Tri-branched gels: Low branching factors make rubbery materials ultra-elastic

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Abstract:

Unlike hard materials, such as metals and ceramics, rubbery materials can endure large deformations due to the large conformational degree of freedom of crosslinked polymer network. However, little is known about the effect of the branching factor on their deformability. Here, we show that the lowest branching factor, which corresponds to tri-branching, results in the greatest deformability. No existing models of rubber elasticity explain this. We propose a new hypothesis about the cross-linking: crosslinks with higher branching factors reduce the conformational degrees of freedom, resulting in a loss of deformability. Although tetra-branched polymers have been preferred since the development of vulcanisation, we believe that our findings on the merits of tri-branching will prompt a paradigm shift in the development of rubbery materials.

Main Text:

Vulcanisation(1) is a chemical process that links polymers containing natural rubber and forms tetra-branched crosslinks, leading to the creation of a three-dimensional (3D) polymer network in which the positions of the constituent polymer chains are fixed. Even when subjected to large deformations, the polymer chains return to their original position when the stress is removed(2). This is the molecular origin of the elasticity of rubber. Such rubbery materials have become essential in our daily lives, as their elasticity and flexibility provide a functionality range that cannot be supplied by hard materials. Despite the usefulness of these materials, the impact of plastic pollution has been revealed recently(3, 4); rubbery materials are a source of microplastic pollutants(5), and the additives used can also cause environmental pollution(6). Thus, there is a need to design new rubbery materials that are more
environment friendly. A methodology for making rubbery materials stronger, without any additives, should help meet that demand.

Although crosslinking is a well-known chemical process, its effect on the deformability of rubbery materials is still not fully understood (7–10). One reason for the poor understanding is the invisibility of the polymer network: it is impossible to visualise the polymer network in rubber because the covalent bonds between the carbon atoms remain almost impossible to visualise using any state-of-the-art microscope. Another reason is the crowding of the polymer chains; the polymer network in a rubbery material is far removed from those shown schematically in Figure 1, instead resembling entangled spaghetti. In fact, the chain entanglements govern the mechanical properties of the rubber and make it difficult to investigate the effects of the crosslinking structure (11).

One means of decreasing the number of chain entanglements is the addition of a diluent to the polymer network. The resultant swollen polymer network is called a polymer gel. In polymer gels, the polymer network architecture plays a vital role in determining the physical properties. Researchers have realised the advantages of such an approach in this century, and many polymer gels with advanced mechanical properties have been developed. These include gels with slidable crosslinks (12), gels consisting of two coexisting independent networks (13), homogeneous gels (14), and self-healing gels (15). Further, the concepts created in gel science have proved to be translatable, allowing the successful design and fabrication of excellent condensed rubbery materials (16–18). In this respect, gel science is an incubation apparatus for developing advanced rubbery materials.

In this study, we focused on a single simple problem. Specifically, we sought to define how the branching factor – the number of strands connected to each branch – influences the deformability and/or strength of a polymer. Previous studies have been mostly focused on tetra-branched networks, and systematic comparison with other branching factors has been limited to weak deformation regimes (19–21). In particular, little is known about tri-branching, which corresponds to the lowest branching factor that can form a network. We find that the lowest branching factor realises the greatest deformability and strength for the polymer gels.

It is well known that the polymerisation of mutually reactive tetra-branched polymeric precursors in aqueous solution gives an ideally homogeneous polymer network, ‘soft diamond’ (tetra-branched gel) (14) (Figure 1a). The tetra-branched gel is also known as a model network for which the structure–property relationships are well understood (8). In this study, we synthesised a homogeneous tri-branched polymer network via a similar reaction with tri-branched precursors, resulting in a ‘soft triamond’ (tri-branched gel). Schematics of both the tetra-branched and tri-branched hydrogels are shown in Figure 1a. As shown in Figure 1b, the tri-branched gel with polymer concentration c of 14 wt.% and strand polymerisation degree N of 610 was ultra-elastic and did not break when stretched up to an elongation ratio of 30. This elongation ratio was the maximum possible deformation that could be
applied using our apparatus with an appropriate sample geometry. After stretching, a strong residual strain was observed for the specimen (Figure 1d), which was mostly recovered over 24 h (Figures 1c and e). Notably, a tetra-branched gel with a similar composition ($c = 14$ wt.% and $N = 450$) broke at an elongation ratio of 10, and little residual strain was observed (Supporting Information). This significant difference suggests that the tri-branched network is more deformable and stronger than the tetra-branched one. In other words, upon subtracting a strand from each crosslink, deformability and strength are drastically enhanced.

