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Grafting-Through ROMP for Gels with Tailorable Moduli and Crosslink Densities

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A new type of chemically-crosslinked polymeric network was synthesized by grafting-through ring-opening metathesis polymerization (gt-ROMP) using well-defined norbornene functionalized macrocrosslinkers. These macromolecular grafted-through networks uniquely possessed two molecular-level dials for tuning network microstructure and mechanical properties. In particular, both facets of the crosslink density, i.e. network junction functionality and molecular weight between crosslinks, could be independently manipulated by varying the macrocrosslinker degree of polymerization or the gt-ROMP degree of polymerization, providing shear storage moduli ranging over an order of magnitude.

Polymer gels have enormous potential in biomedicine,¹⁻² soft electronics,³⁻⁴ actuation,⁵⁻⁶ and additive-manufacturing.⁷⁻⁸ Application-relevant gels, however, can be plagued by poor performance, requiring strength enhancing modifications, or by a limited set of molecular-level dials to control network microstructure for tailored properties and function.⁷⁻⁹ Therefore, new synthetic approaches are an ongoing need in gel engineering, especially those which can impart multi-scale control of structure and architecture, along with, additional parameters for enhancing and controlling physiochemical properties.⁷ Numerous synthetic strategies have been pursued to create high-performance gels with advanced network morphologies using, for example, interpenetrating,¹⁰⁻¹¹ sliding crosslink,¹² and nanocomposite microstructures.¹³

A gel's microstructure can be broadly classified as physically-crosslinked or chemically-crosslinked based upon the nature of the bonds used in network formation.^{7,14} Physically-crosslinked gels can be synthesized through the formation of a range of

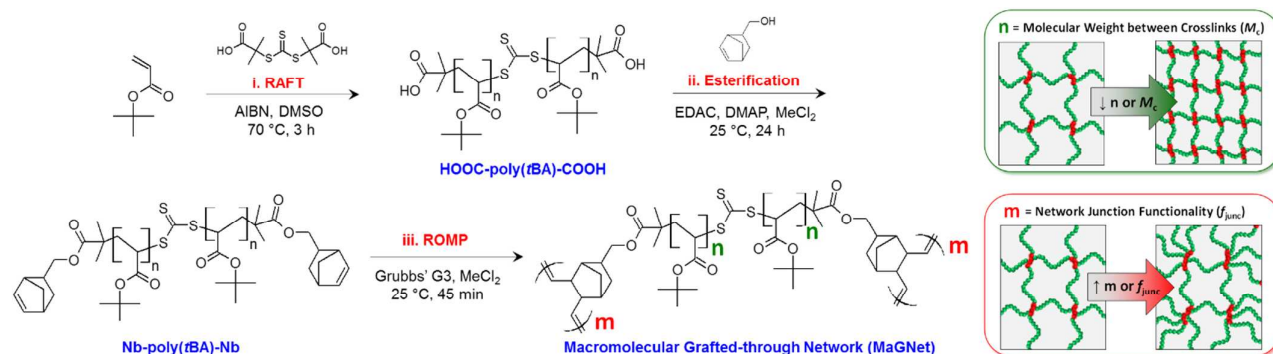
non-covalent associations between polymer chains, rooted in hydrogen-bond,¹⁵⁻¹⁸ electrostatic,¹⁷ hydrophobic,¹⁹ or specific guest-host²⁰ interactions. In contrast, chemically-crosslinked gels are synthesized by the formation of covalent bonds between chains *via* three classic crosslinking approaches, involving step-growth reactions of complimentary multifunctional species, chain-growth reactions of multifunctional species, or vulcanization-like mechanisms entailing the chain end- or backbone-crosslinking of linear precursors.²¹⁻²² Beyond these classic approaches to chemically-crosslinked networks, few others exist, narrowing the scope of accessible microstructures. Recent advances in microstructural control of polymeric networks, for instance, with dual-crosslinked, covalent-adaptable, and homogenous (*i.e.* tetra-PEGs) networks have led to gels with profound stretching, healing, and mechanical properties,²³⁻²⁵ underscoring the value of modular processes that can exert control over network architecture for accessing highly-tailorable materials.

