

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Sol-Gel Condensations to Form Polytetrahydrofuran Networks and Their Elastomeric Behavior

M. K. Hassan^a; G. G. Abdel-Sadek^a; G. Beaucage^b; J. E. Mark^a; M. A. Sharaf^c

^a Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, USA ^b Department of Chemical and Materials Engineering and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, USA ^c Department of Chemistry, Helwan University, Cairo, Egypt

Online publication date: 28 January 2004

To cite this Article Hassan, M. K. , Abdel-Sadek, G. G. , Beaucage, G. , Mark, J. E. and Sharaf, M. A.(2004) 'Sol-Gel Condensations to Form Polytetrahydrofuran Networks and Their Elastomeric Behavior', *Journal of Macromolecular Science, Part A*, 41: 1, 1 – 13

To link to this Article: DOI: 10.1081/MA-120027172

URL: <http://dx.doi.org/10.1081/MA-120027172>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Sol–Gel Condensations to Form Polytetrahydrofuran Networks and Their Elastomeric Behavior

M. K. Hassan,¹ G. G. Abdel-Sadek,^{1,#} G. Beaucage,²
J. E. Mark,^{1,*} and M. A. Sharaf³

¹Department of Chemistry and the Polymer Research Center and ²Department of
Chemical and Materials Engineering and the Polymer Research Center,
The University of Cincinnati, Cincinnati, Ohio, USA

³Department of Chemistry, Helwan University, Ain Helwan, Cairo, Egypt

ABSTRACT

A cationic ring-opening polymerization was used to prepare hydroxyl-terminated polytetrahydrofuran (PTHF) $[-(\text{CH}_2)_4\text{O}-]$ having a number-average molecular weight of $20,700 \text{ g mol}^{-1}$, and a relatively narrow molecular weight distribution. Elastomeric tetrafunctional networks were prepared by hydrolysis–condensation reactions on this polymer and on two others that had been commercially obtained. The synthesis was carried out at 60°C with 3-isocyanatopropyltriethoxysilane as an end-capping molecule and Sn-octoate as a catalyst. Completeness of the end-capping reaction was followed by infrared absorption spectroscopy, which showed gradual decreases of peaks at 2270.7 and 3475 cm^{-1} from the disappearances of isocyanato and hydroxyl groups, respectively, and the appearance of a peak at 3350 cm^{-1} from newly formed NH groups. Analysis of the kinetic data suggest that the $-\text{NCO}$, $-\text{OH}$, and $-\text{NH}-$ peaks tend to exhibit first-order kinetics at the beginning of the reaction and

[#]Current address: G. G. Abdel-Sadek, Ophthonix, Inc., 10455 Pacific Center Court, San Diego, CA 92121, USA.

^{*}Correspondence: J. E. Mark, Department of Chemistry, The University of Cincinnati, Cincinnati, OH 45221-0172, USA; E-mail: markje@email.uc.edu.



reach asymptotic values at extended times. The elastomers thus obtained were studied with regard to their equilibrium swelling in toluene at 25°C, and their stress–strain isotherms in elongation. For some of the samples, high elongations seemed to bring about highly desirable strain-induced crystallization, as evidenced by upturns in the modulus. Swelling of these samples with increasing amounts of the non-volatile diluent dibutyl phthalate caused the upturns to gradually disappear, proving that they did indeed result from strain-induced crystallization rather than limited chain extensibility.

Key Words: Ring-opening polymerizations; Polytetrahydrofuran; Elastomers; Networks; Endcapping; Sol–gel condensation; Cage-like structures; Equilibrium swelling; Stress–strain measurements, Moduli; Strain-induced crystallization.

INTRODUCTION

One of the most striking properties of flexible polymer chains is the rubber-like elasticity they exhibit when crosslinked or end linked into a network structure.^[1] Although the homopolymer polytetrahydrofuran (PTHF) $[-(\text{CH}_2)_4\text{O}-]$ itself has only limited commercial utility, network structures prepared by crosslinking it could yield highly useful elastomeric properties.^[2,3] Endlinking polymer chains by means of a multi-functional crosslinking agent provides an ideal way for obtaining such elastomeric networks, frequently of controlled network chain lengths and chain-length distributions.^[1] In favorable cases, it was possible to prepare elastomeric polymer networks having known cross-link functionality ϕ , and known values of the average molecular weight M_c between cross-links.^[4] The crosslinking agents were either alkoxysilanes^[5–7] or triisocyanates.^[7,8]

