gel time; ^f The weight ratio of gel to monomer in percentage; ^g Number-average molecular weight of segmental chain ($M_{n,seg}$) and its distribution ($\bar{D}$) measured by GPC after cleavage of gel fraction by the method reported in Ref. [6]; ^h Calculated by Eq.(1); ⁱ No gelation occurred.

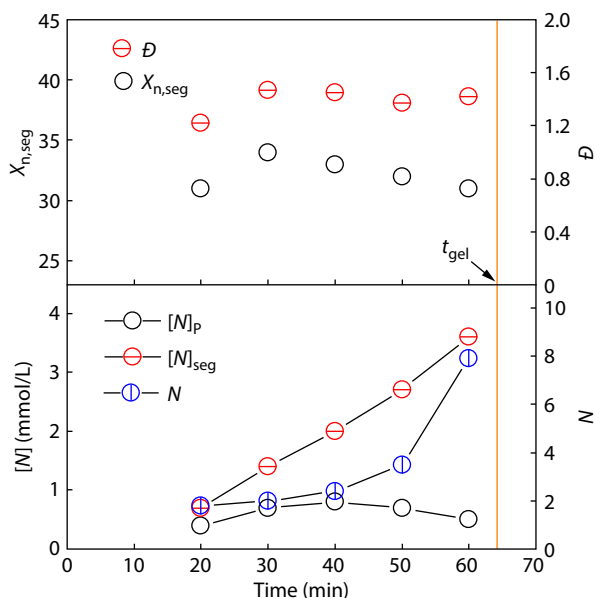


Fig. 1 Variation of the concentration of macromolecule ($[N]_p$) and segmental chain ($[N]_{seg}$), the number of segmental chains per macromolecule (N), the number-average degree of polymerization ($X_{n,seg}$) and its distribution (D) of the segmental chain with polymerization time.

sured one. $X_{n,seg}$ of linear segmental chains is precisely measured by GPC. Thus, the true value of N is greater than its measured one. The above results demonstrate that the network is constructed by stepwise initiation, concurrent chain-growth of segmental chains and stepwise-growth of branch topology via radical coupling.

Tunability of NLRAsCP

According to Eq. (1), the gelation in NLRAsCP is determined by three parameters, a_w , q and ϕ . When two parameters are fixed, the third one can be adjusted to meet the gelation criterion or avoid gelation. Several methods were applied to adjust these parameters.

The a_w of a single PFI is a discrete integer, while a_w of binary PFI composed of I_x and I_y can be continuously adjusted between x and y . NLRAsCP of styrene initiated by the mixture of **A**₂–**A**₄ was conducted. Pentaerythritol dipivalate di(2-bromoisobutyrate) (**A**₂) shown in Scheme 2 was designed to have the structure most like **A**₄ except for functionality. Increasing the ratio $[A_2]/[A_4]$ resulted in low a_w . The minimum a_w required for gelation or the critical weight-average functionality of PFI ($a_{w,c}$) was determined to be 2.07, which corresponded to the ratio $[A_2]/[A_4]$ of 98.2/1.8 (Run 3 in Table 1). According to Eq. (1), the corresponding $q\phi$ value is 0.93 for styrene. Thus, ϕ_{min} is 0.93 at 90 °C if q is assumed to be unity. The obtained ϕ_{min} is between 0.87^[58] and 0.946,^[43] the reported δ of styrene measured by model compound at 90 °C and MALDI-TOF at 90 °C. The binary PFI of **B**₄–**B**₅ with similar structure was applied in NLRAsCP of MMA. The $a_{w,c}$ of MMA was determined to be 4.03, which corresponded to the ratio $[B_4]/[B_5]$ of 97.6/2.4 (Run 6 in Table 1). According to Eq. (1), $q\phi$ value is 1/3.03. ϕ_{min} for MMA is proposed to be 0.33 at 90 °C. This value is between 0.186^[43] and 0.35,^[59] the reported δ of MMA measured by MALDI-TOF at 90 °C and model com-

pound at 80 °C.