One critical property shared by all gels is the shear elastic modulus (G'), spanning a vast range of values from 10^2 to 10^7 Pa,²⁶ which depends on the network's microstructure and crosslink density. Generally, in chemically-crosslinked networks, the crosslink density is controlled by either adjusting the molecular weight between crosslinks (M_c) or the network junction functionality (f_{junc}). Classic theories of network elasticity describe the dependence of G' on these parameters according to the expression, $G' = \nu_{\text{eff}} kT(1-2C/f_{\text{junc}})$, where ν_{eff} is the number density of elastically effective network chains (which is inversely proportional to M_c), k is the Boltzmann constant, T is the absolute temperature, and C is a parameter that varies between 0 and 1 for the affine and phantom network models, respectively.²² Thus, synthetic approaches having simple dials to control both the M_c and f_{junc} within a network's microstructure are desirable for tailoring properties (*e.g.* moduli, swelling, porosity), especially those capable of facile and broad variation to f_{junc} which is traditionally synthetically challenging.

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Scheme 1. Network Synthesis by (i) RAFT polymerization of tert-butyl acrylate, (ii) esterification of polymer chain-ends with norbornene methanol, and (iii) grafting-through ROMP of macrocrosslinker. Illustration of macrocrosslinker DP (n) and gt -ROMP DP (m) on the molecular weight between crosslinks and network junction functionality, respectively.

Motivated by the limitations in structural diversity and available parameters for tuning properties in chemically-crosslinked gels, we strove to develop a new class of gel offering multiple dials to manipulate network structure by *grafting-through* ring-opening metathesis polymerization (gt -ROMP). To the best of our knowledge, gt -ROMP of solely macrocrosslinkers has never been reported for accessing polymer networks, nor the idea of using two separate degrees of polymerization (DPs) to control network microstructure and structure-property relationships within a gel. Outside of this work, one report has utilized gt -ROMP for network synthesis, but with a focus on synthesizing bottlebrush networks by copolymerizing, primarily macromonomers, with only a small fraction of macrocrosslinker.²⁷ Nonetheless, the idea of using macrocrosslinkers to design chemical gels with highly-tailorable M_c and f_{junc} is unexplored, despite their potential in controlling both facets of the crosslink density.

Herein, we propose a way to impose control over network crosslink density by first synthesizing RAFT derived macrocrosslinkers (to control M_c) and then end-crosslinking them by gt -ROMP (to control f_{junc}) as illustrated in Scheme 1. Thus, the resulting polymer networks would theoretically have two simple dials for tuning network crosslink density and structure-property relationships, *via* the macrocrosslinker DP (n) and the gt -ROMP DP (m) during crosslinking. Grafting-through ROMP was primarily chosen because of its ability to polymerize through sterically challenging macromonomers.^{28–29} In addition, gt -ROMP has been shown to rapidly polymerize norbornene macromonomers to quantitative conversions, resulting in bottlebrushes possessing low dispersities, high molecular weights, and diverse chemical structures.^{28, 30–34} We anticipated that the advantages of gt -ROMP would translate into a unique strategy for crosslinking polymer networks. In this work, we describe the synthesis and characterization of this new class of chemically-crosslinked polymer network, which we refer to as a macromolecular grafted-through network (MaGNet), due to its microstructure composed of macromolecular building blocks and crosslinking mechanism achieved by grafting-through polymerization. Furthermore, we

demonstrate how systematic variations of two separate DPs led to networks possessing tailorable shear storage moduli ranging over an order of magnitude.

