



Feature Article

Structure–mechanical property correlations of model siloxane elastomers with controlled network topology

Kenji Urayama^{a,*}, Takanobu Kawamura^b, Shinzo Kohjiya^c

^a Department of Materials Chemistry, Kyoto University, Kyoto 615-8510, Japan

^b Department of Chemical Engineering, Kanazawa University, Ishikawa 920-1192, Japan

^c Department of Chemistry, Mahidol University, Phuthamonthon, Nakorn Pathom 73170, Thailand

ARTICLE INFO

Article history:

Received 6 September 2008

Received in revised form

16 October 2008

Accepted 21 October 2008

Available online 29 October 2008

Keywords:

Elastomers

Polydimethylsiloxane

Rubber elasticity

Viscoelasticity

ABSTRACT

We review our recent studies towards the molecular understanding of mechanical properties–structure relationships of elastomers using model polydimethylsiloxane (PDMS) networks with controlled topology. The model elastomers with controlled lengths of the network strands and known amounts of cross-links and dangling chains are obtained by end-linking the functionally terminated precursor PDMS with known molecular weights using multi-functional cross-linkers. Several modern entanglement theories of rubber elasticity are assessed in an unambiguous manner on the basis of the nonlinear stress–strain behavior of the model elastomers under general biaxial strains. The roles of cross-links and entanglements in the large-scale structure of the swollen state are revealed from small angle X-ray scattering spectra. A remarkably stretchable elastomer with the ultimate strain over 3000% is obtained by optimizing the network topology for high extensibility, i.e., by reducing the amounts of trapped entanglements and the end-to-end distance of the network strands. The model elastomers with unattached chains exhibit a pronounced viscoelastic relaxation originating from the relaxation by reptative motion of the guest chains. The relaxation spectra provide a definite basis to discuss the dynamics of guest linear chains trapped in fixed polymer networks. The temperature- and frequency-insensitive damping elastomers are made by introducing intentionally many dangling chains into the networks.

© 2008 Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

1. Introduction

Elastomers exhibit large reversible deformabilities with distinctly low elastic modulus – which are unparalleled in solid materials – due to the entropic elasticity. Such unique mechanical properties of elastomers originate from the three-dimensional network structure comprising long and flexible polymer chains [1,2]. The amorphous network structure of elastomers is characterized by several topological parameters such as the length of the network strands, functionality of cross-links, and the amounts of entanglements, dangling chains and loops. Extensive research on elastomers has been conducted over the years, and today, elastomers are widely utilized as commercial products. However, the molecular understanding of the network topology–mechanical property relationships still remains incompletely understood. This is primarily because conventional elastomers formed by random cross-linking methods have very obscure structure with a broad network strand length distribution and an unknown number of dangling chains. Well-characterized

model elastomers with known structural parameters can be prepared by the end-linking reaction [2–6]. Functionally terminated precursor chains with known molecular masses are end-linked with cross-linkers of functionality three or more (Fig. 1). The length of the network strands between the cross-links can be controlled by the length of the precursor chains. A finite imperfection in the end-linking reaction invalidates the equivalence of the lengths of the precursor chains and network strands, and this deviation can be quantitatively evaluated on the basis of a nonlinear polymerization model [7] and the quantity of unreacted materials extracted after the reaction. Similarly, the size distribution of the network strands can be controlled by the size distribution of the precursor chains. For example, the end-linking of mixtures of short and long precursor chains resulted in elastomers with bimodal length distribution of network strands [2,5,8]. The trimodal [9] or “pseudo unimodal” (extremely broad unimodal) [5] length distribution of network strands is also possible. Moreover, dangling chains (those tethered to the network at only one end) can be introduced intentionally by using mixtures of mono-functional and bi-functional precursors [2,4,10]. The end-linking of precursors in the solution can vary the amount of trapped entanglements in the resultant elastomers by changing the precursor concentration [11–13]. The end-linking

* Corresponding author.

E-mail address: urayama@rheogate.polym.kyoto-u.ac.jp (K. Urayama).

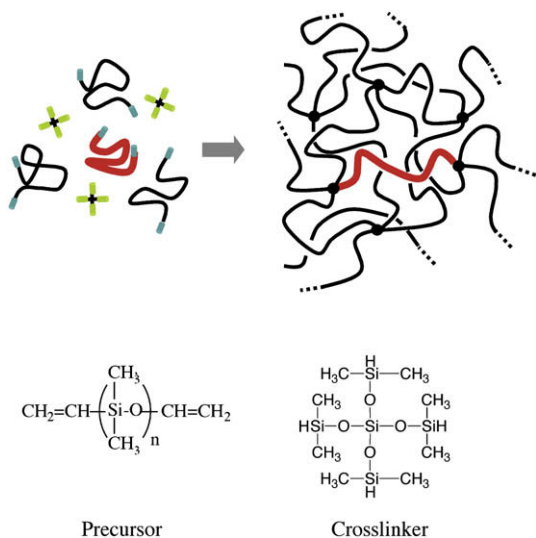


Fig. 1. End-linking telechelic precursors with tetra-functional cross-linkers.

reaction provides the mechanism to fabricate elastomers with a rich variety of topological characteristics.

