Synthesis, Characterization, and Rubber Elasticity of End-Linked Poly(tetrahydrofuran) Elastomer

Lei Jong* and R. S. Stein

Polymer Research Institute, University of Massachusetts, Amherst, Massachusetts 01003

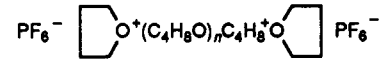
Received May 23, 1990; Revised Manuscript Received November 28, 1990

ABSTRACT: For physical studies of network formation, inhomogeneity, rubber elasticity, and stress-induced crystallization in a model elastomer, an end-linked poly(tetrahydrofuran) network has been synthesized and characterized. Diallyl-terminated poly(tetrahydrofuran) was synthesized by cationic ring-opening polymerization and terminated with allyl alcohol. The functionality, molecular weight, and polydispersity were characterized with GPC, chemical titration, and NMR. The results indicate the average functionality is 2.0 ± 0.1. End-linked elastomer can then be synthesized by reacting the stoichiometric amount of diallylpoly(tetrahydrofuran) with pentaerythritol tetrakis(3-mercaptopropionate), a tetrafunctional thiol. The resultant elastomers were characterized in terms of sol fraction and equilibrium degree of swelling. The average sol fraction of these elastomers is 2%. The thiol–ene addition reaction involved in the network formation was studied by using the small molecules that have similar chemical structures as that of prepolymer and cross-linker. NMR studies of the reaction product indicate that the thiol–ene addition reaction is well-defined, with no observed side reactions. Therefore, it is concluded that the chemical structure of this end-linked elastomer is known. This system is therefore adequate for our investigation of elastomeric properties. Stress–strain behavior of a swollen network was measured and compared with a constrained junction model. The results indicate the molecular weight between junctions by theoretical fitting of experimental data is much smaller than the true M_c between junction points. This implies that the contribution of trapped entanglements as an effective junction points to the modulus of these elastomers.

Introduction

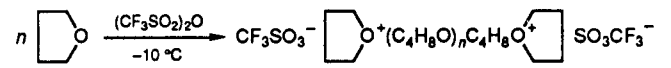
It is known that random cross-linking networks are more complicated than end-linked networks in terms of their chemical structures. End-linked networks are therefore more suitable for use as a model system for the establishment of reliable knowledge of elastomers. From previous studies,[1,2] it was shown that elastic properties of end-linked networks are different for networks formed from different types of polymers. It is therefore helpful to study and accumulate as much information as possible from different types of end-linked networks. On the basis of this realization, end-linked poly(tetrahydrofuran) networks were synthesized and characterized. The advantages of this system is multifold and as follows: (1) Prepolymer can be prepared by a well-defined cationic ring-opening living polymerization. (2) Difunctional initiator is readily available. (3) Glass transition temperature is −78 °C, and the melting point is 35–40 °C. As a result, by a slight manipulation of temperature around the room temperature, one can study the elastomer in both its amorphous and semicrystalline states. (4) Deuterated THF is readily available. Therefore, deuterated PTHF can be synthesized, and the network formation or local orientation can be studied with small-angle neutron scattering, deuterium NMR, or infrared dichroism. Regarding the physical studies of model networks, it is worth mentioning that a clear understanding of network structure is the basic requirement in interpreting the results. Therefore, the synthesis will be presented below in great detail, by starting with the synthesis of prepolymer, diallyl poly(tetrahydrofuran).

Tetrahydrofuran polymerizes only by a cationic ring-opening mechanism.[3–8] The propagating species in THF polymerization is a tertiary oxonium ion associated with a negatively charged species, the counterion. More firmly bonded elements in a complex ion lead to more stable and more suitable counterion for THF polymerization and to fewer side reactions. Stable counterions are complex ions including anions like PF_6^-, AsF_6^-, SbF_6^-, $SbCl_6^-$, BF_4^-, $SO_3CF_3^-$, SO_3F^-, and ClO_4^-. Several initiators and mechanisms are available.[9] However, only a few difunctional initiators can be used in the synthesis of a difunctional PTHF prepolymer. These difunctional initiators include terephthaloyl hexafluoroantimonate,[10] adipoyl hexafluoroantimonate,[10] bisdioxolenium perchlorate,[11] trifluoromethanesulfonic anhydride,[12] disulfuryl fluoride, complex



prepared from THF and PF_5,[13] compounds formed from dialkyl halide and $AgClO_4$ or $AgPF_5$,[14] and silenium dication,[15,16] which has the structure $ClO_4^-Si^+(CH_3)_2(OSi(CH_3)_2)_5OSi^+(CH_3)_2ClO_4^-$. Among the above difunctional initiators, only trifluoromethanesulfonic anhydride can be used to yield poly(tetrahydrofuran) with both narrow molecular weight distribution and homogeneous polymer backbone.

One effective experimental condition is to polymerize THF in bulk at −10 °C by using trifluoromethanesulfonic anhydride as the initiator.[12] The molecular weight can be controlled by adjusting the concentration of the initiator and the time of polymerization. The reaction mechanism is as follows:

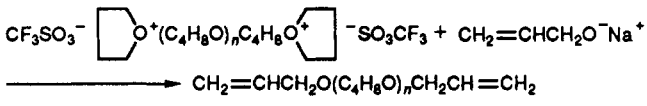


Because oxonium ion groups can react with nucleophiles, various end groups can be introduced into prepolymer. By termination of the living polymer with water, alcohol, ammonia, amines, carboxylic acids, and thiols,[17,18] resultant end groups can be used in further reactions to form networks.