q can be adjusted by varying the ratio $[Mn_2(CO)_{10}]/[PFI]$. NLRAsCPs of MMA was promoted by $Mn_2(CO)_{10}$ /visible light under various $[Mn_2(CO)_{10}]/[B_5]$ ratios at 30 °C were carried out. The minimum value of the ratio $[Mn_2(CO)_{10}]/[B_5]$ required for gelation of MMA was 1.94 (Run 7 in Table 1). This corresponded to q of 0.78 if the *in situ* formed manganese pentacarbonyl radical abstracted bromide atom from PFI with 100% efficiency. The ϕ value estimated by Eq. (1) is 0.32 at 30 °C for MMA, which is close to that estimated by $a_{w,c}$ (Run 6 in Table 1).

The termination mode of macroradicals is determined by their nature, so ϕ depends on the radical structure, but hardly changes with polymerization time before an autoacceleration in the polymerization rate occurs. Previously we have reported the synthesis of well-defined polyacrylate networks by endlinking of 3-armed bromo-polyacrylate *via* RACR with α -methyl styrene (AMS).^[60] The mechanism of RACR is shown in Scheme 1 (A), in which X is a kind of non-homopolymerizable compound. RACR is also an efficient protocol for synthesis of block copolymers from two different monobromo polymers in the presence of different double bonds.^[7,10,11] Inspired by this strategy, a small amount of AMS was added to adjust ϕ in NLRAsCP of MMA initiated by **B**₄. The minimum ratio of 4[**B**₄]:[AMS] was determined to be 10 (Run 8 in Table 1), which corresponded to ϕ_{min} of 1/3.

NLRAsCP provides a simple method to determine ϕ through gelation process and only a_w and q are required. a_w can be adjusted by selection of a pair of PFIs with similar structure, while q is easily and precisely stoichiometrically adjusted by the feed ratio. ϕ is approximately equal to δ if chain transfer is negligible.

Variation of t_{gel} and $M_{n,seg}$ with Polymerization Time

Because ϕ hardly changes during the polymerization, the growth of branch topology depends on the increment of q in one specific polymerization. q is determined by the initiation rate. According to Eq. (1), the gelation occurs at q_c for a selected monomer. Therefore, the gel time (t_{gel}) is determined by the initiation rate and not by the propagation rate. NLRAsCP of styrene initiated by **A**₃/ $Mn_2(CO)_{10}$ /visible light under the same condition except the ratio $[St]/[A_3]$ was conducted and the results were given in Table S3 (in ESI). As shown in Fig. 2, when $[M]/(3[A_3])$ was increased from 20 to 87 (bulk polymerization), t_{gel} slightly changed and yields of gel were around 20%, which confirms that both t_{gel} and yields of gel are not affected by the ratio $[M]/[PFI]$. The monomer concentration does not affect the rate of crosslinking at constant rate of initiation was previously reported by Bamford *et al.*^[18] $X_{n,seg}$ linearly increased with the ratio $[St]/3[A_3]$, which provides a method to adjust the segmental chain length which affects the crosslink density of the network.

Comparison of NLRAsCP and NLRP

Although NLRP and NLRAsCP are methods to synthesize polymer network from vinyl monomers, they are different in the following aspects. (1) NLRP follows the chain polymerization mechanism, while NLRAsCP follows stepwise mechanism although it involves radical addition reaction. (2) PVM is the source of branching in NLRP, while PFI is the source in NLRAsCP. (3) As shown in Scheme 4, the cleaved products of networks