Figure 1. Schematics of target polymer networks and photos of stretching experiment. a, Schematic illustrations of a tetra-branched gel (left), tri-tetra-branched gel (middle), and tri-branched gel (right). These gels were systematically synthesised by mixing various ratios of tetra-branched and tri-branched precursors. b, Photographs of a stretched tri-branched gel at $\lambda = 1$ and 30. Photographs of a dumbbell-shaped tri-branched gel sample c, before and d, after stretching ($\lambda = 30$). In d, the gel is outlined by an overlaid dotted line as a guide to the eye. e, When equilibrated at 25 °C without drying, the gel recovered its dumbbell shape.
To provide a systematic comparison, in addition to the tetra-branched and tri-branched gels, we fabricated intermediate samples (tri-tetra-branched gels) by reacting tri-branched and tetra-branched precursors with various concentration ratios (Figure 1a). Figure 2a shows typical relationships between the stress $\sigma$ and elongation ratio $\lambda$ of gels with different branching factors and a polymer concentration of 14 wt.%. The polymer concentration, c, and strand polymerisation degree, $N$, were selected based on a published model (Supporting Information)(22), which allowed us to safely stretch and break the specimens using our apparatus. As shown in Figure 2c, the maximum elongation ratio $\lambda_{\text{max}}$ of the tetra-branched gels with selected $c$ and $N$ obeys the model prediction, shown as the dotted line ($\lambda_{\text{max}} \sim c^{1/3} N^{2/3}$), reflecting the homogeneity of the tetra-branched gel. When the fraction of tri-branched crosslinks was gradually increased, $\lambda_{\text{max}}$ systematically deviated from the predicted value for the tetra-branched gel, reaching a maximum for the purely tri-branched gel. It should be noted that the transition from the tetra-branched to tri-branched gel inevitably changes $N$ from 230 to 300, in addition to altering the branching factor, which increases the stretchability of the gel. However, the systematic deviation from the model prediction suggested that the enhanced deformability of the tri-branched gel might be a function of its branching factor. Therefore, it indicates that the influence of the branching factor on the deformability, which is not predicted by any existing models, exists.

