



Title	Fracture energy of polymer gels with controlled network structures
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Citation	The Journal of Chemical Physics, 139(14), 144905 <a href="https://doi.org/10.1063/1.4823834">https://doi.org/10.1063/1.4823834</a>
Issue Date	2013-10-11
Doc URL	<a href="http://hdl.handle.net/2115/53822">http://hdl.handle.net/2115/53822</a>
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Type	article
File Information	1.4823834.pdf



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Citation: *The Journal of Chemical Physics* **139**, 144905 (2013); doi: 10.1063/1.4823834

View online: <http://dx.doi.org/10.1063/1.4823834>

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## Fracture energy of polymer gels with controlled network structures

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(Received 1 August 2013; accepted 17 September 2013; published online 11 October 2013)

We have investigated the fracture behaviors of tetra-arm polyethylene glycol (Tetra-PEG) gels with controlled network structures. Tetra-PEG gels were prepared by AB-type crosslink-coupling of mutually reactive tetra-arm prepolymers with different concentrations and molecular weights. This series of controlled network structures, for the first time, enabled us to quantitatively examine the Lake-Thomas model, which is the most popular model predicting fracture energies of elastomers. The experimental data showed good agreement with the Lake-Thomas model, and indicated a new molecular interpretation for the displacement length ( $L$ ), the area around a crack tip within which the network strands are fully stretched.  $L$  corresponded to the three times of end-to-end distance of network strands, regardless of all parameters examined. We conclude that the Lake-Thomas model can quantitatively predict the fracture energy of polymer network without trapped entanglements, with the enhancement factor being near 3. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823834>]

### I. INTRODUCTION

A fracture is to disunite a material into two or more pieces, during which process a crack formation is followed by crack propagation. Because the fracture is the critical event for structural materials, the fracture behavior is of extreme practical and fundamental importance.<sup>1–12</sup> The ease of crack propagation in a material is characterized by a fracture energy ( $T_0$ ). The most popular model predicting fracture energies of elastomeric materials is the Lake-Thomas theory.<sup>6</sup> The Lake-Thomas theory provides us a molecular interpretation for the fracture phenomena, and describes  $T_0$  as the energy needed to break the chemical bonds per unit cross-section on the fracture surface as

$$T_0 = \left(\frac{3}{8}\right)^{1/2} \nu L N U, \quad (1)$$

where  $\nu$  is the number of elastically effective chain per unit volume,  $L$  is the displacement length,  $N$  is the degree of polymerization of network strand, and  $U$  is the energy required to rupture a monomer unit. They assumed that  $L$  is related to the end-to-end distance of the network strand as  $L \approx R_0 \approx aN^{1/2}$  ( $a$ : monomer length) and  $U$  is the sum of the bond energies in monomeric unit. Because  $U$  and  $a$  are defined only by the chemical structure of backbone,  $\nu$  and  $N$  are of the interest for the verification of the Lake-Thomas theory.

The applicability of the Lake-Thomas theory has been vigorously examined for elastomers with different species and degrees of dilution.<sup>4,11</sup> Although  $T_0$  measured under the quasi-static condition obeyed Eq. (1) in scaling,  $T_0$  was larger than what is predicted by the Lake-Thomas theory. The upward deviation of  $T_0$  was accommodated by introducing an enhancement factor.<sup>2,9,13</sup> However, the molecular origin of

the enhancement factor has never been clarified, because of the difficulty in quantitative verification of  $T_0$ .

This difficulty is mainly caused by the ambiguities in the experimentally estimated values of  $\nu$  and  $N$ . Practically, both  $\nu$  and  $N$  are estimated from the elastic modulus ( $G$ ) as<sup>11</sup>

$$G = \nu k_B T \quad (\text{affine network model}), \quad (2)$$

$$\nu = \frac{\rho \phi_0}{m N}, \quad (3)$$

where  $\rho$  is the density of backbone,  $\phi_0$  is the polymer volume fraction, and  $m$  is the molecular weight of monomeric unit. Here, we show the prediction of the affine network model; however, there are three candidate models predicting  $G$ : the affine network model,<sup>14</sup> phantom network model,<sup>15</sup> and junction affine model,<sup>16,17</sup> leading to the different values of  $\nu$  and  $N$  from the same  $G$ . Because we do not know the requirement conditions for each model or even the validity of each model, we cannot estimate the credible values of  $\nu$  and  $N$ . Thus, at this stage, the relationship we can confirm is not exactly Eq. (1) but the following equation:<sup>4</sup>

$$T_0 \sim \nu L N \sim G^{-1/2}. \quad (4)$$

The variety in the existing models also makes it difficult to compare the experimental results by different authors.