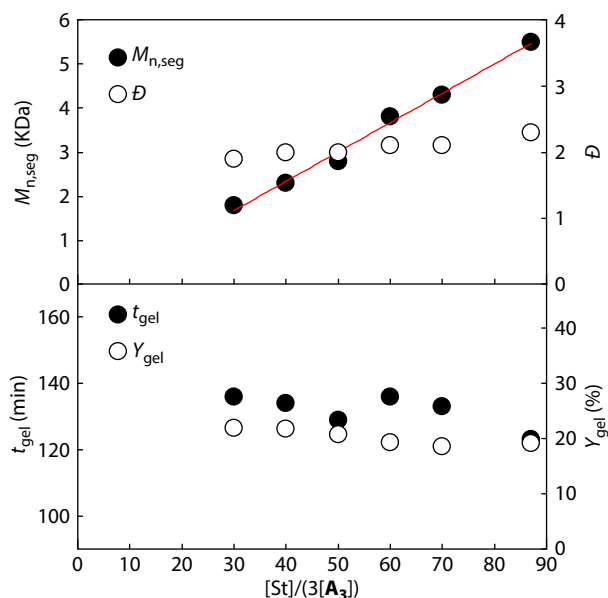
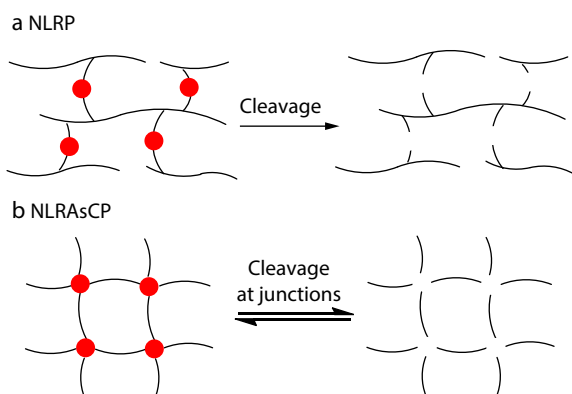


Fig. 2 Variation of gel time (t_{gel}), yield of gel (Y_{gel}), the number-average molar mass of cleaved gel fraction ($M_{n,seg}$) and its polydispersity index ($\bar{D}$) with the ratio $[St]/(3[A_3])$ under the same $[A_3]$.



Scheme 4 Comparison of the cleaved products of polymer networks prepared by NLRP and NLRAsCP.

produced by two methods are distinctly different if networks are cleavable. The cleavage occurs at junctions in the network synthesized by NLRAsCP, which leads to linear chains being almost the same as segmental chains within the precursor network. If cleavable PVM used in NLRP, the network can be degraded to linear chains that is irrelevant to segmental chains since junctions are not totally cleaved. Therefore, the cleaved product of NLRAsCP preserves the structural information of its precursor network.

The characteristic of NLRAsCP is the “heritable” architecture of its product. The cleavage of junctions in the network results in linear chains having almost the same structure as the segmental chains of its precursor network. This allows reverse deducing network structure from its cleaved products, such as crosslinking density and distribution of junctions of the network deduced from the number-average molar mass and its distribution of cleaved segmental chains. This opens a way to understand the network structure by simple experimental methods. NLRAsCP enables experimental study on the

relationship between the properties and structure of the network, such as the effect of crosslinking density on the swelling behavior. Additionally, the functionality and the structure of PFI can be tailored. This allows to control the functionality and performance of junctions in the network.

CONCLUSIONS

We demonstrate the synthesis of polymer networks by MVM's NLRAsCP involving both radical addition and coupling reactions. The course of NLRAsCP has been theoretical analyzed, and the gelation criterion has been proposed. NLRAsCP includes stepwise initiation, chain-growth of segmental chain and successive *in situ* endlinking of macroradicals. The gelation depends on the weight-averaged functionality (a_w) and the extent of initiation (q) of the PFI, and the termination factor (ϕ). These parameters can be adjusted by various experimental methods. The uniform branched PFI plays a triple role of initiation, branching and cleavable site in NLRAsCP. NLRAsCP opens a facile and versatile strategy for the synthesis of various polymer networks with heritable architectures using cleavable PFIs. The cleavage at junctions derived from PFI allows segmental structure of the network to be preserved. The segmental structure of the network can be reversely deduced from its cleaved products. The directly experimental study on the relationship between the properties and structure of the network will be expected.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2788-z>.

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