Figure 2. Mechanical properties of tri-branched, tri-tetra-branched, and tetra-branched gels. a, The $\sigma$–$\lambda$ relationships of a tri-branched gel (blue), tri-tetra-branched gels (green) with different molar fractions of tri-branched crosslinks and a tetra-branched gel (black). The polymer concentration, $c$, was the same for all the gels (14 wt.%). b, $\lambda_{\text{max}}$ as a function of $c^{1/3} N^{2/3}$ for the tri-branched gels (blue triangles; $N = 300$, $c = 14$ and 23 wt.%), tri-tetra-branched gels with different $s$ (green rhombuses), and tetra-branched gels with different $c$ and $N$ (black squares). The values of $\lambda_{\text{max}}$ of the tetra-branched gels with $c < 14$ wt.% were reproduced from our previous study(22). The dashed line represents the model prediction $\lambda_{\text{max}} \sim c^{1/3} N^{2/3}$ for the tetra-branched gels. c, The $\sigma$–$\lambda$ relationships of tri-branched gels with $c = 23$ wt.% under a cyclic loading test.
To investigate the structural changes that occurred during stretching, we performed small/wide angle X-ray scattering (SAXS/WAXS). Figure 3a shows the two-dimensional (2D) SAXS patterns of the tri-branched and tetra-branched gels acquired during a loading–unloading cycle; the samples were stretched close to $\lambda_{\text{max}}$ and then relaxed. Under the initial condition, we only observed isotropic featureless patterns, indicating that the tri-branched and tetra-branched gels had amorphous structures, unlike true tridiamond or diamond crystals. Under moderate deformation conditions ($\lambda < 5$), all the samples showed isotropic SAXS patterns, suggesting that the structure was isotropic, even under deformation(23). This is in contrast to conventional polymer gels, which showed abnormal butterfly patterns under stretching due to structural heterogeneity(24). The absence of specific patterns in this region indicated good structural homogeneity for the tri-branched and tetra-branched gels. In contrast, under strong deformation conditions ($\lambda > 8$), a streak appeared in the SAXS patterns along the direction perpendicular to the stretching axis, suggesting the formation of strain-induced structure. Notably, highly diluted polymer networks rarely show any strain-induced structure. Among the three sample types, the tri-branched gels produced the strongest SAXS pattern streak. This disappeared during the unloading process, indicating the reversibility of the strain-induced structure.
Figure 3. Results of SAXS/WAXS analyses of hydrogels during stretching. a, 2D SAXS patterns of tri-branched and tetra-branched gels with c = 14 wt.% acquired at various points during a loading–unloading cycle. b, 2D SAXS/WAXS patterns of a 23 wt.% tri-branched gel acquired in the range of $\lambda = 1.0$–18 during a loading–unloading cycle. The red circles and yellow arrows have been overlaid to highlight diffraction spots and sharp streaks, respectively. The pink and blue arrows indicate (100) and (010) reflections of planar zig-zag PEG crystals. c, Schematic of the planar zig-zag PEG crystal lattice with trans conformation.

To further investigate the strain-induced structures of tri-branched gels, we increased the polymer concentration from 14 wt.% to 23 wt.%. When the structural changes under deformation were investigated by SAXS/WAXS (Figure 3b and S1, and Table S1), the tri-branched gel (23 wt.%, $N = 300$) showed a sharp streak above $\lambda = 13$ and diffraction spots at $\lambda = 18$. The diffraction spots were indexed as (100) and (010) reflections of planar zig-zag crystals of the backbone polymer (polyethylene glycol; PEG) in the trans conformation (Figure 3c), suggesting that strain-induced crystallisation (SIC) had occurred. The high crystallinity (up to 80%) was surprising, because the polymer segments in
the crystal must have phase-separated from the water occupying the remaining 77% of the material. Such high crystallinity is possibly due to the efficient ordering of the polymer backbone along the stretching axis. In addition, the characteristic diffraction pattern disappeared after removing the stress, demonstrating the reversibility of the crystallisation. In a cyclic loading test \((\lambda = 18)\), almost constant stress-elongation curves were measured for the tri-branched gel, with slight mechanical hysteresis loss observed at the second and further loadings (Figure 2c). The slight mechanical hysteresis may be because of a small amount of residual crystal that did not dissolve on the timescale of the loading cycle. This significant deformability near the fracture point \((\lambda_{\text{max}} = 19.4 \pm 1.2)\) cannot be observed in tetra-branched polymer gels without the occurrence of SIC. In addition, the unvarying stress-elongation relationship distinguishes these polymer gels from self-healing gels, which undergo massive mechanical hysteresis. The robust mechanical profile is due to SIC, which works as an on-demand reinforcement device. When a stress concentration occurs within a meso-scale region, SIC occurs and hardens the region, inhibiting further stress concentration. This result constitutes the first observation of a reversible SIC in a covalently bonded polymer gel. This indicates the possibility that polymer networks with reduced branching factors can be efficiently reinforced by SIC.

Finally, we explain the enhanced deformability and ordering of the tri-branched gels. Based on conventional theories of polymer networks, the deformability decreases with crosslinking, because crosslinking decreases the conformational degree of freedom of the polymer chains. Here, we extend the theory of deformability to include the quality of the crosslinks in addition to the quantity of crosslinks, hypothesising that higher branching factors exclude more conformational degrees of freedom than lower ones.