The strong correlation between  $\nu$  and  $N$  causes an experimental difficulty as well. The conventional ways to make polymer networks use random polymerization of monomer and crosslinker, and random crosslinking of crosslinkable-prepolymer. We can tune  $\nu$  by controlling the crosslinker concentration or crosslinking density in these systems. However, when we tune the crosslinker concentration or crosslinking density,  $N$  varies at the same time. Thus, it is difficult to tune the values of  $\nu$  and  $N$  independently. Of course, the

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heterogeneity of polymer networks, which is known as an inherent nature, also inhibits the precise control and estimation of  $\nu$  and  $N$ . Because of these difficulties, the quantitative verification of the Lake-Thomas theory, especially the enhancement factor, has been practically impossible until now. Overcoming this difficulty in experimental investigations requires a systematic work that is based on a set of polymer networks that are all derived from the same polymer with precisely controlled and definitely identified  $\nu$  and  $N$ .

Recently, we have succeeded in fabricating a near-ideal polymer network called tetra-arm polyethylene glycol (Tetra-PEG) gel, which is formed by A-B type cross-end coupling of two TetraPEG units that have mutually reactive amine (TetraPEG-NH<sub>2</sub>) and activated ester (TetraPEG-OSu) terminal groups, respectively.<sup>18–20</sup> Although the connectivity and spatial heterogeneities were observed, the degree of heterogeneity was much smaller than that of conventional gels.<sup>21–23</sup> In previous studies, we have revealed the requirement conditions for the models predicting  $G$  of Tetra-PEG gel, and estimated the credible values of  $\nu$  and  $N$ .<sup>14–17</sup> Thus, we can calculate and use the values of  $\nu$  and  $N$  from feed condition with no ambiguity.

In our previous paper, we have investigated the fracture energy of Tetra-PEG gel. We independently tuned  $N$  and  $\phi_0$ , and confirmed the validity of the scaling form of the Lake-Thomas model. However, our previous study had at least two problems. One is the estimation method of  $N$ . We used  $N$  computed from the molecular weight of prepolymers without any justification. There is a possibility that  $N$  is larger than the computed value because of the imperfect connection of the network. The other is the pure effect of  $\phi_0$  on  $T_0$ . Because the enhancement factor is known to correlate with the chain entanglement, there is a possibility that the enhancement factor increases with increase in  $\phi_0$ . These two problems inhibited the quantitative examination of the Lake-Thomas theory.

In order to overcome these problems, in this study, we employed the connectivity ( $p$ )-tuned Tetra-PEG gels. The  $p$ -tuned Tetra-PEG gels enable us to tune  $\nu$  without changing  $N$  and  $\phi_0$  and allow us to know the pure effects of imperfect connection and  $\phi_0$ . First, we evaluated the  $p$ -tuned Tetra-PEG gels, then reevaluated the conventional Tetra-PEG gels with different  $N$  and  $\phi_0$ . Through the analysis, the Lake-Thomas model was qualitatively examined. Finally, the fracture energy of Tetra-PEG gels was compared to those of other polymer network systems.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

Tetraamine-terminated PEG (TetraPEG-NH<sub>2</sub>) and Tetra-OSu-terminated PEG (TetraPEG-OSu) were purchased from Nippon Oil and Fats Co., Ltd. (Tokyo, Japan). The product name and molecular weight in TetraPEG-NH<sub>2</sub> was SUNBRIGHT PTE-50 PA, PTE-100PA, PTE-200PA, and PTE-400PA. The product name and molecular weight in TetraPEG-OSu was SUNBRIGHT PTE-50HS, PTE-100HS, PTE-200HS, and PTE-400HS. Disodium hydrogen phosphate, sodium dihydrogen phosphate,

TABLE I. Experimental conditions for the Tetra-PEG gels and  $p$ -tuned Tetra-PEG gels.