In our case, terminating end groups were selected according to the following requirements: (1) It should react only with one living end of the polymer. This is to prevent the formation of functional groups along the polymer chain and the broadening of the molecular weight distribution. (2) It can be used in large quantity. This

0024-9297/91/2224-2323$02.50/0

is to obtain instant termination and therefore to prevent the broadening of molecular weight distribution. (3) The resultant functional groups should be stable during the purification and storage for further reactions with multifunctional cross-linker. (4) The resultant functional groups can undergo addition reactions with polyfunctional cross-linkers available. On the basis of these requirements, the sodium salt of allyl alcohol was used to give diallyl-terminated PTHF



Alternatively, a large quantity of allyl alcohol can be used to obtain instant termination. It has been shown in our experiments that both the sodium salt of allyl alcohol and allyl alcohol yield the same results.

In the network formation, two cross-linking reactions are potentially useful. One is a silane–vinyl addition reaction and another is a thiol–ene addition reaction. The silane addition reaction is not suitable for use in this case because it can cause the rearrangement of allyl functional groups[19] due to the immediate adjacency of the allyl functional group to an ether linkage. Therefore, the thiol–ene addition reaction was chosen. The addition of thiol to olefins to form thiol ethers is a reaction that has been extensively studied since its discovery by Posner in 1905.[20] The reaction is generally considered to proceed via a multistep chain mechanism,[21,22] which includes initiation, addition, chain transfer, propagation, and termination.

For the purpose of model network synthesis, only the addition of thiols to terminal olefins should be considered. In these reactions, the kinetic chain length is usually high and the yields of the chain termination products are consequently very low. Generally, these products have not been detected.[23] Also, in the reaction mixtures of equal molar amounts of reactants, the 1:1 adduct will predominate due to the high chain-transfer constant of thiol. The free-radical addition of thiols to terminal olefins proceeds in an anti-Markovnikov manner, with exceptionally high yields and usually without telomer formation.[24] These were observed from several experiments with the yield of 1:1 adduct more than 95%.[25-30]

Polymers prepared by this reaction such as polyalkylene sulfides have been studied extensively.[31-38] The infrared spectrum of one polyalkylene sulfide prepared from hexamethylenedithiol and 1,5-hexadiene was compared with the IR spectrum of another polyalkylene sulfide prepared from hexamethylenedithiol and 1,6-dibromohexane. It was concluded that a linear polymer by the addition of dithiol to diolefins was obtained.[31] This is an indication that telomer formation, which can lead to a branching polymer, is not significant. The NMR study of the polymer prepared by the polymerization of 1,4-butanediol–di-*N*-allyl carbamate and ethylene glycol di-β-mercaptopropionate also indicated that no significant vinyl polymerization occurred competitively with the thiol–ene addition reaction because the proton on a tertiary carbon in the NMR spectrum of this polymer was not observed.[39]

Elastomers from polymers with a terminal double bond and polyfunctional thiols have also been claimed in a few patents.[40,41] Divinylpoly(tetrahydrofuran) prepared from dihydroxypoly(tetrahydrofuran) and allyl isocyanate and then cross-linked with pentaerythritol tetrakis(3-mercaptopropionate) under UV has been reported.[39] However, the network was not characterized to indicate its conversion, and it is likely that the functionality of this prepolymer is greater than 2.0 because of the allophanate formation.

From the previous studies of thiol–ene reactions, it is seen that this reaction can be used as a means in the synthesis of model networks with only an insignificant amount of side reactions. Therefore, diallylpoly(tetrahydrofuran) was cross-linked with pentaerythritol tetrakis(3-mercaptopropionate) to form an end-linked elastomer.

The reaction was initiated with a heat-activated free-radical generator, benzopinacole. Benzopinacole is a special initiator, which can only be activated effectively above 80 °C.[41] Consequently, cross-linking reaction does not occur when the prepolymer is mixed with cross-linker at room temperature in a good solvent. Conventional free-radical generators such as organic peroxides and azo compounds cannot be used in this case because they can initiate the reaction even under ambient conditions.

Experimental Section

Synthesis of Diallylpoly(tetrahydrofuran). In a typical case, 3 mL of anhydrous trifluoromethanesulfonic anhydride was added to 250 mL of THF, which was freshly distilled from lithium aluminum hydride. The reaction mixture was then stirred with a constant-speed mechanical mixer at −10 °C for 2 h. To introduce the functional groups and terminate the reaction, 50 mL of anhydrous allyl alcohol distilled from potassium carbonate and 180 mL of anhydrous dichloromethane distilled from CaH_2 were then added to the living polymer solution. After 30 min of stirring, 18 mL of triethylamine was added into the reaction mixture in order to precipitate the acid generated during the termination. Afterward, the mixture was stirred for another 30 min and the temperature raised to room temperature. White precipitate of acid–base complex was observed. Solvents including THF, allyl alcohol, dichloromethane, and triethylamine were evaporated under vacuum at ambient temperature. The remaining mixture of salt and polymer was diluted with ether and exhaustively extracted with water. The ether solution of polymer was dried over magnesium sulfate and then filtered through a 0.7-μm glass-fiber filter. After the evaporation of ether, polymer was diluted with benzene and freeze-dried. The yield was 67% with a number-average molecular weight of 8286 and a polydispersity of 1.28.