Our hypothesis is supported by the mathematical theory of structural rigidity proposed by J. C. Maxwell. The model treats networks as a collection of rigid rods with \(f\)-branched flexible links (Figure 4). Because the rigid rods do not deform and only rotational motion around the links is allowed, it can be used to describe the conformational degrees of freedom relating to branched structures. Figures 4a, b, and c show 2D schematics describing the deformation of 3-, 4- and 8-branched networks, respectively. The dotted blue lines represent the flexible axes, along which the network can collapse; the network collapses more easily in the presence of a higher number of flexible axes. The 3-branched network has more flexible axes than the 4-branched network, while the 8-branched network does not have any such axes. According to the model, the network structure does not collapse if the following conditions are satisfied: \(f > 4\) in 2-D space and \(f > 6\) in 3-D space. This model clearly shows that networks with smaller \(f\) values have higher degrees of freedom and greater deformability. Therefore, 3-branched polymer networks, with the smallest \(f\) that allows the formation of a network structure, has the greatest deformability.
Figure 4. Structural rigidity model. Schematics showing the rigidities of 2D \( f \)-branched bonded networks (\( f = 3 \) (a, triangles), 4 (b, squares), and 8 (c, octagons)). The blue dashed lines represent the flexible axes. The networks with \( f = 3 \) and 4 can be collapsed along the flexible axes, while the network with \( f = 8 \) cannot be collapsed.

This study experimentally demonstrated that a polymer network with the lowest branching factor is endowed with ultra-elastic mechanical properties. Hence, the branching factor could be used as an additional design metric, in addition to the other well-known factors \( c \) and \( N \). This could allow the deformability to be more easily optimised and drastic expansion of the range of mechanical properties realised by rubbery materials. SIC, as observed in tri-branched gel, acts as an on-demand reinforcement device and contributes to the robustness and high strength of these gels. This work is the first to have revealed the importance of tuning the branching factor, which is expected to facilitate further advancements in polymer science and help to solve the global problems caused by rubbery materials.

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Supporting Materials

Materials and Methods

Fabrication of the gels. Tri-amine-terminated poly(ethylene glycol) (tri-PEG-PA), tri-NHS-glutarate-terminated poly(ethylene glycol) (tri-PEG-HS), tetra-amine-terminated poly(ethylene glycol) (teta-PEG-PA), and tetra-NHS-glutarate-terminated poly(ethylene glycol) (teta-PEG-HS) were purchased from NOF Co. (Tokyo, Japan). The weight-average molecular weights \(M\) of the tri-branched prepolymers were 10k, 20k, and 40k, while the tetra-branched precursors had \(M\) values of 5k, 10k, 20k, and 40k. The molecular weights were measured by gel permeation chromatography with linear PEG as the standard. All precursors were used without further purification and were first dissolved in phosphate (PB) or phosphate-citric acid (CPB) aqueous buffers.\(^\text{16}\) To control the reaction rate, the optimal ionic strength and pH were used (Table S2). To fabricate the tri- and tetra-branched gels, equal amounts of the two corresponding prepolymer solutions were mixed, and the resulting solution was poured into a dumbbell-shaped mould (JIS K6251 No. 7). At least 12 h was allowed for the reaction to reach completion before the following experiments were performed. The value of \(N\) was calculated as follows:

\[
N = \frac{M}{44f}
\]

where \(f\) is the branching factor of the prepolymer.

To fabricate tri-tetra-branched gels, tri-PEG and tetra-PEG precursors with \(M = 20k\) were dissolved in PB or CPB (Table S2) to give different molar fractions of tri-branched crosslinks \(s\), where \(s\) is defined as follows.

\[
s = \frac{[\text{tri-PEGs}]}{[\text{tri-PEGs} + [\text{tetra-PEGs}]]}
\]

Tri-tetra-branched gels were formed for \(0 < s < 1\), while \(s = 0\) or \(1\) corresponds to the pure tetra-branched or tri-branched gels, respectively. Gels with \(s\) values of 0, 0.25, 0.5, 0.75, and 1 were prepared. In the tri-tetra-branched gels, all four precursors were selected and mixed so that the number of mutually reactive groups are matched with the determined \(s\). The polymer solutions were moulded and reacted using the process used for the other sample types. The \(N\) values of the tri-tetra-branched gels were calculated as the number average:

\[
N = 303s + 227(1 - s)
\]