In this study, PTHF networks were prepared using hydroxyl-terminated polytetrahydrofuran (designated HO–PTHF–OH), with 3-isocyanatopropyltriethoxysilane as the end-capping molecule. The end-capping reaction was found to be highly selective, and was followed by FTIR spectroscopy. The networks thus prepared were characterized with regard to their extents of equilibrium swelling, and moduli in elongation at 25°C (in both swollen and unswollen states). The melting temperature T_m of the high molecular weight polymer itself has been reported to be approximately 57°C,^[9] but the network structure introduced could reduce this to the extent that the polymer is amorphous at ambient temperature (as required for rubberlike elasticity).^[1] It would be even better if elongation would increase its T_m to the extent that strain-induced crystallization would occur. This would be of considerable importance since the crystallites thus formed would act as reinforcing particles and greatly improve the mechanical properties of the elastomer.^[1]

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was obtained from the Fischer Company as HPLC grade and then distilled over potassium metal. Trifluoromethanesulfonic acid anhydride (triflic anhydride) was used as received from the Aldrich Company, and sodium hydroxide and diethyl ether were similarly used without further purification.



3-Isocyanatopropyltriethoxysilane (95%) was purchased from United Chemical Technologies, Inc. Stannous octoate was obtained from Pfaltz & Bauer, Inc. and used without further purification. For purposes of comparison, two low molecular weight PTHF samples were obtained from the Aldrich Chemical Company, with quoted number average molecular weights of 650 and 2900 g mol⁻¹.

Synthesis of Hydroxyl-Terminated Polymer

Tetrahydrofuran was polymerized by a cationic ring opening mechanism.^[2,10-12] The details of the procedures of synthesis are as follows:^[2,10] triflic anhydride of 2.5 mL was added to 200 mL of distilled THF. The mixture was mechanically stirred at -5°C for 90 min and the polymerization permitted to proceed under an inert atmosphere (dry Ar). A 20 mL of 3% aqueous NaOH solution was added to the polymer thus formed, and the mixture was then stirred for 30 min at 0°C. This gave hydroxyl-terminated polymer, which was extracted by adding 350 mL of diethyl ether to the mixture with vigorous shaking. The ethereal layer was washed several times with distilled water using a separatory funnel to remove the excess NaOH and the sodium salt of triflic anhydride. The ether was then evaporated and the HO-PTHF-OH obtained was dried at 60°C under vacuum for about 30 hrs.

Characterization of the Prepared Polymer

The hydroxyl-terminated polytetrahydrofuran obtained was characterized using gel permeation chromatography (Waters GPC model 501) with toluene as solvent, and with polystyrene standards. Infrared measurements were carried out using a Perkin-Elmer (Spectrum One) spectrophotometer.

Synthesis of the Elastomeric Networks

The PTHF networks were prepared by end-capping the hydroxyl-terminated PTHF with 3-isocyanatopropyltriethoxysilane, using Sn-octoate (tin-2-ethyl hexanoate) as catalyst under an Ar atmosphere, the polymer was dissolved in anhydrous THF and stirred continuously at 60°C, after which Sn-octoate (1.2% of the wt. of polymer) was added and the stirring continued for 10 min. A stoichiometric amount of 3-isocyanatopropyltriethoxysilane was added with continuous stirring for 10 min at the same temperature. Some additional formulations were made with stoichiometric imbalance, with the compositions characterized by the molar ratio $r \equiv [\text{end linker}]/[\text{polymer}]$. Each reaction mixture was poured into an aluminum mold, subsequently sealed with Teflon, and the reaction carried out on a hot press at 70–80°C for 24–30 hr. The resulting networks were extracted with toluene at room temperature, gradually deswelled with methanol, and then dried in a vacuum oven for two days.



Characterization of the Networks

Equilibrium swelling measurements were carried out on portions of each network strip, in toluene at 25°C. The extent of swelling was characterized by v_2 , the volume fraction of the (already extracted) polymer at equilibrium swelling.

Stress–strain measurements were conducted using a sequence of increasing values of the elongation $\alpha = L/L_i$ with some inclusions of values out of sequence to test for reversibility.^[1] Values of the elastic force f were recorded only after they had become sensibly constant. In some cases, measurements were carried out on both the unswollen elastomer and as swollen with known amounts of the non-volatile diluent dibutyl phthalate (boiling point 278°C).

RESULTS AND DISCUSSION

Polytetrahydrofuran

The number-average molecular weight M_n and the polydispersity index of the polymer prepared were found by GPC measurements to be 20,700 g mol⁻¹ and 1.26, respectively. Its IR spectrum is shown in Fig. 1. The broad band at $\cong 3400$ cm⁻¹ clearly demonstrates the presence of the desired hydroxyl chain ends.

End-capping of the hydroxyl-terminated PTHF chains was successfully carried out by attaching their terminal –OH functional groups to the terminal isocyanato group of the end linker. This has been followed by a hydrolysis–condensation reaction between the end-capping ethoxy and the (–OH) groups. This end-capping reaction is a novel approach that differs significantly from those in previous studies of PTHF and poly(dimethylsiloxane) networks.^[4,7] The suggested mechanism is shown in Sch. 1.