Synthesis of Elastomer from Diallylpoly(tetrahydrofuran) and Pentaerythritol Tetrakis(3-mercaptopropionate). A stoichiometric amount of diallylpoly(tetrahydrofuran) and pentaerythritol tetrakis(3-mercaptopropionate) was mixed in benzene first, and 0.1% of benzopinacole was then added into this solution. The weight fraction of benzene is about 70%. The reaction in benzene was allowed to proceed for 20–30 min at 60 °C. During this period, all cross-linkers should already have reacted with at least one prepolymer chain. This is necessary in the prevention of phase separation between cross-linker and prepolymer after the evacuation of benzene. Whether or not the phase separation occurs can be checked from the extraction of a well-cured unimodal network. If the segregation is significant, the sol fraction will be large because the number of effective cross-linkers required to produce a perfect network is reduced. The results of sol fraction presented in this paper indicate that the condition used here is proper in producing a homogeneous network. The homogeneity of these networks will be mentioned in the last section of this paper. After the mixing, a flat dish containing this reaction mixture was placed in a vacuum oven and benzene was removed by flushing with nitrogen and simultaneously evacuating with a pump. Most of the benzene was evacuated within 30 min because no more condensation of benzene was observed in the solvent trap. Thus, the network can be considered to be formed in the absence of solvent. The pumping and flushing with nitrogen was continued for 2 h at 88 °C, and the network was then cured for 2 days under nitrogen.

Reaction of Allyl Phenyl Ether and Methyl 3-Mercaptopropionate. In order to determine the extent of the side

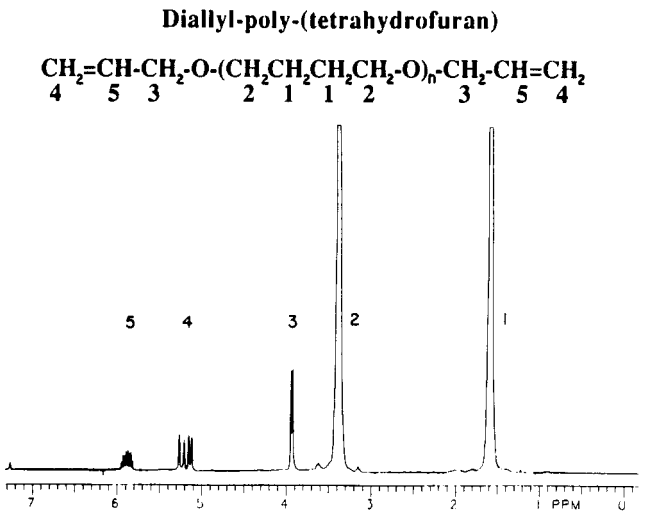


Figure 1. NMR spectrum of poly(tetrahydrofuran) in $CDCl_3$, M_n = 990.

reactions involved in the cross-linking reaction, the reaction was simulated with small molecules, which have the same chemical structure as that of prepolymer and cross-linker. Allyl phenyl ether has a structure equivalent to an allyl functional group in the diallyl-terminated PTHF. Methyl 3-mercaptopropionate has a chemical structure equivalent to one arm of tetrafunctional cross-linker used in the network formation. A stoichiometric amount of allyl phenyl ether and methyl 3-mercaptopropionate was mixed in benzene and allowed to react in the same conditions as that of network formation. After the reaction, benzene, unreacted allyl phenyl ether, and unreacted methyl 3-mercaptopropionate were evaporated under vacuum at room temperature. The remaining products were then subjected to NMR measurements.

Characterization Methods. All NMR spectra presented here were measured with a Varian XL-300 NMR spectrometer. $CDCl_3$ was used as a solvent, and a 5-mm standard NMR tube was used as the sample cell. The number of accumulations in free induction decays is over 300. Molecular weight and polydispersity were measured with gel permeation chromatography equipped with an Ultrastyragel linear column (Waters Chromotography Division, Millipore Corp.). THF was used as solvent. The calibration standards used are the PTHF of low polydispersity purchased from Polyscience. By end-group titration, the iodine bromide method[42] was used in the determination of the number-average molecular weight of diallylpoly(tetrahydrofuran). In a typical case, 0.546 g of prepolymer was dissolved in 40 mL of CCl_4 and 25 mL of Hannus' solution was added to the mixture. The mixture was allowed to stand for 25 min, and then 30 mL of 15% aqueous KI solution was added to the reacted solution. The solution was vigorously shaken for a few minutes, and then 60 mL of water was added. The resultant solution containing iodine was then titrated with a 0.1 N $Na_2S_2O_3$ solution.

Sol fraction of model networks was measured as follows: A network of approximately 0.25 g was extracted with 60 mL of toluene at 50 °C for 2 days. The extracted swollen network was then successively deswelled with the proper amount of methanol, and the deswelled network was dried in a vacuum oven at 50 °C for 1 day. The sol fraction of networks can be calculated from the weight of the networks before and after extraction. The volume fraction of a polymer in a swollen network at the equilibrium degree of swelling was measured with an electronic balance. The volume ratio of a network in its dry state and its swollen state is the volume fraction of the polymer, assuming that the volume of the solvent and that of the polymer are additive.