In order to construct network architectures with tailorable M_c 's and f_{junc} 's, custom telechelic norbornene functional macrocrosslinkers were synthesized using RAFT polymerization followed by a carbodiimide-mediated esterification. RAFT provided a facile route to carboxylic acid functionalized polymers (Scheme 1-i, HOOC-poly(t BA)-COOH) having targeted degrees of polymerization, narrow dispersities, and high chain-end fidelity with S,S'-bis(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (BDATC) as the chain-transfer agent.^{35–36} BDATC was synthesized according to literature and its structure confirmed by nuclear magnetic resonance (NMR) (Fig. S1).³⁶ To ensure high degrees of carboxylic acid chain-end functionality for the subsequent esterification step, all RAFT polymerizations were formulated to promote high livingness *via* a large [BDATC]:[initiator] ratio, *e.g.* 40:1, which minimizes the fraction of unfunctionalized initiator-derived polymer chains while maximizing those bearing α,ω -terminal carboxylic acid groups.^{37–38} Under such reaction conditions, control of the macrocrosslinker's molecular weight was established through kinetic analysis, revealing a linear increase in the number-average molecular weight from SEC ($M_{n,SEC}$) with increasing monomer conversion (Fig. S2A). Furthermore, over the course of polymerization, narrow dispersity values ($D \leq 1.2$) and monomodal distributions were maintained at each molecular weight as confirmed by SEC (Fig. S2A-B). Utilizing similar RAFT conditions, a series of six macrocrosslinker precursors bearing α,ω -terminal carboxylic acid groups were synthesized having $M_{n,SEC}$ values ranging from 3.2–8.9 kg/mol and D 's ≤ 1.1 , as summarized in Table S1.

Norbornene functionality was next introduced onto the polymer chain-ends through a carbodiimide-mediated esterification (Scheme 1-ii), between the carboxylic acid groups of HOOC-poly(t BA)-COOH and alcohol group of *iso*-5-norbornene-2-methanol (Nb-OH). After purification, ¹H NMR, SEC, and

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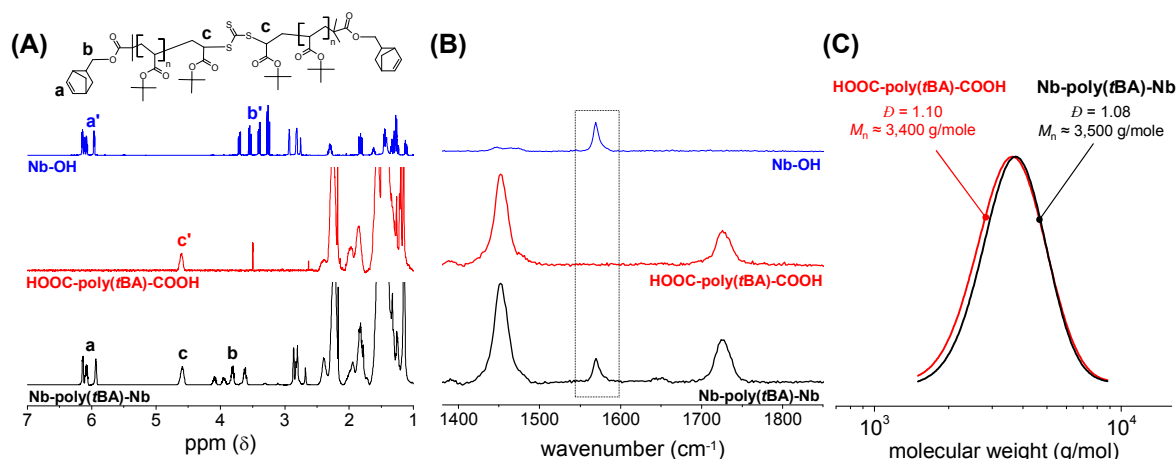


Figure 1. Structural characterization of norbornene functionalized macrocrosslinker. (A) ¹H NMR and (B) Raman spectra of reactants, norbornene methanol (Nb-OH) and α,ω -carboxylic acid functional poly(*t*BA), and resultant macrocrosslinker, Nb-poly(*t*BA)-Nb. (C) SEC traces of precursor and macrocrosslinker before and after esterification.

Raman spectroscopy were employed for end-group analysis and structural verification of the resulting norbornene functional macrocrosslinkers (Nb-poly(*t*BA)-Nb). Comparisons between the ¹H NMR spectra of Nb-OH, HOOC-poly(*t*BA)-COOH, and Nb-poly(*t*BA)-Nb in Fig. 1A led to the identification of key resonances confirming functionalization, aided by literature,^{32, 39-40} including the norbornene double bond (**a**, 6.15-5.94 ppm), methylene (**b**, 4.10-3.64 ppm), and ultimate methine protons adjacent to the trithiocarbonate (**c**, 4.59 ppm). Of note, the resonances of the methylene protons shifted downfield relative to Nb-OH (**b'**, 3.66-3.25 ppm), characteristic of a change in the electronic environment due to ester formation at the polymer chain-ends.⁴⁰ Furthermore, the norbornene and methylene proton peaks were noticeably broader in the Nb-poly(*t*BA)-Nb spectrum compared to Nb-OH, indicating their attachment to the polymer chain-end. Additional peak assignments for the isomers of Nb-OH, HOOC-poly(*t*BA)-COOH, and Nb-poly(*t*BA)-Nb are available in the supplementary information (SI) (Fig. S3-S5).