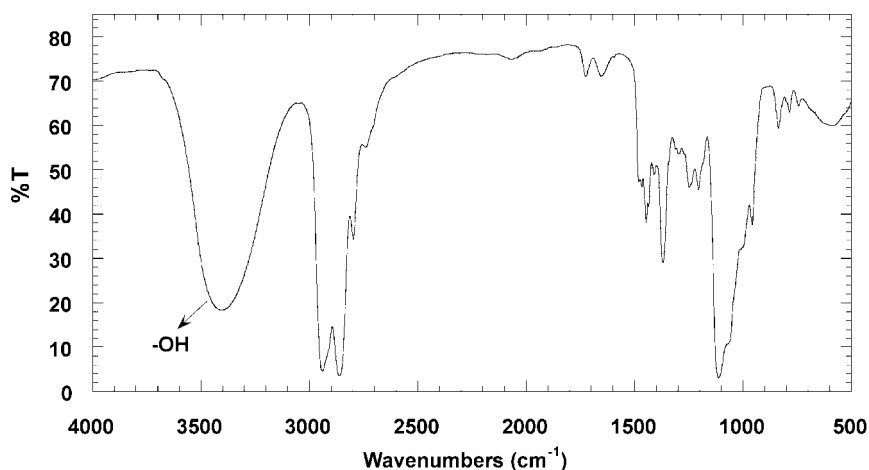
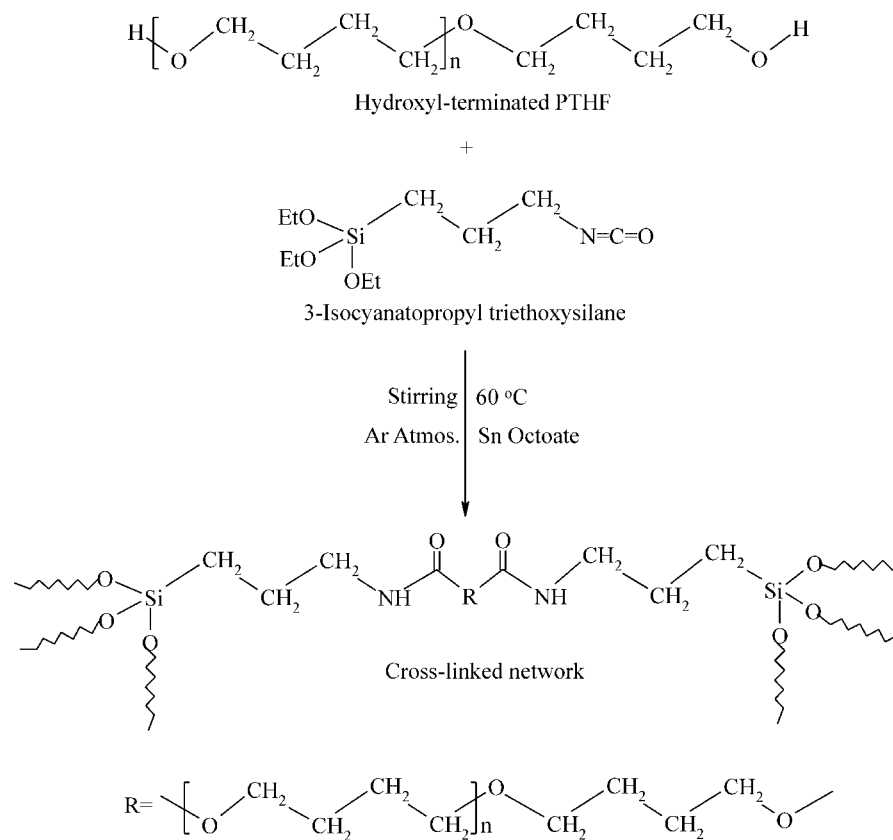


Figure 1. Typical infrared spectrum for the hydroxyl-terminated PTHF.





Scheme 1. Hydrolysis–condensation preparation of PTHF networks.

Quantitative Kinetic Analysis

Since infrared spectroscopy was found to be a sensitive tool for checking the presence of relevant functional groups, it was used to follow the reaction during network formation. Figure 2 shows the infrared absorption spectra of a network film at different times, from the beginning to the point at which the reaction was terminated. The $\nu(\text{OH})$ absorption band of the polymer was observed at 3475 cm^{-1} , and the $\nu(\text{NCO})$ absorption band of the end linker was observed at 2270.7 cm^{-1} . With time, gradual decreases of the intensities of the OH and NCO reactant bands occurred, while a new absorption band gradually grew at 3350 cm^{-1} , from the NH -groups forming the network structure. These changes are consistent with the reaction mechanism given in Sch. 1. In further analysis, the extent of reaction P for the OH and NCO peaks was calculated as follows:^[13]