Results and Discussion

The typical ^1H NMR spectra of a diallylpoly(tetrahydrofuran) with a M_n equal to 990 are shown in Figures 1 and 2. The assignment of resonance lines was obtained by comparing the NMR spectrum of the prepolymer with that of allyl alcohol or that of allyl phenyl ether. No

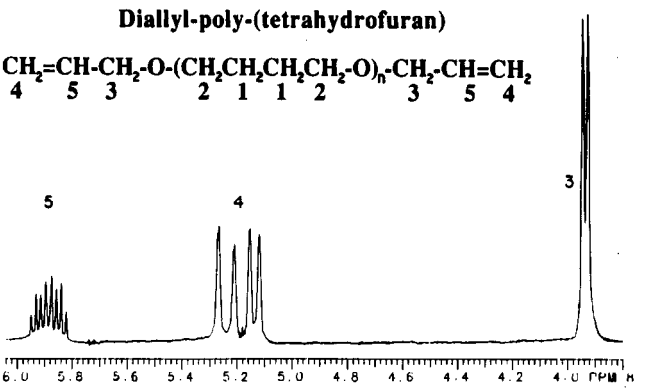


Figure 2. NMR spectrum of allyl functional groups of poly(tetrahydrofuran) in $CDCl_3$, M_n = 990.

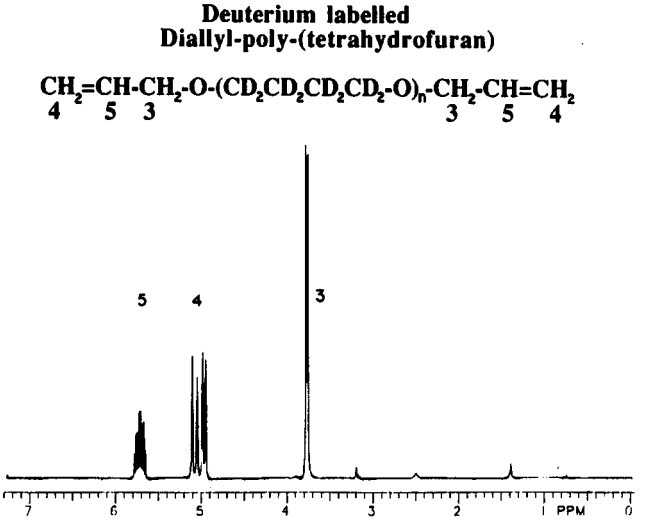


Figure 3. NMR spectrum of deuterated poly(tetrahydrofuran) in $CDCl_3$, M_n = 995.

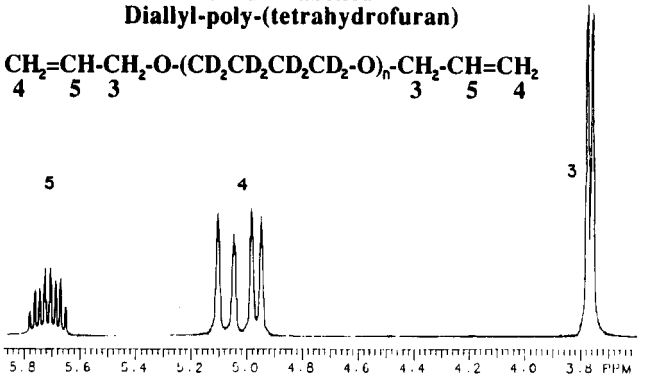


Figure 4. NMR spectrum of allyl functional groups of deuterated poly(tetrahydrofuran) in $CDCl_3$, m_n = 995.

significant side reactions during the polymerization have been observed from the NMR spectrum. In order to check whether there are resonance lines superimposed with the resonance lines of hydrogen in the polymer backbone, deuterium-labeled diallylpoly(tetrahydrofuran) was synthesized by the same method mentioned in the Experimental Section. The deuterium-labeled monomer used in the polymerization was ordered from the Cambridge Isotope Laboratory and Aldrich Chemical Co. with 99.5 atom % D. The ^1H NMR spectra of deuterium-labeled prepolymers with a M_n equal to 995 are shown in Figures 3 and 4. Except for an approximately 0.5% hydrogeneous monomer unit, no other significant side reactions were observed. An IR spectrum of amorphous diallylpoly(tet-

Table I
Characterization of Diallylpoly(tetrahydrofuran)

M_n(chemical titration)	M_n(GPC)	M_n(NMR)	M_w/M_n(GPC)	functionality
1210		1260		
1360		1319		
5783	6038		1.14	2.09
5880	6098		1.29	2.07
8286	8335		1.28	2.01
8292	8723		1.22	2.10
11490[a]	11520		1.33	1.99
13160	13475		1.54	2.05

[a] This polymer is hydroxyl-terminated.

Table II
Equilibrium Swelling of Model Poly(tetrahydrofuran) Networks in Toluene[a]

$10^{-3}M_n$	W_s (sol fraction)	V_2 (volume fraction)
2.00	0.022	0.3057
2.52	0.008	0.2876
5.88	0.032	0.2150
5.88	0.006	0.2270
5.88	0.018	
8.29	0.015	0.2031
8.29	0.021	0.1973
8.29[b]	0.023	0.1759
8.29	0.034	0.1780
13.16	0.030	0.1500
13.16	0.030	0.1430

[a] The molar ratio S—H/C=C is 1.00. The average functionality of the cross-linker is 3.88. [b] Bimodal network: $(M_n)_L$ = 13 160, $(M_n)_S$ = 2520. Molar fraction: X_L = 0.5425, X_S = 0.4575.

rahydrofuran) was also obtained. No hydroxyl groups were observed in the spectrum. This is an indication that the initiator, monomers, and chemicals used in terminating polymerization are sufficiently dry. The number-average molecular weight of this prepolymer was measured by using GPC, NMR, and chemical titration. The results including polydispersity and functionality are tabulated in Table I. The fluctuating error involved in the calculation of the functionality of a prepolymer is mostly from the fluctuation in the eluting speed of the GPC used. The true functionality should be less than 2.0 per polymer chain. Also, the true polydispersity of these polymers should be less than the values shown in Table I because of the band-broadening effect in the GPC used. The number-average molecular weight obtained from several techniques such as NMR, GPC, and chemical titration is in reasonably good agreement with M_n estimated from polymerization kinetics established by Smith and Hubin.[12] From these experimental observations, it is concluded that the chemical structure, molecular weight, polydispersity, and functionality of these prepolymers are well-defined.