Molecular weight of Tetra-PEGs (g/mol)	$\phi_0$	Ionic strength of buffers (mM)	Incubation time of Tetra-PEG-OSu (min)
5k	0.034	50	0
	0.050	50	0
	0.066	50	0
	0.081	100	0
	0.12	100	0
10k	0.034	25	0
	0.050	25	0
	0.066	25	0
	0.081	50	0
	0.12	50	0
20k	0.034	50	0
	0.050	50	0
	0.066	50	0
	0.081	100	0
	0.12	100	0
40k	0.034	25	0
	0.050	25	0
	0.066	25	0
	0.081	50	0
	0.12	50	0
20k	0.081	100	20
			80
			120
			160
			200
			240
			320
			400

and citric acid were purchased from Wako Pure Chemical Co., Inc. (Japan, Tokyo).

### B. Fabrication of Tetra-PEG gels

Equimolar quantities of TetraPEG-NH<sub>2</sub> and TetraPEG-OSu ( $\phi_0$ : 0.034–0.12) were dissolved in phosphate buffer (pH 7.4) and phosphate-citric acid buffer (pH 5.8), respectively. The ionic strength of buffer solution was varied to maintain the solution pH. In order to tune the reaction conversion ( $p$ ), the TetraPEG-OSu solution was incubated at 25 °C for a series of times ( $t_{\text{deg}}$ ). After the incubation time, TetraPEG-NH<sub>2</sub> and TetraPEG-OSu solutions were mixed, and the resulting solution was poured into the mold. At least 12 h were allowed for the completion of the reaction before the following experiment was performed. The detailed experimental conditions are listed in Table I.

### C. Infrared (IR) measurement

The gels were prepared as cylinder shape (diameter: 15 mm, height: 7.5 mm). Prepared gel samples were immersed in H<sub>2</sub>O for 2 days at room temperature and then air-dried. The dried samples were cut into thin films (thickness:

40  $\mu\text{m}$ ) using a microtome (SM2000R, Leica). These dried samples were soaked in  $\text{D}_2\text{O}$ , and then soaked in a mixture solvent of  $\text{D}_2\text{O}$  and PEG ( $M_w = 0.40$  kg/mol) with volume ratio of 1:1. IR spectra of these samples were obtained using a JASCO FT-IR-6300 at room temperature. For each sample, more than 2 independent samples were tested, and 128 scans were co-added at a resolution of  $4\text{ cm}^{-1}$ .

#### D. Tearing test

The tearing test was carried out using a stretching machine (Tensilon RTC-1150A, Orientec Co.). The gels were cut using a gel cutting machine (Dumb Bell Co., Ltd.) into the shape specified by JIS K 6252 as 1/2 sizes (50 mm  $\times$  7.5 mm  $\times$  1 mm, with an initial notch of 20 mm). The two arms of the test sample were clamped and one arm was pulled upward at a constant velocity (40 and 500 mm/min), while the other arm was maintained stationary. The tearing force  $F$  was recorded.

### III. RESULTS AND DISCUSSION

#### A. Intrinsic fracture energy was estimated from the minimum value of tearing force

We performed the tearing test for trouser-shaped specimens.<sup>24</sup> Each trouser was pulled at a constant speed and the tearing force ( $F$ ) was recorded. The fracture energy is given as

$$T_0 = \frac{2F}{h}, \quad (5)$$

where  $h$  is the thickness of the gel samples. The tearing force,  $F$ , fluctuated during the experiment, showing the stick-slip-like behavior. We estimated different  $T_0$ 's from the maximum, average, and minimum values of  $F$ , and confirmed that  $T_0$ 's computed from the maximum and average values of  $F$  were strongly affected by the magnitude of stick-slip behavior, while  $T_0$  computed from the minimum values of  $F$  was not affected by the magnitude of stick-slip behavior and systematically changed against the feed conditions. Thus, we used  $T_0$  computed from the minimum values of  $F$ , which indicates the minimum energy required to propagate a crack. The detailed tearing behavior will be discussed in our forthcoming paper. It is widely known that  $T$  depends on the tearing speed;  $T$  is constant when the tearing speed is below a specific value, and called the intrinsic fracture energy ( $T_0$ ). We performed the tearing measurements at a constant velocity of 40 and 500 mm/min, and confirmed  $T$  was constant in this velocity range. Thus, we succeeded in measuring  $T_0$ .