$$P = 1 - \frac{A_t}{A_0} \quad (1)$$



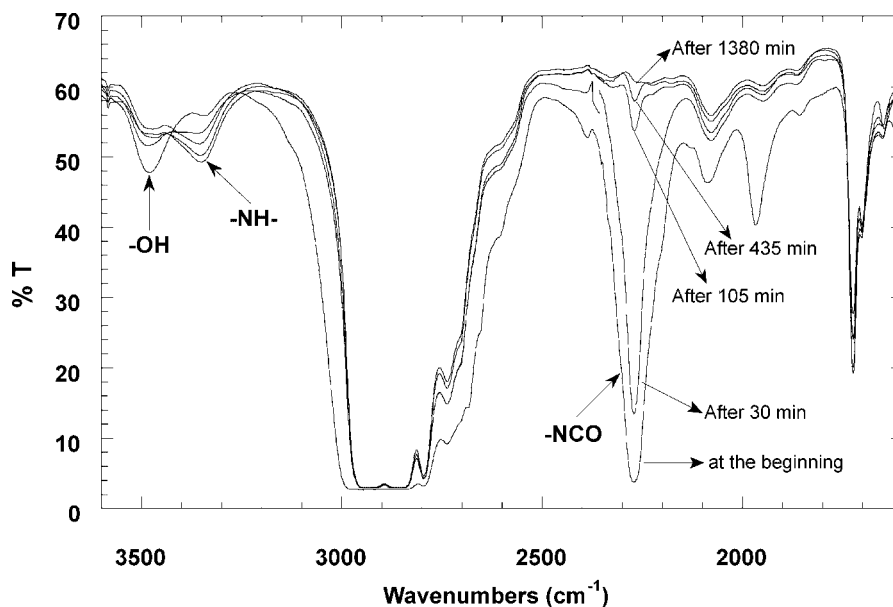


Figure 2. The evolution of the infrared spectra as the end-linking reaction proceeded.

where A_t is the absorbance at time t and A_0 is the absorbance at the beginning of the reaction. For the -NH- peak that belongs to the reaction products, the extent of reaction is defined as:

$$P = \frac{A_t}{A_\infty} \quad (2)$$

where A_∞ is the absorbance at the end of the reaction. This assumes that peak absorbance is proportional to concentration. The extent of reaction for -NCO , -OH , and -NH- vs. reaction time is shown in Fig. 3. It is clear that the peak intensity changes rapidly with time initially, and then reaches asymptotic values at longer times. Also, for the -NCO and -NH- peaks, the reaction reaches almost 90% of completion after 105 min. But, in the case of the -OH peak, the reaction reaches a little less than 50% of its completion and does not change much afterward. This might be explained in terms of an increase in the concentration of the -OH groups due to the hydrolysis of the end-capped -OEt groups that are then involved in the condensation and formation of the network. This plausible suggestion is supported by the correspondence obtained in the values of the extents of reaction P for the -NCO and -NH groups. This is a clear indication of the near completion of the end-capping reaction. This makes it very difficult to determine how many of -OH groups are being used in each reaction step, in particular the hydrolysis–condensation. The difference in reactivities of the -NCO and -OEt groups with the -OH terminal group of the prepolymer supports the idea that the -OH groups of the polymer are being attached by the -NCO groups of the end-capping molecule. It is also feasible that a condensation reaction between the remaining -OH groups of the polymer and the -OEt groups of the end linker takes place. Therefore, the network formation reaction can be



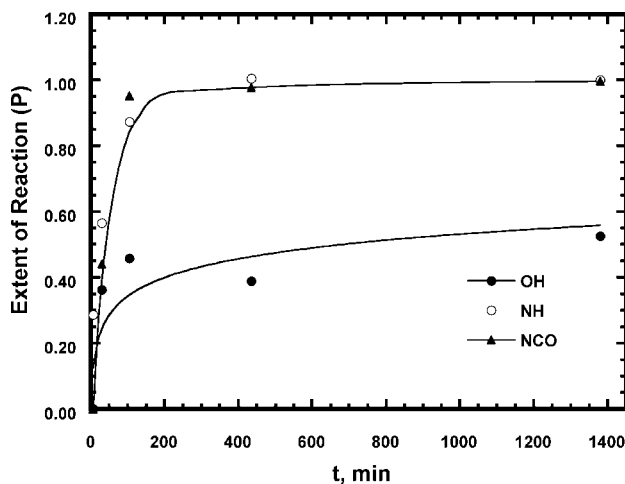


Figure 3. Extent of reaction P as a function of time for different peaks.