The characterization of networks includes the measurement of the sol fraction, the volume fraction at equilibrium swelling in a good solvent, and the study of cross-linking reactions. The results of the sol fraction and volume fraction are presented in Tables II and III for toluene and ethyl acetate, respectively. It is seen that the average sol fraction is about 2%. The sol fraction of elastomers varies with each preparation of the network from the same prepolymer. However, that most of networks have a sol fraction less than 2% indicates that the preparation method is adequately reproducible. A total of 2% of the sol fraction may result from the accuracy in measuring small amounts of cross-linker and/or the steric effect, which controls the diffusion rate of prepolymer and cross-linker in the later stage of curing. Nonetheless, this type of network provides the minimum value of M_c between junctions. The true value of M_c is slightly larger

Table III
Equilibrium Swelling of Model Poly(tetrahydrofuran) Networks in Ethyl Acetate[a]

$10^{-3}M_n$	W_s (sol fraction)	V_2 (volume fraction)
2.00	0.022	0.4209
2.52	0.008	0.3723
5.88	0.011	0.3561
5.88	0.012	0.3554
5.88[b]	0.013	0.3427
8.29	0.012	0.3110
8.29	0.014	0.3135
8.29	0.034	0.2492
10.16	0.036	0.2426

[a] The molar ratio S—H/C=C is 1.00. The average functionality of the cross-linker is 3.88. Temperature = 25 °C. [b] Bimodal network: $(M_n)_L$ = 8286, $(M_n)_S$ = 990. Molar fraction: X_L = 0.6694, X_S = 0.3306.

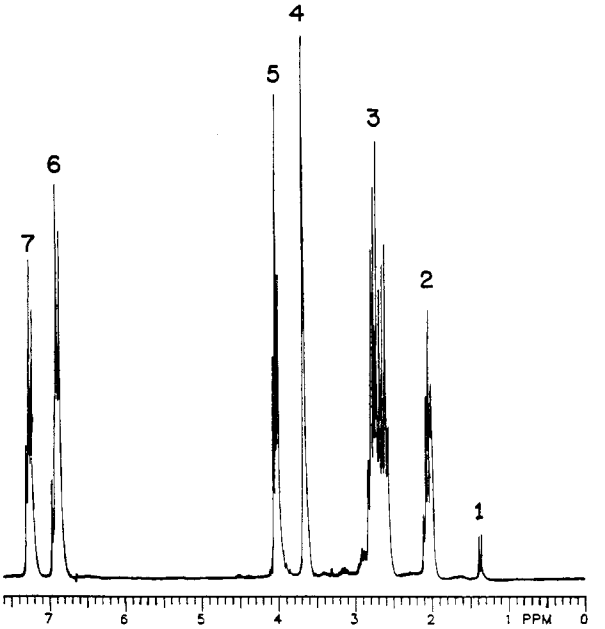


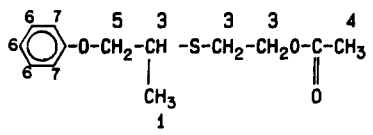
Figure 5. NMR spectrum of the reaction product of allyl phenyl ether and methyl 3-mercaptopropionate.

than the M_n of the prepolymer, depending on the amount of the sol fraction. The use of such information to address the entanglement effect in a network will be discussed in the following section.

The nature of the cross-linking reaction has been reviewed in the Introduction. The added evidence of small-molecule reactions conducted by the author will be presented here. The ^1H NMR spectrum of reaction products of allyl phenyl ether and methyl 3-mercaptopropionate is shown in Figure 5. The assignment of resonance lines was done by using NMR spectra of similar compounds compiled in the published literature. The combination of the area integration and the assignment of resonances lines yields the two possible structures shown in Figure 6. The relative number percentage of each product shown was obtained from the ratio of the area of resonance line 1 and that of resonance line 4 in Figure 5. By inspection of the NMR spectrum in Figure 5, it is also seen that no other significant side reactions are observable.

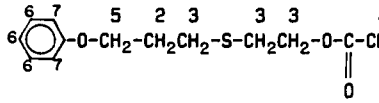
As far as the high-temperature stability of this network is concerned, previous degradation studies of PTHF[43] yielded 29 and 45 kcal/mol for the activation energy of degradation in air and in a vacuum, respectively. By using these values, one can conclude that, under the nitrogen atmosphere, the molecular weight should undergo insignificant change during the network curing at 88 °C for 48 h. Although the thermal degradation of PTHF may begin

(1) MARKOVNIKOV ADDITION



6 %

(2) ANTI-MARKOVNIKOV ADDITION



94 %

Figure 6. Reaction products of allyl phenyl ether and methyl 3-mercaptopropionate, obtaining the NMR spectrum shown in Figure 5.

to occur above 90 °C, physical studies of amorphous elastomer can be performed at a temperature well below 90 °C because of the low melting point of PTHF.

Rubber Elasticity

A few theoretical models have been proposed to account for entanglement effects in rubber networks. These include sliplink models,[44,45] in which each network chain threads its way through a number of rings, tube models,[46-52] in which each network chain is confined within a tube, and the constrained junction model,[53,54] in which each network junction is subjected to a domain of constraint. The experimental results presented here are compared with the constrained junction model only.