Poly(dimethylsiloxane) (PDMS) is known as one of the most flexible polymers [14]. The high flexibility of PDMS originates from the structural features of the Si–O bonds; they have a longer bond length, larger bond angle, and significantly lower torsional potential than C–C bonds. This leads to a very low glass transition temperature (ca. -120°C) for PDMS. PDMS undergoes crystallization at considerably low temperatures of below -30°C . Usually, crosslinked PDMS does not exhibit strain-induced crystallization at room temperature. These features of PDMS are beneficial for fundamental studies of rubber elasticity. In fact, PDMS has often been employed as a precursor in end-linked elastomers. There are several types of chemical reaction that facilitate end-linking. The addition reaction between vinyl groups and Si–H groups by the use of a Pt catalyst is one of the most well-known reactions (Fig. 1). This reaction was employed for sample preparation in all our studies introduced in this article.

In this article, we review our recent studies on different types of PDMS elastomers with controlled network topology. Section 2 describes the nonlinear elasticity of model elastomers under general biaxial strains. Several modern entanglement theories for rubber elasticity are strictly assessed using stress–strain data obtained in different types of deformations. Section 3 discusses a large-scale structure present in the swollen model elastomers with controlled lengths of network strands on the basis of small angle X-ray scattering spectra. Section 4 introduces that the remarkably extensible elastomers with the unusual network topology tuned to high extensibility which are prepared by end-linking in semi-dilute solutions and subsequently drying. Section 5 describes the viscoelastic properties of the model elastomers with low concentration of unattached chains and model irregular elastomers with a known amount of dangling chains. The model elastomers with low concentrations of unattached chains provide a basis for discussion of the dynamics of free guest chains in fixed (crosslinked) polymer networks. The model irregular elastomers with a known amount of dangling chains result in an elastomer with high damping, which is insensitive to temperature and frequency.

2. Nonlinear elasticity characterized by general biaxial strains

Elastomers exhibit large (and recoverable) deformabilities due to small forces. The relation between stress and strain is linear only

at very small strains, and it is significantly nonlinear at moderate and large strains. Uniaxial deformation has often been employed to characterize nonlinear elasticity because of its experimental simplicity. Uniaxial deformation, however, is one of the different types of deformations, and it provides limited information about nonlinear elasticity. In contrast, general biaxial strains that vary independently in two orthogonal directions (Fig. 2) cover the entire range of physically accessible deformations in incompressible elastomers [1,15,16]. The significance of general biaxial strains was recognized a long time ago, but there are few corresponding experiments [17–19] due to the complexity of the instruments required. Several researchers [1,16,20–24] have stated that analysis relying only on uniaxial data often leads to an erroneous understanding of nonlinear rubber elasticity – however, this important fact appears to be largely neglected. A typical example is the overestimation of the familiar Mooney–Rivlin plot using uniaxial data: the linearity in this plot is often superficial because the free energy estimated from this plot does not describe the biaxial data [20–24].

The biaxial data of well-characterized elastomers provide a definite basis for the molecular understanding of rubber elasticity. Many entanglement models have been proposed to improve the flaws in the classical theories [5]: the classical theories consider neither the topological interaction (entanglement effect) arising due to the uncrossability of network strands nor their finite extensibility. Most of the past assessments of these entanglement theories relied only on uniaxial data. Uniaxial deformation is not sensitive enough to distinguish one model from another [21,25]. In addition, the structural parameters in the models are often treated as additional fitting parameters because of obscurity of structural parameters of the randomly crosslinked elastomer samples. This treatment lends more ambiguity to the assessments. We investigated the nonlinear stress–strain relations of the model elastomers of end-linked PDMS under general biaxial deformations by using a custom-built tester to obtain an unambiguous basis for testing the theories [23,24,26–28]. The typical size of square sheet samples is ca. 50 mm width and ca. 1 mm thickness. The precursor PDMS chains used are highly entangled before end-linking due to the high molecular weight ($M_w = 89,500$). This molecular weight is considerably larger than the critical molecular weight for the formation of entanglement couplings ($M_c \approx 17,000$) [29] as well as the molecular weight between adjacent entanglements ($M_e \approx 10,000$) [30]. The mesh of the resultant networks is dominated by trapped entanglements instead of chemical cross-links. The PDMS elastomers with various amounts of trapped entanglements were prepared by varying the weight fraction of precursor PDMS (ϕ_0) in the solutions at end-linking. An oligodimethylsiloxane was employed as nonvolatile solvent. “As-prepared” samples (i.e., including the solvent) were used for biaxial experiments.

Fig. 2 shows the nominal biaxial stresses σ_x and σ_y for the end-linked PDMS elastomer of $\phi_0 = 0.70$ with as functions of the principal ratios λ_x and λ_y [23]. It should be emphasized that the stresses are the quasi-equilibrium ones with no appreciable time effect because they were obtained from the quasi-plateau stresses after sufficiently long time at each strain. It can be observed from the figure that the uniaxial stretching (triangular symbols; $\sigma_y = 0$) is only a part of the examined deformations. It should be noted that the uniaxial stretching data were obtained by another tensile tester using a rectangular strip of ca. 10 mm diameter and ca. 40 mm length which was cut from the sheet specimen used for biaxial measurements.

Using the biaxial data in Fig. 2, we assessed five entanglement models [26]: – the diffused-constraint model [31], the three different versions of the tube model [32–34], and the slip-link model [35,36]. We evaluated the structural parameters such as the numbers of elastically effective network strands and cross-links from the reaction conditions by using a nonlinear polymerization

Download English Version:

<https://daneshyari.com/en/article/5185372>

Download Persian Version:

<https://daneshyari.com/article/5185372>

[Daneshyari.com](https://daneshyari.com)