Stretching tests. Uniaxial tensile tests were conducted using a Shimadzu AG-X Plus universal tester (Shimadzu Corporation, Japan) at room temperature. Dumbbell-shaped specimens (JIS K6251 No. 7) were uniaxially stretched at an initial strain rate of \(~0.07\) s\(^{-1}\) (results in Figure 1) or \(~0.16\) s\(^{-1}\) (results in Figure 2). The different strain rates were selected to minimise the effect of water evaporation from the specimen. The stress–elongation ratio (\(\sigma–\lambda\)) curves were automatically recorded by the universal tester. Uniaxial tensile tests were conducted at least three times for each sample type, and typical results are shown in Figure 2a. The average \(\lambda\) at rupture and its standard deviation were used as the representative \(\lambda_{\text{max}}\) and the experimental error shown in Figure 2b, respectively.

Loading–unloading tests for the tri-branched gel were conducted using a SUN RHEO METER 150ST and CR-500DX system (Sun Scientific Corporation, Japan). Rectangular samples (5 mm wide, 1 mm thickness, and approx. 3.7 mm long) were stretched to \(\lambda \approx 18\) and then released to return to their original length at an initial strain rate of \(~0.3\) s\(^{-1}\). The \(\sigma–\lambda\) curves were automatically recorded by the tester. The experiments were conducted in a custom-designed liquid paraffin chamber to prevent solvent evaporation at 25 °C.

In-situ small/wide angle X-ray scattering. In-situ SAXS/WAXS measurements were conducted at the BL05XU beamline of the SPring-8 synchrotron, Japan. An X-ray wavelength of 1.0 Å was used, and the sample-to-detector distances were 3950 mm and 300 mm, respectively for SAXS and WAXS tests. The samples were exposed to X-ray irradiation for 1 s while being stretched using a custom tensile-testing apparatus. The stretching rate was \(~0.3\) s\(^{-1}\). The scattering patterns were obtained using a 2D detector.
(Pilatus 1M; Dectris, Switzerland). The transmittance was calculated from the ratio of the incident beam intensity, measured using an ionisation chamber, to the transmitted beam intensity, measured using a PIN diode embedded in a beam stopper.

The 2D WAXS patterns were converted to 1D intensity profiles from the direction perpendicular to stretching by symmetric sector averaging over azimuthal angles of $90 \pm 2.5^\circ$. The average scattering intensity was normalised by the transmission intensity and sample thickness and then plotted against the amplitude of the scattering vector ($q$):

$$q = \frac{4\pi}{\lambda} \sin \left(\frac{\theta}{2}\right) \quad (4)$$

where $\theta$ is the scattering angle calibrated from the diffraction pattern of silver behenate. The obtained 1D WAXS profiles were fitted with Gaussian functions and were decomposed into a number of constituent peaks (Figure S1). Characteristic WAXS diffraction peaks were indexed to the reflections from the crystal lattice, based on the agreement between the measured and the calculated d-spacing, $d_m$ and $d_{hkl}$, respectively (Table S1). The values of $d_m$ and $d_{hkl}$ were calculated as follows:

$$d_m = \frac{2\pi}{q} \quad (5)$$

$$d_{hkl} = \frac{2\pi}{|ha^*+kb^*+lc^*|} \quad (6)$$

where $h$, $k$, and $l$ are the Miller indices, and $a^*$, $b^*$, and $c^*$ are the basic translation vectors of the reciprocal lattice, which were calculated from the crystal lattice structures\(^{11}\). The crystallinity $X$ was calculated as follows:

$$X = \frac{A_c}{A_c + A_a} \quad (7)$$

where $A_c$ is the integrated area of the peaks assigned to the crystalline phase, and $A_a$ is that of the peaks assigned to the amorphous phase.