In a constrained junction model, the force in a uniaxially stressed rubber network is expressed as the sum of two terms[55,56]

$$f = f_{ph} + f_c \tag{1}$$

The first term, f_{ph}, represents the contribution of the corresponding phantom networks, and f_c is due to the constraint on the junction because of the presence of other chains. Experimentally, the most used definition of the modulus in elongation is

$$[f^*] = f^* v_2^{1/3}/(\alpha - \alpha^{-2}) \tag{2}$$

where f^* is the nominal stress f/A^0, f is the equilibrium value of the elastic force, A^0 is the undeformed cross-sectional area of the swollen sample, and v_2 is the volume fraction of polymer in the swollen network. The theoretical expression of reduced force is given as

$$[f^*] = v_{2c}^{-1/3}(\xi kT/V^0)[1 + f_c/f_{ph}] \tag{3}$$

The explicit form of eq 3 is detailed in ref 54.

Uniaxial Stress-Strain Experiment

Samples used in this experiment were prepared in the same way as that described previously. A rectangular shape of the sample is cut from the network sheet and swelled in dibutyl phthalate for a certain period of time. The degree of swelling can be controlled by the immersion time. These networks are then enclosed in a bottle for 3 days until they are swollen homogeneously by eye inspection. The volume fraction of each network is measured by assuming that the volume fraction of polymer and that of solvent are additive. From the volume fraction of polymer in the swollen network and the dimension of dry network, the swollen dimension was calculated. The typical dimension of a swollen network is $60 \times 6 \times 1$ mm^3. Two fiducial marks with about a 30-mm separation are drawn on the swollen sample with red ink.

Table IV
Stress-Strain Measurements of Swollen Model Poly(tetrahydrofuran) Networks[a]

$10^{-3}M_n$	W_s (sol fraction)	V_2 (volume fraction)	$2C_1$, N/mm^2	$2C_2$, N/mm^2	A_4
8.29	0.0214	0.689	0.340	0.523	1.156
		0.544	0.452	0.216	1.534
		0.337	0.500	0.093	1.670
8.29[b]	0.0230	0.698	0.312	0.267	1.059
		0.532	0.320	0.172	1.086
		0.257	0.365	0.064	1.240
10.16	0.0364	0.681	0.313	0.325	1.305
		0.486	0.342	0.159	1.425
		0.275	0.359	0.093	1.494

[a] The diluent is dibutyl phthalate; bp = 340 °C. The average functionality of the cross-linker is 3.88. [b] Bimodal network: $(M_n)_L$ = 13160, $(M_n)_S$ = 2520.

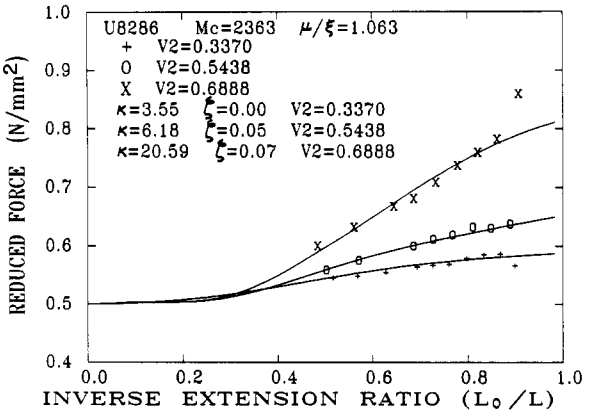


Figure 7. Theoretical fitting of experimental data for the unimodal network of M_n = 8286.

The stress-strain measurements are performed by fixing one end of the sample and suspending different weights on the other end of the sample. They are allowed to reach equilibrium for at least 20 min. It was found that the elongation under a constant weight remained the same for the equilibration time of either 20 min or 3 h. The distance between two marks was measured with a cathetometer, which is accurate to 0.02 mm. Reversibility is also checked by the out-of-sequence measurements.

Stress-Strain Isotherms of Swollen Networks

Table IV shows the results of stress-strain measurements of swollen networks. $2C_1$ and $2C_2$ are the phenomenological Mooney-Rivlin constants. A_4 is the structure factor at infinite deformation. The general expression of the structure factor for any functionality of junction is

$$A_\phi = 2C_1/(\rho RT/M_n) \tag{4}$$

where ρ is the density of the polymer and M_n is the number-average molecular weight of the prepolymer. For a perfect end-linked elastomer of functionality ϕ, the structure factor is equal to $(1 - 2/\phi)$. In the case of model PTHF elastomer, ϕ is equal to 3.88, and the theoretical value of A_ϕ is therefore 0.4845. Experimental values shown in Table III are much greater than 1.0, which is the top limit of the structure factor for networks with any functionality. This indicates that the M_c between junctions is much smaller than the M_n of the prepolymer.

The fitting of experimental data with the constraint junction model[54-56] is shown in Figures 7-9. The fitting parameters are M_c, κ, and ζ. Two unimodal networks are designated as U8286 and U10160 with M_c equal to 8286 and 10 160, respectively. The bimodal network is designated as B8292 with M_c equal to 8292. The best fit between

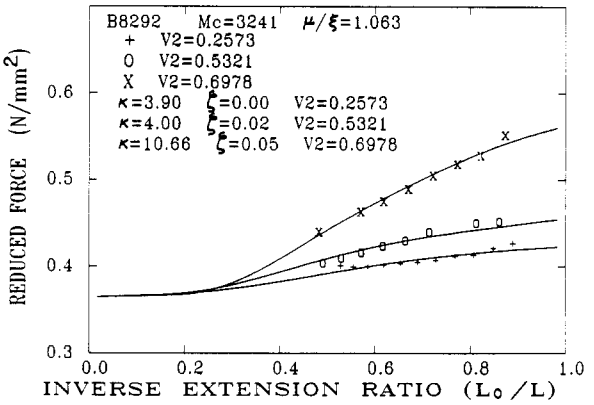


Figure 8. Theoretical fitting of experimental data for the bimodal network of M_n = 8292.