considered to occur through the formation of a urethane bridge between PTHF polymer chains and the end-capping molecules in the first step, followed by a condensation reaction between the $-OH$ groups of the polymer and the end-capping $-OEt$ groups. It is important to note here that the crosslinking system used is a complex system, since it involves hydrolysis of, and then condensation of $-Si-OEt$ groups. In essence, the reactions are of the sol-gel type.^[14-17] One does not have any control over the sol-gel kinetics or mechanism, since it is carried out in bulk. It also depends on the choice of catalyst, here tin-octoate. The choice of the crosslinking system leads to a network that is not clearly defined topologically in terms of functionalities, chain length, and whether it would be a hybrid, with a small fraction of cage-like silsesquioxane structures possibly formed.^[14-17] Results from published kinetic studies, the near bulk conditions used, and the choice of catalyst (tin-octoate) would be favorable to more gelation (condensation) than the formation of a hybrid silsesquioxane-like structures.^[14-18] However, this is difficult to gauge or quantify under the conditions employed. Undoubtedly, when the stoichiometry of end capping is unbalanced, excess crosslinker could lead to either the formation of sol-gel structures or silsesquioxane-like cages. Competitive chain extension will come into play, given the amount of catalyst used (1.2%) particularly when it is tin-octoate.^[18] This would certainly lead to irregularly branched polysilsesquioxane structures that would result in favoring the gelation of PTHF networks. This is apparently reflected in the very low values of the sol fraction w_s , reported in Table 1. Also, the isocyanate reaction is extremely moisture sensitive. Although dry conditions were used, residual moisture may have led to unbalanced stoichiometries.

The well-behaved nature of the peaks in the spectra of the reaction steps with time encouraged us to look at the rates of these different steps. The first-order reaction kinetics can be expressed in terms of the extent of reaction P as follows^[13]

$$\ln\left(\frac{A_t}{A_0}\right) = \ln(1 - P) = -kt \quad \text{for the reactant } -NCO \text{ and } -OH \text{ peaks} \quad (3)$$



Table 1. Characterization of the PTHF networks.

Sample	M_n (g mol^{-1}) ^a	r^b	w_s^c	v_2^d	Swelling		Stress-strain	
					M_c (g mol^{-1}) ^e	$2C_1$ (N mm^{-2})	M_c (g mol^{-1}) ^f	
A1	650	0.85	0.040	0.222	2,430	—	—	—
A2		0.90	0.025	0.245	1,900	—	—	—
A3		1.00	0.032	0.359	570	—	—	—
A4		1.10	0.026	0.212	2,610	—	—	—
A5		1.20	0.005	0.333	870	—	—	—
B1	2,900	0.85	0.022	0.136	7,760	0.084	0.084	9,430
B2		0.90	0.012	0.117	10,830	0.069	0.069	11,470
B3		1.00	0.023	0.150	6,320	0.191	0.191	4,130
B4		1.10	0.008	0.117	10,560	0.073	0.073	10,840
B5		1.20	0.016	0.134	8,070	0.280	0.280	2,800
C1	20,700	1.00	0.013	0.128	9,190	—	—	—
C2		1.20	0.019	0.123	9,960	—	—	—

^aAverage number molecular weight of PTHF endcapped pre-polymer.

^bStoichiometric imbalance ratio $r = [\text{end linker}]/[\text{polymer}]$.

^cNetwork extracted sol fraction.

^dVolume fraction of polymer in the network at swelling equilibrium.

^eAverage molecular weight of chains between cross links calculated from the swelling data of the networks in toluene at room temperature, using polymer-solvent interaction parameter $\chi = 0.43$ and Eq. (5).

^fAverage molecular weight of chains between cross links calculated from $2C_1$ values obtained from the intercepts of the stress-strain isotherms given in Fig. 5 based on Eq. (8).



and,

$$\ln\left(\frac{A_\infty}{A_t}\right) = \ln\left(\frac{1}{P}\right) = kt \quad \text{for the product-NH peak} \quad (4)$$

where k is the reaction constant and t is the time.

In Fig. 4, the $-\text{NCO}$, $-\text{OH}$, and $-\text{NH}$ peaks tend to exhibit first-order kinetics up to ≈ 105 min, as shown by the straight dashed lines, and before the reaction reaches asymptotic values at longer times. Probably more points would be desired from the beginning of the reaction and up to 105 min to clearly identify the order of the reaction for the three peaks, but that was not within the scope of the present study.

Although the reaction scheme presented above appears to indicate first-order kinetics for $-\text{NCO}$, $-\text{OH}$, and $-\text{NH}$, the infrared results only weakly support first-order kinetics for $-\text{NCO}$ but seem to display more complicated kinetics for $-\text{OH}$ and $-\text{NH}$. In the case of $-\text{OH}$, it is still possible that it can be involved in simultaneous hydrolysis/condensation reactions with the crosslinking agent. The behavior of the $-\text{NH}-$ absorption cannot be explained in this way since the cross linker does not contain any $-\text{NH}-$ functionality.