#### B. Reaction conversion was tuned by the pre-dissociation of Tetra-PEG-OSu

In order to investigate the effect of the number of elastically effective chain per unit volume ( $\nu$ ) on the fracture energy ( $T_0$ ), we tuned the reaction efficiency ( $p$ ) and fabricated  $p$ -tuned Tetra-PEG gels. By tuning  $p$ , we can control  $\nu$  while maintaining  $\phi_0$  and  $N$  unchanged, which will help understand

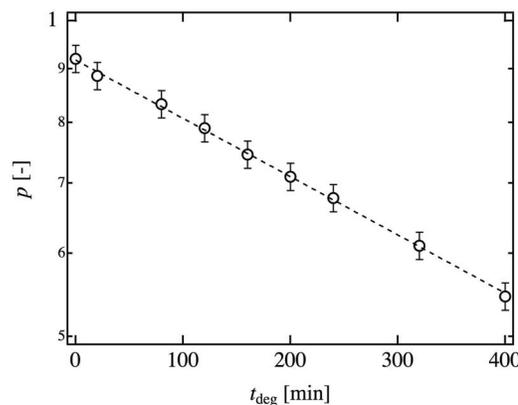


FIG. 1. Reaction conversion ( $p$ ) as a function of  $t_{\text{deg}}$ . The dashed line is the guide line showing the relationship,  $p \sim \exp(-t_{\text{deg}})$ .

the pure effect of  $\nu$  on  $T_0$ . The  $p$ -tuned Tetra-PEG gels were fabricated by hydrolyzing the activated esters on TetraPEG-OSu for a certain period of time ( $t_{\text{gel}}$ ) prior to the reaction initiation.<sup>25</sup> Using FT-IR,  $p$  was estimated as the peak intensity ratio of amide to sum of amide and carboxyl groups.<sup>21</sup> Fig. 1 shows the reaction conversion as a function of  $t_{\text{deg}}$ .  $p$  decreased exponentially with increasing  $t_{\text{deg}}$ , reflecting the pseudo-first order manner of hydrolyzation. The values of  $p$  were successfully controlled from 0.55 to 0.92. We calculated  $\nu$  from  $p$ ,  $\phi_0$ , and  $N$ , according to the tree-like theory as<sup>26</sup>

$$\nu = \frac{\rho\phi_0}{m_{\text{EG}}N} \left\{ \frac{3}{2} \binom{4}{3} (1 - P_\infty)^3 \cdot P_\infty + \frac{4}{2} \binom{4}{4} (1 - P_\infty)^4 \right\}, \quad (6)$$

$$P_\infty = p \cdot P_\infty^3 + (1 - p), \quad (7)$$

where  $\rho$  ( $= 1.129\text{ g/cm}^3$ ) is the density of PEG,  $m_{\text{EG}}$  ( $= 44\text{ g/mol}$ ) is the molecular weight of monomeric unit of PEG,  $P_\infty$  is the probability that an arm does not lead to an infinite network, and  $\binom{x}{y}$  is the usual notation for the number of combinations of  $x$  items taken  $y$  at a time:  $x! / y!(x-y)!$ .

#### C. Fracture energy in $p$ -tuned Tetra-PEG gel

Fig. 2(a) shows  $T_0$  against  $\nu$ . The dashed line represents the scaling prediction of Eq. (1),  $T_0 \sim \nu$ .  $T_0$  increased linearly with increasing  $\nu$  in the region of  $\nu > 4.0$  ( $p > 0.65$ ), well corresponding to the Lake-Thomas prediction. The linear relationship also indicates that the term  $LNU$  does not depend on  $p$ . On the other hand, in the region of  $\nu < 4.0$ ,  $T_0$  deviated upward from the guideline. This region corresponds well to the region where the elastic modulus cannot be predicted from the tree-like theory.<sup>25</sup> A massive amount of dangling chains may inhibit the mean-field-like treatment in this region.