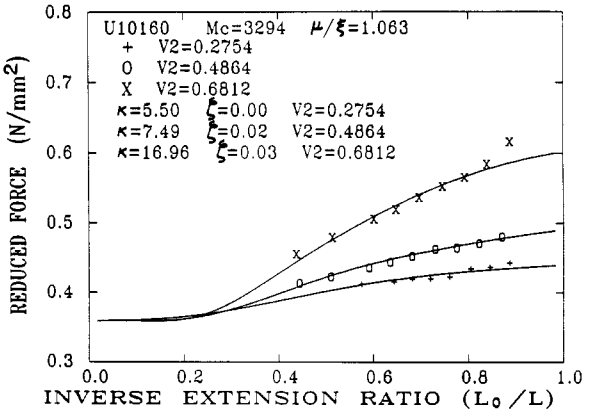


Figure 9. Theoretical fitting of experimental data for the unimodal network of M_n = 10 160.

theory and experiment can only be obtained by using a value of M_c much smaller than the M_n of the prepolymer, but the true M_c between chemical junctions should be greater than the M_n of the prepolymer because the end-linked network is never a perfect network. Two possible reasons can explain the deviation from the theory. These are the presence of physical entanglements and/or the stress-induced crystallization. Inhomogeneity of these well-cured networks prepared by the author has been demonstrated to have a correlation length of 10 Å by small-angle neutral scattering.[57] This means that the segregation effect is insignificant. Homogeneity of the network was controlled by reacting the cross-linker with the prepolymer in benzene under agitation for a sufficient period of time before casting. The change of reaction time in the benzene and the amount of initiator can lead to the variation in the homogeneity of networks, especially in the bimodal network, as demonstrated by the results of small-angle neutron-scattering studies.[58] The proper control of these factors will produce a homogeneous network as those presented here. The inhomogeneity is therefore of no concern in this case. For the isotropic swollen networks, the crystallization was not observed from X-ray diffraction at 25 °C due to the melting point depression. Orientation may increase the melting point and the crystallinity of the networks as demonstrated in 1,4-polybutadiene networks,[59] but the influence of the draw ratio on the final melting point becomes important only for an elongation ratio greater than a certain value, depending on the cross-linking density. In this case, it is doubtful that the draw ratio of about 100% can increase the melting point significantly. From our theoretical fitting of experimental data, the elastically active junctions are more than twice as many as the chemical junctions, assuming that all junctions are tetrafunctional. This indicates more than 50% of the active junctions are physical junctions. If one assumes that stress-induced crystallization can occur in these networks, the number of crystallites acting as effective junctions should increase from zero to a certain value, proportional to the elongation ratio. According to our estimation from fitting, the number of physical junctions is more than that of the chemical junctions in these networks. Such significant increases in the number of active junctions should already have exerted the effect on the stress–strain curve as an up-turn, as is usually observed in stressed rubber when the stress-induced crystallization is effective,[60] but this was not found. This reasoning can be further understood by comparing the stress–strain curves of the model network with $M_c = M_n$ and that of the network with $M_c = 2M_n$. Therefore, we think the possibility of stress-induced crystallization in these swollen networks is not significant. The contribution of the physical junction in these experiments, in our opinion, is more likely due to the contribution of the physical entanglement instead of the error involved in the stress–strain equilibration and/or the stress-induced crystallization. The observation of such effective physical junctions, is, however, not unique. Some previous reports[1,61,62] have also indicated such an effect. Our concluding remark of this investigation is that trapped physical entanglement is likely to play a significant role in the contribution to the modulus of the PTHF network within the range of strain measured. It also suggests that the previous assumption in the constraint junction model, which assumes the trapped entanglement does not act as elastically active junction, may require reconsideration.

Acknowledgment. We acknowledge the CUMIRP (Center for UMass-Industry Research on Polymers) and the National Science Foundation for their support of this investigation.