Swelling Results

Sol fractions obtained from the swelling experiments did not exceed 5 wt% of the dry network, indicating that the preparation method was effective. The value of the interaction parameter $\chi = 0.43$, required to interpret the swelling equilibrium results in toluene, was available in the literature.^[2] Values of the average molar mass of chains between crosslinks, M_c , were calculated using the standard relationship:

$$M_c = \frac{\rho(1 - 2/\phi)v_1v_{2c}^{2/3}v_2^{1/3}}{\ln(1 - v_2) + \chi v_2^2 + v_2} \quad (5)$$

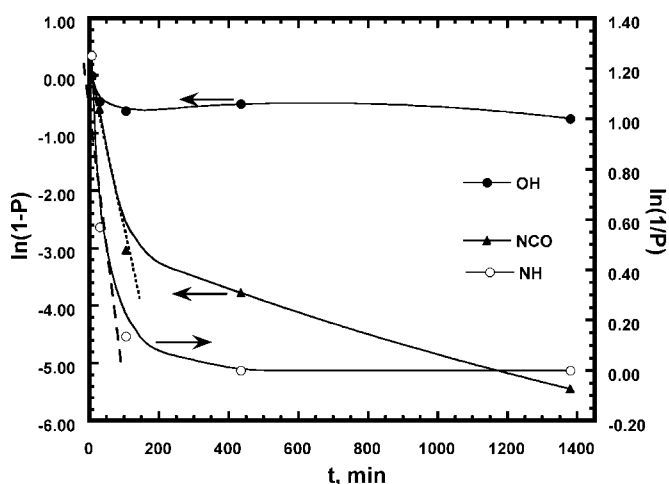


Figure 4. First-order kinetics initially, for all three peaks.



where v_{2c} is the volume fraction of polymer during end linking, ϕ is the average junction functionality, is presumably equal to 3, according to previous arguments about the prevalence of chain extension. V_1 is the molar volume of solvent. Values of sol fractions, v_2 , and M_c are given in Table 1.

Values of M_c from Eq. (5) obtained for the lower molecular weight polymers are much higher than those of M_n for the polymer used to form the network, even in the case of stoichiometric balance ($r = 1.0$). This could be due partly to inaccurate values of the presumably concentration-dependent χ for the specific values of the polymer concentration in the swollen networks. However, incomplete end linking is probably the major reason. In contrast, the networks from the higher molecular weight polymer had values of M_c that were much lower than M_n of the starting polymer. Entanglements among these longer chains are frequently cited as being partly responsible for such differences.

Stress–Elongation Measurements

The end-linked polymers showed good rubber-like properties at ambient temperature, indicating that the PTHF chains had significantly depressed melting temperatures when in these network structures. The uniaxial stress–strain data were analyzed as usual in terms of the reduced stress or modulus $[f^*]$ defined by:^[19–22]

$$[f^*] \equiv \frac{fv_2^{1/3}}{A^*(\alpha - \alpha^{-2})} \quad (6)$$

where f is the elastic force, A^* is the cross-sectional area of the undeformed strip, v_2 is the volume fraction of polymer in the network, and α is the elongation L/L_i , where L and L_i are the deformed and the undeformed lengths, respectively. Experimental values of $[f^*]$ were then plotted against the reciprocal elongation α^{-1} , as suggested by the semiempirical equation of Mooney and Rivlin:^[23,24]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (7)$$

in which $2C_1$ and $2C_2$ are constants independent of α . Thus, the value of the modulus is $2C_1$ in the limit of large deformations ($\alpha^{-1} \rightarrow 0$), and $2C_1 + 2C_2$ in the limit of small deformations, ($\alpha^{-1} \rightarrow 1$). Typical stress–strain isotherms for networks with various cross-link densities are shown in Fig. 5. The limited extensibility of samples from the polymer with molecular weight 650 g mol^{-1} is clearly evident, and expected. Samples from the polymer with the higher molecular weight (2900 g mol^{-1}) showed higher extensibilities.

Values of M_c were obtained from the elongation results using the equation:^[6,7]

$$2C_1 = \left(1 - \frac{2}{\phi}\right) \cdot \frac{\rho RT}{M_c} \cdot v_{2c}^{2/3} \quad (8)$$

where ϕ is the network functionality (as cited above, considered to be equal to 3), ρ is the density of the network in g mm^{-3} , R is the gas constant in $\text{J mol}^{-1} \text{K}^{-1}$, T is the temperature in K, and v_{2c} is the volume fraction of polymer successfully incorporated in the network structure. Values of $2C_1$ and the associated values of M_c are included in Table 1. They show some parallels with those from the swelling equilibrium results.