Here, we focus on the individual parameters  $L$ ,  $N$ , and  $U$  in Eq. (1). The invariance of  $LNU$  against  $p$  indicates that we can use representative values of  $L$ ,  $N$ , and  $U$ , irrespective of  $p$ . As for  $N$ , we can use the constant value computed from the molecular weight of a prepolymer; under the stoichiometrical condition,  $N$  of network strand equals to half of the

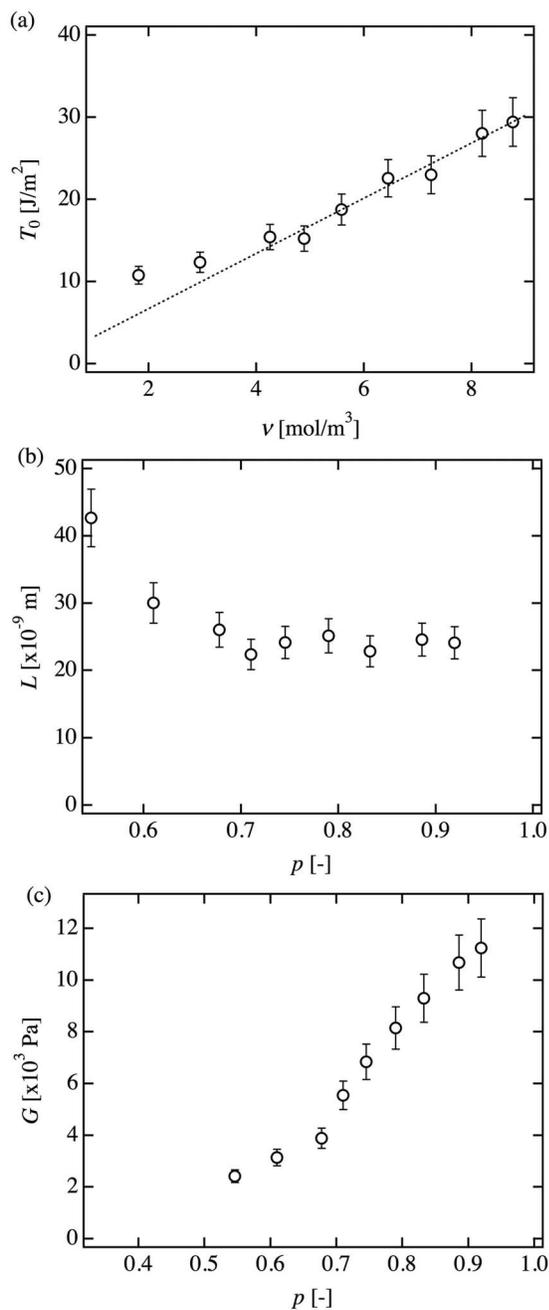


FIG. 2. (a) Fracture energy ( $T_0$ ) as a function of  $v$ . The dotted line is the linear fitting showing the relationship,  $T_0 \sim v$ . (b)  $L$  as a function of  $p$ . (c)  $G$  as a function of  $p$  for  $p$ -tuned Tetra-PEG gel.

molecular weight of a prepolymer. As for  $U$ , we can calculate  $U$  as a sum of bonding energies in the monomer unit of PEG: two CO bond and a CC bond ( $= 1.0 \times 10^6$  J/mol). Using the constant values of  $N$  and  $U$ , we can calculate  $L$  from the slope of Fig. 2(a) (Fig. 2(b)). The value of  $L$  was almost constant ( $\approx 25$  nm) against  $p$  in the region of  $p > 0.65$ , then increased with decreasing  $p$  in the region of  $p < 0.65$ , reflecting the breakage of the linear relationship,  $T_0 \sim v$ . The absolute value of  $L$  is discussed in Sec. III D.