References and Notes

(1) Llorente, M. A.; Riande, E.; Guzman, J. *Macromolecules* **1984**, *17*, 1048.
(2) Llorente, M. A.; Mark, J. E. *Macromolecules* **1980**, *13*, 681.
(3) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528.
(4) Meerwein, H.; Delfs, D.; Morshel, H. *Angew. Chem.* **1960**, *72*, 927.
(5) Furukawa, J.; Saegusa, T. *Polymerization of Aldehydes and Oxide*; Interscience: New York, 1963.
(6) Saegusa, T.; Kobayashi, S. *Prog. Polym. Sci., Jpn.* **1973**, *6*, 107.
(7) Enikolopian, N. S.; Ponomarenko, V. V.; Rakova, G. V. *Vysokomol. Soedin.* **1977**, *A19*, 1924 (in Russian). Translated in *Polym. Sci. USSR* **1977**, *19*, 2200.
(8) Rosenberg, B. A.; Irshak, W. I.; Enikolopin, N. S. *Inter-chain Reaction in Polymeric System*; Khimiya: Moscow, USSR, 1975.
(9) Dreyfuss, P. *Polytetrahydrofuran*; Gordon and Breach Science: New York, 1982.
(10) Franta, E.; Reibel, L.; Lehmann, J. *J. Polym. Sci., Symp. Ser.* **1976**, *56*, 139.
(11) Yamashita, Y.; Hirota, M.; Matsui, H.; Hirao, A.; Nobutoki, K. *Polym. J.* **1971**, *2* (1), 43.
(12) Smith, S.; Hubin, A. J. *J. Macromol. Sci. A* **1973**, *7* (7), 1399.
(13) Hoene, R.; Reichert, K. H. W. *Makromol. Chem.* **1976**, *177*, 3545.
(14) Burgess, F. J.; Cunliffe, A. V.; Richards, D. H.; Thompson, D. *Polymer* **1978**, *19*, 334.
(15) Kucera, M.; Lanikova, J.; Spousta, E. Czech. 11064, Dec 27, 1963.
(16) Kucera, M.; Spousta, E. *J. Chem. Soc.* **1965**, 1478.
(17) Smith, S.; Hubin, A. J. U.S. Patent 3,824,220, July 16, 1974.
(18) Smith, S.; Hubin, A. J. U.S. Patent 3,824,219; U.S. Patent 3, 824,198.
(19) March, J. *Advanced Organic Chemistry, Reactions, Mechanism, and Structures*, 3rd ed.; Wiley-Interscience: New York, 1985.
(20) Posner, T. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 646.

(21) Karasch, M. S.; Read, A. T.; Mayo, F. R. *Chem. Ind. (London)* **1938**, *57*, 752.
(22) Back, R.; Trick, G.; McDonald, C.; Sivertz, C. *Can. J. Chem.* **1954**, *32*, 1078.
(23) Stacey, F. W.; Harris, J. F., Jr. *Org. React.* **1963**, *13*, 165.
(24) Kellogg, R. M. In Thiyl Radicals. *Methods in Free-Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; Vol. 2.
(25) Shostakovskii, M. F.; Prilezheava, E. N.; Shapiro, E. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1958**, *7*, 1021.
(26) Prilezhaeva, E. N.; Shostakoskii, M. F. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1958**, *7*, 1071.
(27) Rust, E. E.; Vaughan, W. E. U.S. Patent 2,392,294; *Chem. Abstr.* **1946**, *40*, 2453.
(28) Evans, T. W.; Vaughan, W. E.; Rust, E. E. Brit. Pat. 567,524; *Chem. Abstr.* **1947**, *41*, 2745.
(29) Smith, B.; Hernestam, S. *Acta Chem. Scand.* **1954**, *8*, 1111.
(30) Hendrickson, J. G.; Hatch, L. F. *J. Org. Chem.* **1960**, *25*, 1747.
(31) Marvel, C. S.; Chambers, R. R. *J. Am. Chem. Soc.* **1948**, *70*, 993.
(32) Marvel, C. S.; Aldrich, P. H. *J. Am. Chem. Soc.* **1950**, *72*, 1978.
(33) Marvel, C. S.; Nowlin, G. *J. Am. Chem. Soc.* **1950**, *72*, 5026.
(34) Marvel, C. S.; Markhart, A. H. *J. Am. Chem. Soc.* **1951**, *73*, 1046.
(35) Marvel, C. S.; Markhart, A. H. *J. Polym. Sci.* **1951**, *6*, 711.
(36) Marvel, C. S.; Baumgarten, H. E. *J. Polym. Sci.* **1951**, *6*, 127.
(37) Marvel, C. S.; Robert, C. W. *J. Polym. Sci.* **1951**, *6*, 717.
(38) Marvel, C. S.; Caesas, P. D. *J. Am. Chem. Soc.* **1951**, *73*, 1097.
(39) Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci.* **1977**, *15*, 627.
(40) Morgan, C. R. U.S. Pat. 3,784,524, Jan 8, 1974.
(41) Morgan, C. R. U.S. Pat. 4,020,233, April 26, 1977.
(42) Siggia, S. *Quantitative Organic Analysis via Functional Groups*; John Wiley and Sons, Inc.: New York and London, 1963.
(43) Davis, A.; Golden, J. H. *Makromol. Chem.* **1965**, *81*, 38.
(44) Marrucci, G. *Rheol. Acta* **1979**, *18*, 193.
(45) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *46*, 67.
(46) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
(47) DiMarzio, E. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9* (1), 256.
(48) de Gennes, P.-G. *J. Phys. Lett.* **1974**, *35*, L-133.
(49) Edwards, S. F. *Br. Polym. J.* **1977**, *9*, 140.
(50) Gaylord, R. J. *Polym. Eng. Sci.* **1979**, *19*, 263.
(51) Marrucci, G. *Macromolecules* **1981**, *14*, 434.
(52) Gaylord, R. J. *J. Polym. Bull.* **1983**, *9*, 181.
(53) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(54) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(55) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(56) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363.
(57) Jong, L. Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1989.
(58) Wu, W.; Laurence, D. C.; Jong, L.; Hanyu, A.; Stein, R. S. *Macromolecules* **1990**, *23*, 348.
(59) Cesari, M.; Perego, G.; Zazzetta, A.; Gargani, L. *Makromomol. Chem.* **1980**, *181*, 1143.
(60) Su, T.-K.; Mark, J. E. *Macromolecules* **1977**, *10*, 120.
(61) Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039.
(62) Meyers, K. O.; Bye, M. L.; Merrill, E. W. *Macromolecules* **1980**, *13*, 1045.