Upturns are seen in the modulus $[f^*]$ at higher elongations, specifically at $\alpha \approx 2.4$ for the sample from the polymer with molecular weight 2900. They could be due to either



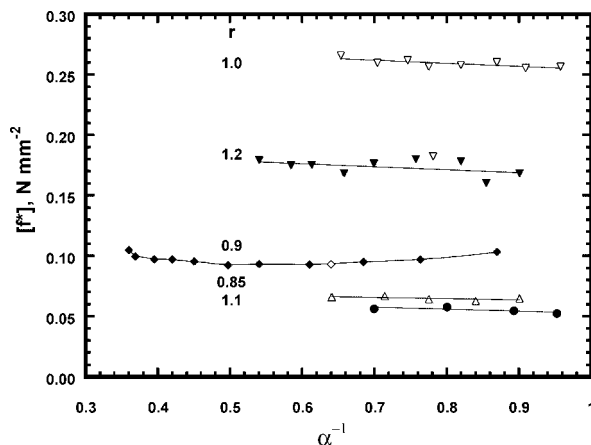


Figure 5. Stress-strain isotherms in elongation for unswollen PTHF networks prepared from the polymer having a molecular weight of 2900 g mol^{-1} . Values of the composition molar ratio are specified for each curve.

limited chain extensibility or to strain-induced crystallization.^[25,26] For networks with the higher molecular weight (20,700) of the pre-polymer, the upturns in the modulus at high elongations do not persist with swelling in dibutyl phthalate, as is demonstrated in Fig. 6. The magnitudes of the increases in $[f^*]$ are seen to decrease with swelling, indicating that although swelling may facilitate the first appearance of strain-induced crystallization, it clearly diminishes the total amount of crystallinity attainable (Fig. 6). Also, this increase in $[f^*]$ generally disappears at higher dilutions, specifically at $v_2 = 0.4$. This indicates that the upturn is due to strain-induced crystallization rather than to limited chain extensibility. Another aspect of the behavior of PTHF is different from that of some other crystallizable

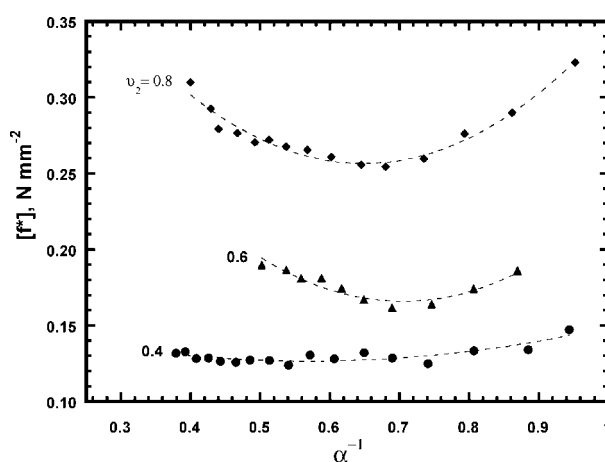


Figure 6. The effects of swelling on some of the stress-strain isotherms, at the indicated values of the polymer volume fraction v_2 present in the elastomers.



polymers, specifically in that in the PTHF networks there is no downturn in the reduced stress just prior to the upturns at higher elongations.^[27,28] In any case, the upturns are due to crystallites acting as a physical crosslinks and filler particles. Detailed interpretation of the strain-induced crystallization behavior at high elongations is very important in a practical sense, since it corresponds to a significant toughening of the elastomer.^[1]

CONCLUSION

Novel PTHF networks were prepared by a selective sol–gel condensation reaction. The kinetics of the complex and competing reactions involved has been followed by FTIR spectroscopic techniques. The reaction favoring the formation of the desired networks seems to reach about 90% completion in about 105 min and the peaks tend to exhibit first-order kinetics up to that time. Swelling equilibrium results and stress–strain isotherms in elongation were used to characterize these elastomers. One important result was the demonstration of strain-induced crystallization, which is an important inherent reinforcing mechanism shared by several commercially-important elastomers, specifically natural rubber, high *cis*-1,4-polybutadiene, and polyisobutylene.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Egypt-US Grant INT-9605191.