Here, it should be noted that  $G$  decreased with a decrease in  $p$  with obeying Eqs. (6) and (7), while  $L$  remained unchanged (Fig. 2(c)). The  $G$ -independent  $L$  and  $N$  clearly

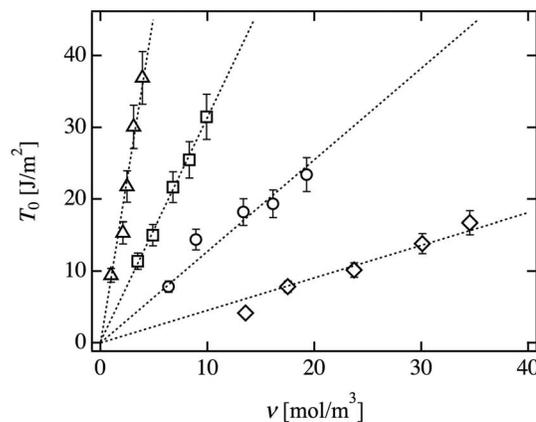


FIG. 3.  $T_0$  as a function of  $v$  in the Tetra-PEG gels (5k, rhombus; 10k, circle; 20k, square; 40k, triangle). Linear fitting of the data are shown as the dotted lines.

conflict with the prediction of Eq. (3), and show the failure of conventional method to predict  $N$  from  $G$ . The decrease in  $p$  in Tetra-PEG gels may only generate dangling chains and not increase  $N$ . We should consider this effect of dangling chains, which lowers the influence of  $G$  on  $N$ , even in the conventional polymer networks. When we use the polymer volume fraction of non-dangling element instead of  $\phi_0$ , Eq. (3) will provide us a better prediction. In this study, we can use the representative values of  $N$  and  $U$  regardless of  $p$  in the region  $p > 0.65$ , because we clarified the pure effect of  $p$ .

#### D. Fracture energy in Tetra-PEG gel

In order to discuss the effects of  $N$  and  $\phi_0$  on  $T_0$ , we reevaluated  $T_0$  of the Tetra-PEG gels with different  $N$  and  $\phi_0$ . Fig. 3 shows the  $T_0$  against calculated  $v$ , which is calculated from  $p$ ,  $N$ , and  $\phi_0$  according to Eqs. (6) and (7). The values of  $p$  were almost constant against  $\phi_0$  and higher than 0.7.<sup>24</sup> Thus, we can ignore the effect of  $p$  on  $N$ ,  $U$ , and  $L$ , and use the representative values of  $N$  and  $U$ . Because the reaction conversion was almost constant against  $\phi_0$ ,  $v$  obeyed a simple scaling relationship  $v \sim \phi_0$ . Thus, the change in  $v$  of each symbol is originated from change in  $\phi_0$ . As shown in Fig. 3,  $T_0$  increased with increases in  $v$  and  $N$ , indicating that polymer networks with dense and longer strand tend to be tough materials.  $T_0$  of the same  $N$  was proportional to  $v$ , indicating that the slope ( $LNU$ ) is independent of  $\phi_0$ , but dependent of  $N$ . From the linear fitting, the slopes are estimated to be 0.45, 1.28, 3.15, and 9.18 for 5k, 10k, 20k, and 40k Tetra-PEG gels, respectively. We set  $U = 1.0 \times 10^6$  (J/mol), and  $N = 57, 114, 227, \text{ and } 454$  g/mol for 5k, 10k, 20k, and 40k Tetra-PEG gels, respectively, and estimated  $L$ .

Fig. 4 shows  $L$  of Tetra-PEG gels with different  $N$ .  $L$  increased from 13.0 to 33 nm with an increase in  $N$ . We also show  $R_0$  of virtual network chains with polymerization degree of  $N$ , which corresponds to  $L$  in the original Lake-Thomas model. The values of  $R_0$  are calculated as  $b_k N_k^{1/2}$ , where  $b_k$  (0.65 nm)<sup>27–29</sup> and  $N_k$  are the length and number of Kuhn segments, respectively. The values of  $N_k$  are derived as  $N_k = 0.68N$ , where we assume that the bond angles are 109.5°, and bond length of C–C and C–O are 0.154 and 0.145 nm,