Similarly, a Raman spectrum of reagent Nb-OH was acquired and then compared to the spectra of HOOC-poly(*t*BA)-COOH and Nb-poly(*t*BA)-Nb (Fig. 1B). The spectra of Nb-OH showed a strong peak at 1570 cm⁻¹, which was assigned to the ν(C=C)

stretch of norbornene's double bond based upon literature.⁴¹⁻⁴² Furthermore, the 1570 cm⁻¹ peak was absent in the spectrum of HOOC-poly(*t*BA)-COOH but present in the spectrum of Nb-poly(*t*BA)-Nb, supporting conclusions from ¹H NMR that the norbornene functionality was indeed installed. The identification of the norbornene peak in Raman also provided a unique handle for verifying norbornene conversion in MaGNet gels after crosslinking with *gt*-ROMP. Once functionalization was established, the fraction of chains with norbornene functional groups (f_{Nb}) was quantified, which was essential for determining the amount of macrocrosslinker that could participate in *gt*-ROMP. From the ¹H NMR spectrum of purified Nb-poly(*t*BA)-Nb (Fig. 1A, S5A), the f_{Nb} was calculated using integration values from the norbornene double-bonds relative to the ultimate methine peaks (see Table S1 and S3). For all esterification reactions, f_{Nb} was found to be $\geq 93\%$, indicating that HOOC-poly(*t*BA)-COOH chain-ends underwent high to near-quantitative conversion to yield the desired norbornene-functionalized macrocrosslinker. Finally, SEC traces of the polymers before and after esterification were found to be monomodal and of low dispersity ($D = 1.08-1.10$) (Fig. 1C, Fig. S3B, Fig. S5B, Table S1); thus, ensuring the integrity of our macrocrosslinkers after esterification.

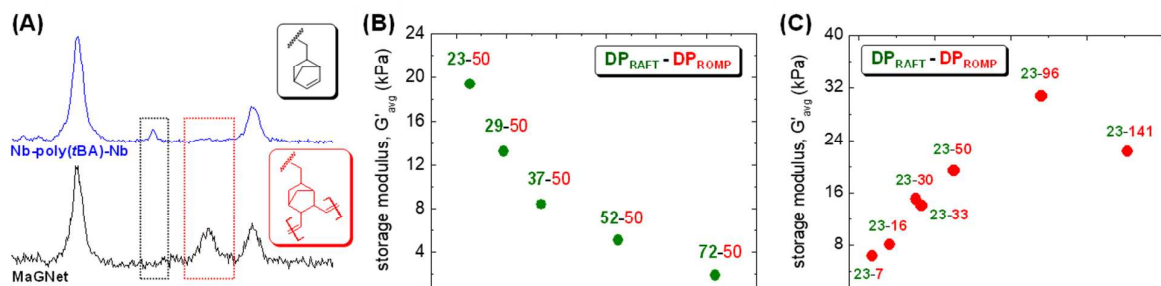


Figure 2. Spectroscopic and average storage modulus values of MaGNet gels. (A) Raman spectra of the macrocrosslinker and grafted MaGNet gel after *gt*-ROMP. (B) Average storage modulus (G'_{avg}) versus DP_{RAFT} for a series of MaGNet gels having a constant DP_{ROMP} of 50. (C) G'_{avg} versus DP_{ROMP} for a series of MaGNet gels with a constant DP_{RAFT} of 23.