REFERENCES

1. Erman, B.; Mark, J.E. Model elastomers. In *Structures and Properties of Rubberlike Networks*; Oxford University Press: New York, 1997.
2. Jong, L.; Stein, R.S. Synthesis, characterization, and rubber elasticity of end-linked poly(tetrahydrofuran) elastomer. *Macromolecules* **1991**, *24* (9), 2323–2329.
3. Roland, C.M.; Buckley, G.S. Thermal crystallization of polytetrahydrofuran networks. *Rubber Chem. Tech.* **1991**, *64* (1), 74–82.
4. Mark, J.E.; Sung, P.-H. Model polyurethane networks prepared from poly(ethylene oxide) and poly(tetramethylene oxide). *Eur. Polym. J.* **1980**, *16* (12), 1223–1227.
5. Mark, J.E. Model elastomeric networks. *Rubber Chem. Tech.* **1981**, *54* (4), 809–819.
6. Mark, J.E.; Sullivan, J.L. Model networks of end-linked polydimethylsiloxane chains. I. Comparisons between experimental and theoretical values of the elastic modulus and the equilibrium degree of swelling. *J. Chem. Phys.* **1977**, *66* (3), 1006–1011.
7. Llorente, M.A.; Mark, J.E. Model networks of end-linked polydimethylsiloxane chains. IV. Elastomeric properties of the tetrafunctional networks prepared at different degrees of dilution. *J. Chem. Phys.* **1979**, *71* (2), 682–689.
8. Johannes, B.R.; Stephens, J.P.; Arend, J.W.; Willem, J.M. Phase transition of hydroxy-telechelic side-chain liquid crystalline polyethers and polyurethane networks derived thereof. *Macromol. Chem. Phys.* **1996**, *197*, 1031–1041.
9. Mark, J.E. *Polymer Data Handbook*; Mark, J.E., Ed.; Oxford University Press: New York, 1999.



10. Hassan, M.K. The University of Cincinnati; Ph.D. Thesis in Chemistry, 2003.
11. Booth, C.; Devoy, C.J. Thermodynamics of mixtures of poly(ethylene oxide) and benzene. *Polymer* **1971**, *12* (5), 309–319.
12. Dreyfuss, P. Kinetics of condensation (step-growth) polymerization. In *Polytetrahydrofuran*; Gordon and Beach Science: New York, 1982.
13. Allcock, H.R.; Lampe, F.W.; Mark, J.E. Kinetics of condensation (step-growth) polymerization. In *Contemporary Polymer Chemistry*, 3rd Ed.; Prentice-Hall, Inc.: Englewood Cliffs, N.J., 2003.
14. Lichtenhan, J.D.; Otonari, Y.A.; Carr, M.J. Linear hybrid polymer building blocks: methacrylate-functionalized polyhedral oligomeric silsesquioxane monomers and polymers. *Macromolecules* **1995**, *28* (24), 8435–8437.
15. Baney, R.H.; Itoh, M.; Sakakibara, A.; Suzuki, T. Silsesquioxanes. *Chem. Rev. (Washington, D.C.)* **1995**, *95* (5), 1409–1430.
16. Matejka, L.; Dukh, O.; Brus, J.; Simonsick, W.J., Jr.; Meissner, B. Cage-like structure formation during sol-gel polymerization of glycidylxypropyltrimethoxysilane. *J. Non-Cryst. Solids* **2000**, *270* (1–3), 34–47.
17. Loy, D.A.; Shea, K.J. Bridged polysilsesquioxanes. Highly porous hybrid organic-inorganic materials. *Chem. Rev. (Washington, D.C.)* **1995**, *95* (5), 1431–1442.
18. Clarson, S.J. Private discussions.
19. Mark, J.E.; Flory, P.J. Stress-strain isotherms for poly(dimethylsiloxane) networks. *J. Appl. Phys.* **1966**, *37* (13), 4635–4639.
20. Mark, J.E. An experimental comparison of the theories of elasticity of polymer networks. *J. Am. Chem. Soc.* **1970**, *92* (25), 7252–7257.
21. Flory, P.J.; Tatara, Y. Elastic free energy and the elastic equation of state. Elongation and swelling of poly(dimethylsiloxane) networks. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13* (4), 683–702.
22. Mark, J.E. The constants $2C_1$ and $2C_2$ in phenomenological elasticity theory and their dependence on experimental variables. *Rubber Chem. Tech.* **1975**, *48* (3), 495–512.
23. Mooney, M. Thermodynamics of a strained elastomer. I. General analysis. *J. Appl. Phys.* **1948**, *19*, 434–444.
24. Rivlin, R.S. Some applications of elasticity theory to rubber engineering, Proc. 2nd Rubber Technol. Conf. (London), 1948; 204–212.
25. Mark, J.E.; Erman, B. Strain-induced crystallization and ultimate properties. In *Rubberlike Elasticity. A Molecular Primer*; Wiley, Interscience: New York, 1988.
26. Su, T.-K.; Mark, J.E. The effect of strain-induced crystallization on the elastomeric properties of *cis*-1,4-polybutadiene networks. *Macromolecules* **1977**, *10* (1), 120–125.
27. Mark, J.E. Stress-strain isotherms for polymer networks at very high elongations. *Polym. Eng. Sci.* **1979**, *19* (4), 254–259.
28. Mark, J.E. The effect of strain-induced crystallization on the ultimate properties of an elastomeric polymer network. *Polym. Eng. Sci.* **1979**, *19* (6), 409–413.

Received July 2003

Accepted August 2003