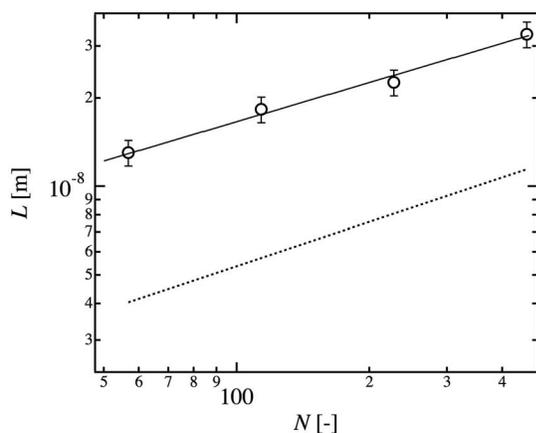


FIG. 4.  $L$  as a function of  $N$  in Tetra-PEG gel. The solid line is the fitting line of a power function ( $L \sim N^{0.45}$ ), and the dashed line is the guide showing the computed  $R_0$  of network chain with polymerization degree of  $N$ .

respectively. The values of  $L$  and  $R_0$  have similar magnitude and  $N$ -dependence, but are different from each other. Thus, we need to add the enhancement factor ( $k$ ) to Eq. (1) even in the case of ideally homogeneous network structure

$$T_0 = \left(\frac{3}{8}\right)^{1/2} k \nu R_g N U. \quad (8)$$

In order to discuss the values of  $k$ , we computed  $k$  for each  $N$  and plotted it against  $N$  in Fig. 5. The values of  $k$  decreased slightly with an increase in  $N$ . However, they are almost in the range of experimental error and all have the values of approximately 3, indicating that network strands within  $3R_0$  from the crack tip are extended at the fracture. The value of  $k$  is a universal value and is equal to approximately 3 regardless of  $p$ ,  $\phi_0$ , and  $N$  in the range examined.

### E. Comparison with different system

Although the conventional method predicting  $T_0$  from  $G$  according to Eqs. (1)–(3) is not always correct, it is interesting to compare the result of Tetra-PEG gels with other systems. Finally, we estimated  $T_0$  of Tetra-PEG gels by the conventional method and compared with those by different authors.<sup>30</sup>

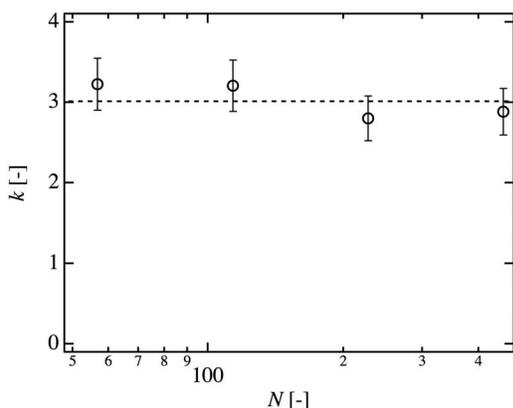


FIG. 5. The prefactor  $k$  as a function of  $N$ . The dotted line is the guide showing  $k = 3$ .

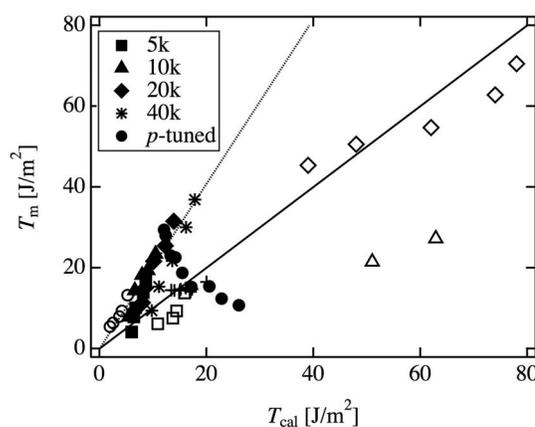


FIG. 6. The fracture energy measured ( $T_m$ ) and calculated ( $T_{cal}$ ) for Tetra-PEG gels with different  $p$ ,  $N$ , and  $\phi_0$ . The values of  $T_m$  and  $T_{cal}$  of different gels and elastomers are taken from the literatures: cis-polyisoprene, unfilled triangles;<sup>4</sup> poly(dimethylsiloxane), unfilled rhombuses;<sup>4</sup> swollen poly(dimethylsiloxane), crosses;<sup>4</sup> polyacrylamide hydrogels, unfilled circles;<sup>31</sup> and squares.<sup>32</sup> The solid line shows the relationship  $T_m = T_{cal}$ , and dotted line shows the guide of the linear relationship between  $T_m$  and  $T_{cal}$  of Tetra-PEG gels.