Utilizing our newly synthesized Nb-poly(*t*BA)-Nb, an array of MaGNet gels were fabricated by crosslinking with *gt*-ROMP (Scheme 1-iii) to elucidate the impact of network microstructure on the shear storage modulus. In particular, network M_c and f_{junc} were independently controlled by varying the DP of the employed macrocrosslinker (DP_{RAFT}) or the targeted DP during ROMP crosslinking (DP_{ROMP}), respectively. To this end, two series of gels were synthesized: (1) a RAFT series, in which the DP_{RAFT} was systematically varied while employing a similar DP_{ROMP} , and (2) a ROMP series, in which the DP_{ROMP} was varied while employing a similar DP_{RAFT} . During all crosslinking reactions using *gt*-ROMP, high concentrations of macrocrosslinker were employed (~ 8.7 wt.% in MeCl₂), similar to conditions for bottlebrush synthesis,³³⁻³⁴ in order to maximize intermolecular reactions and minimize

topological defects,^{26, 43} e.g. intramolecular loops from one propagating chain grafting-through both norbornenes of the same macrocrosslinker. Furthermore, we employed Grubbs' 3rd generation catalyst for its rapid kinetics, steric and functional-group tolerance, and enhanced reactivity compared to its 1st and 2nd generation analogues.⁴⁴ Subsequent discussions of MaGNet gels utilize two integer values to describe network microstructure (e.g. Gel 20-50), which designates the first value as DP_{RAFT} and the second as DP_{ROMP} . Furthermore, the reported DP_{RAFT} , or M_c , for each macrocrosslinker was taken as an average value determined from three independent M_n calculations using NMR (M_n, NMR), SEC (M_n, SEC), and a theoretical value based upon monomer conversion ($M_n, theo$) reported in Table S1.

After gel synthesis and before inclusion of storage modulus values into either data series, Raman spectroscopy was carried out on each MaGNet gel to verify quantitative conversion of the norbornene groups after crosslinking. The existence of any unreacted norbornene groups would impact the gel's rheological properties by reducing its effective DP_{ROMP} , i.e. f_{junc} , and by introducing dangling chain-ends which would act as additional defects in the network structure. For all gels reported in this work, the norbornene conversion was found to be quantitative according to Raman, as evidenced by the disappearance of the 1570 cm⁻¹ peak in gel spectra (Fig. 2A, S6). In addition, each gel spectra showed the formation of a new peak, at 1651 cm⁻¹, representative of the crosslinked junction and $\nu(C=C)$ stretch of the poly(norbornene) backbone.⁴² An average storage modulus (G'_{avg}) was then calculated for each gel using storage moduli collected during an angular frequency sweep (ω) between 0.1-100 rad/s at constant strain (γ) (Fig. S7A-B, S8A-B). The constant strain value employed during these analyses ($\gamma = 0.1-0.5\%$) was selected to reside below the critical strain before strain-softening and permanent network deformation, estimated from amplitude sweeps (Fig. S7C-D, S8C-D). Furthermore, for all gels, the storage modulus was found to be independent or weakly dependent on frequency, characteristic of chemically-crosslinked gels.⁴⁵

For the RAFT gel series, G'_{avg} was studied as a function of five different M_c 's, controlled *via* the macrocrosslinker DP_{RAFT} used during *gt*-ROMP (Fig. 2B, Table S1-S2). We found that as the DP_{RAFT} increased from 23 to 72 across the gel series, the G'_{avg} decreased by one order of magnitude from *ca.* 20 to 2 kPa. The decreased G'_{avg} reflects a reduction in the elastically effective network chains arising from a larger M_c , i.e. ν_{eff} is inversely proportional to M_c , which is in agreement with classical affine and phantom network theories of elasticity.⁴⁶⁻⁴⁸ This data also shows that a greater range of G'_{avg} values were accessible when employing lower M_c macrocrosslinkers, evidenced by a 11 kPa difference in G'_{avg} progressing from Gel 23-50 to 37-50 (14 units) and only a 6.5 kPa difference from Gel 37-50 to 72-50 (35 units). For each RAFT gel, we found that G' exceeded G'' for all values of ω confirming their solid-like response to deformation (Fig. S7A-B), with exception only to the largest M_c microstructure at high frequencies where $G' \approx G''$ (Gel 72-50). Furthermore, the magnitude by which G' exceeded G'' generally decreased from lower to higher M_c values indicating a transition from stronger to weaker gels. Qualitatively, color changes were also observed going from a dark to light yellow when using low to high DP_{RAFT} macrocrosslinkers respectively, a consequence of the trithiocarbonate concentration within the matrix. Unique to MaGNet gels is the ability to control the junction functionality through the targeted DP_{ROMP} , providing a second molecular-level dial for tailoring the crosslink density and G'_{avg} .