### Supporting Text

**Empirical model of ultimate elongation.**

The maximum elongation ratio of polymeric materials ($\lambda_{\text{max}}$) is estimated as the ratio of the fully stretched length to the original length of a polymeric strand connecting neighbouring crosslinks\(^{30}\).

$$\lambda_{\text{max}} = \frac{a}{d_0} \quad (S1)$$

where, $a$ is the effective length of the monomer segment, $N$ is the degree of polymerization of the polymeric strand, and $d_0$ is the initial length between neighbouring crosslinks. For simplicity, we assumed that $d_0 \text{ [m]}$ is correlated to the number density of elastically effective chains ($\nu \text{ [1/m}^3\text{]}$), as described previously\(^{22}\).

$$d_0 \sim \nu^{-\frac{1}{3}} \quad (S2)$$

When all end groups of $f$-branched prepolymers react with each other and no dangling chains are left in the obtained network, $\nu$ is correlated to the number density of crosslinks ($\mu$):

$$\nu = \frac{f}{2} \mu \quad (S3)$$

Here, $\mu$ was calculated as follows:

$$\mu = \frac{cN_A}{M} \quad (S4)$$

where $c$ is the polymer concentration, $N_A$ is the Avogadro number, and $M$ is the molecular weight of an $f$-branched prepolymer. By combining Equation M1, S1, S2, S3, and S4, we obtained:

$$\lambda_{\text{max}} \sim \left(\frac{cN_A}{4N}\right)^{\frac{1}{3}} aN \sim c^{\frac{1}{3}}N^{\frac{2}{3}} \quad (S5)$$

Our previous study using tetra-branched gels\(^{20}\) confirmed the validity of Equation S5.
Figure S1. 1D WAXS profile of a tri-branched gel with a polymer concentration of 23 wt.%. The red, black, yellow, and blue lines represent the raw data, the best fitting result, the crystalline peaks, and the amorphous halo, respectively. The green dotted line represents the baseline.

Figure S2. Typical $\sigma$-$\lambda$ curve of a tri-branched gel (blue) and a tetra-branched gel (black). Here, the polymer concentration was 14 wt.%, and the molecular weight of the prepolymer was 40k.
Table S1. Crystal lattice parameters. Measured d-spacing ($d_m$) and calculated d-spacing ($d_{hkl}$) values, and the crystallinity ($X$) of a tri-branched gel with a polymer concentration of 23 wt.%.

| $q$ ($\text{Å}^{-1}$) | $d_m$ (Å) | Reflection surface | $d_{hkl}$ (Å) | Type of crystal    | $X$ (%) |
|-----------------------|-----------|--------------------|----------------|-------------------|---------|
| 1.5                   | 4.3       | Triclinic (100)    | 4.4            | planar zig-zag    | 81      |
| 1.8                   | 3.6       | Triclinic (010)    | 3.7            | planar zig-zag    |         |

Table S2. Fabrication conditions of tri-branched, tri-branched, and tetra-branched gels.

| Type of gel          | $s$ [-] | $N$ (-) | Polymer concentration (wt%) | Buffer for PA | Buffer for HS |
|----------------------|---------|---------|-----------------------------|---------------|---------------|
| Tri-branched gel      | 1       | 14      | 150                         | PB pH7.4 100 mM | CPB pH5.8 100 mM |
|                       |         |         | 14                          | PB pH7.4 100 mM | PB pH7.4 100 mM |
|                       |         |         | 23                          | PB pH7.4 100 mM | CPB pH5.8 100 mM |
|                       |         |         | 610                         | PB pH8.0 100 mM | PB pH7.4 100 mM |
| Tri-tetra-branched gel| 0.75    | 280     | 270                         | PB pH7.4 100 mM | CPB pH5.8 100 mM |
|                       | 0.5     | 270     | 14                          | PB pH7.4 100 mM | CPB pH5.8 100 mM |
|                       | 0.25    | 250     |                              |                |                |
| Tetra-branched gel    | 0       | 57      | 110                         | CPB pH5.8 100 mM | CPB pH5.8 100 mM |
|                       |         |         | 230                         | PB pH7.4 100 mM | CPB pH5.8 100 mM |
|                       |         |         | 460                         | PB pH7.4 50 mM  | CPB pH5.8 50 mM  |