Fig. 6 shows  $T_0$  measured from Eqs. (1)–(3) ( $T_m$ ) against  $T_0$  calculated ( $T_{cal}$ ).

The values of  $T_{cal}$  and  $T_m$  of Tetra-PEG gels except  $p$ -tuned samples roughly obey a linear relationship (dotted line in Fig. 6), showing the qualitative agreement with Eqs. (1)–(3). Quantitatively,  $T_m$  of Tetra-PEG gels are higher than the prediction of Eqs. (1)–(3) and those of samples with similar  $T_{cal}$  from literature, suggesting the fracture toughness of homogeneous network. On the other hand,  $p$ -tuned Tetra-PEG gels show opposite behavior;  $T_{cal}$  decreased with an increase in  $T_m$ . This opposite behavior is mainly caused by the failure of Eq. (3); a decrease in  $\nu$  does not lead to the increase in  $N$ . As mentioned above, in  $p$ -tuned Tetra-PEG gels, the decreased connectivity only generates dangling chains, but does not increase  $N$ . Thus, Eq. (3) is not correct even qualitatively in the case of the samples with substantial amount of dangling chains. According to this interpretation, the samples showing downward deviations from dotted line have substantial amount of dangling chains, and their  $N$  are overestimated by Eq. (3), leading to the overestimation of  $T_{cal}$ . It should be noted that  $T_0$  of Tetra-PEG gels are estimated from the minimum values of  $F$ , while those of literatures are from average or maximum values of  $F$ . Thus, all of the data in previous literatures are practically under the dotted lines, suggesting the existence of substantial amount of dangling chains.

### IV. CONCLUSION

The major findings of this paper are as follows: (i)  $T_0$  increased linearly with an increase in  $\nu$  calculated from  $p$ ,  $\phi_0$ , and  $N$ ; (ii)  $L$  was independent of  $p$  and  $\phi_0$  and only dependent of  $N$ ; (iii)  $L$  was proportional to the end-to-end distance of virtual network chains,  $R_0$ , with the values of approximately  $3R_0$ ; (iv)  $T_0$  of Tetra-PEG gels are higher than other polymer gels with similar  $T_{cal}$ .

As mentioned in the Introduction, the previous studies estimated  $\nu$  and  $N$  from  $G$ ; in a strict sense, they only investigated the relationship between  $G$  and  $T_0$ . Equation (3) is not valid in the polymer network with substantial amount of dangling chains, and the conventional method overestimate  $T_0$ . Thus, it is difficult to examine the validity of the Lake-Thomas model from the data of previous literatures. By controlling the feed parameters independently, our study offers a new insight on  $L$ , which was originally considered as the strand length of the network,  $L \approx R_0 \approx aN^{1/2}$ . Our result indicates that there is an enhancement factor of “3,” which is universal value regardless of the experimental parameters examined in this study. It should be noted that, the Tetra-PEG gels, from which we observed the prefactor, are free from trapped entanglement.<sup>24</sup> Thus, we conclude that we need the enhancement factor being near “3” even for predicting the fracture energy of polymer network without trapped entanglements. The trapped entanglements may increase the interaction between polymer segments, leading to a further increase in the enhancement factor.<sup>2,9,13</sup>

## ACKNOWLEDGMENTS

This work was supported by the Japan Society for the Promotion of Science (JSPS) through the Grants-in-Aid for Scientific Research, the Center for Medical System Innovation (CMSI), the Graduate Program for Leaders in Life Innovation (GPLLI), the International Core Research Center for Nanobio, and the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST program); the Ministry of Education, Culture, Sports, Science, and Technology in Japan (MEXT) through the Center for NanoBio Integration (CNBI); the Japan Science and Technology Agency (JST) through the S-innovation program; and Grant-in-Aids for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (Grant Nos. 12J07983 to Y.A., 23700555 to T.S., and 24240069 to U.C.).

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