In essence, the number of chains emanating from one network junction should be proportional to the number of chains grafted through during ROMP, *i.e.* $f_{\text{junc}} = \text{DP}_{\text{ROMP}} = ([\text{Nb}]/[\text{G3}]) \times \text{Nb}_{\text{conversion}} \times f_{\text{Nb}}$. Gels made using higher DP_{ROMP} values should yield higher crosslink densities and larger storage moduli, having network junctions resembling that of a bottlebrush-like architecture. Indeed, our experimentation revealed that as DP_{ROMP} increased from 7 to 50 across the ROMP gel series, the G'_{avg} increased from 6.4 to 20 kPa (Fig. 2C), indicative of the network becoming more restricted from higher network junction functionalities. However, at values of $\text{DP}_{\text{ROMP}} \geq 50$, the G'_{avg} appeared to reach an upper threshold and maximum plateau of *ca.* 20–30 kPa. Consistent with the phantom network model, the modulus is predicted to increase with larger f_{junc} until a horizontal asymptotic limit is reached, where the modulus will yield minimal increases even with large increases in f_{junc} .^{22, 49–50} In light of these findings and in conjunction with the RAFT series, lower DP_{ROMP} values appear to be ideal for tailoring gel strength as the greatest changes in G'_{avg} occur at lower DP_{ROMP} values. Furthermore, we found that each gel in the ROMP series had G' values consistently larger than G'' confirming their solid-like behavior (Fig. S8A–B), except Gel 23–16 in a small range at $\omega \geq 20$ rad/s.

Conclusions

In summary, well-defined norbornene functional macrocrosslinkers were synthesized with high chain-end reactivity toward *gt*-ROMP, and subsequently, employed as macromolecular building blocks for microstructural control of chemically-crosslinked networks. Rheological analysis of macrocrosslinker-derived gels revealed that by changing DP_{RAFT} (*i.e.*, M_c) or DP_{ROMP} (*i.e.*, f_{junc}), the resulting gels had tailorable storage moduli varying from *ca.* 2 to 32 kPa. In principle, this *gt*-ROMP approach to network formation is amenable to any macrocrosslinker composition, allowing for the synthesis of chemically diverse networks with flexible design of the molecular weights between crosslinks and network junction functionalities. Furthermore, junction functionalities could be easily varied over a wide range of values for tailorable properties, by simply changing the targeted DP during *gt*-ROMP. Future studies will further investigate the extent of this synthetic approach and the applicability of these materials in biomedical and separation technologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

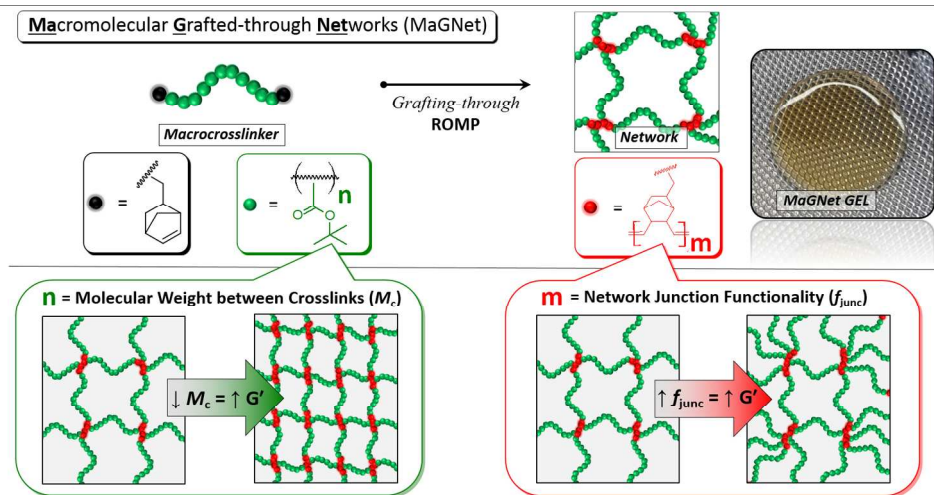
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