Macromolecules **1987,** *20,* 2569–2574

(9) For example: Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*: Plenum: New York, 1981. Frish, H. L.; Frish, K. C.; Klempner, D. In *Chemistry and Properties of Crosslinked Polymers*; Labana, S. S., Ed.; Academic: New York, 1976; p 205.
(10) Flory, P. J. *J. Am. Chem. Soc.* **1956**, *78*, 5222.
(11) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(12) Erman, B. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 893.
(13) Tschoegl, N. W.; Gurer, C. *Macromolecules* **1985**, *18*, 680.
(14) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(15) Edwards, S. F.; Vilgis, Th. *Polymer* **1986**, *27*, 483.
(16) Posthuma de Boer, A.; Pennings, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 187.
(17) Iwata, K. *J. Chem. Phys.* **1982**, *76*, 6363; **1982**, *76*, 6375; **1985**, *83*, 1969.
(18) Hayes, R. A. *Rubber Chem. Technol.* **1986**, *59*, 138.
(19) *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975.
(20) Flory, P. J. *J. Chem. Soc., Faraday Discuss.* **1970**, *49*, 7.
(21) Eichinger, B. E.; Flory, P. J. *Trans. Fraday Soc.* **1968**, *64*, 2035.
(22) Tirell, M. *Rubber Chem. Technol.* **1984**, *57*, 523.
(23) Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules*, in press.

Solution-Cross-Linked Networks. 2. Viscoelastic Behavior of Guest Polyisoprene in Natural Rubber Networks

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ABSTRACT: Viscoelastic behavior of *cis*-polyisoprene (*cis*-PI) entrapped in natural rubber networks (NR) was investigated. Two kinds of networks were used: one had the molecular weight M_x between cross-links similar to the molecular weight M_e (=5000 for bulk *cis*-PI) between entanglements, while the other had M_x smaller than M_e. The molecular weight M of the guest *cis*-PI ranged from 5000 to 3×10^4. Master curves of storage (E') and loss (E'') Young's moduli were constructed for the pure networks and network/guest systems. From these data we determined "extra" relaxation associated with the entrapped guest *cis*-PI molecules. The terminal relaxation of the guest polymers of higher M appeared at lower frequencies. From the relaxation spectra of the guest polymer in the network determined by Tschoegl's method, the longest relaxation time, τ_{mg}, was evaluated. The τ_{mg} in the network with $M_x < M_e$ was found to be longer by about 0.6 decades than that τ_m in the uncross-linked *cis*-PI. On the other hand, in the case of $M_x \simeq M_e$, τ_{mg} was equal to τ_m within experimental error.

Introduction

In the preceding paper (part 1),[1] we reported swelling behavior of networks of natural rubber (NR) which were cross-linked in the solution state and afterword the solvent was removed from the networks. We called such networks *high free energy networks* because such networks were expected to have lower conformational entropy and hence higher free energy than bulk-cross-linked networks. Our study on their swelling behavior demonstrated such was the case: these networks absorb polymers to an appreciable amount when they are soaked in a polymer solution. The network containing free polymer molecules is expected to be an interesting model system for investigating dynamic properties of entangled polymers.

The effect of entanglement on dynamics of polymers has been a subject of long-lasting interest in polymer physics.[2,3] In fact, a few molecular models have been proposed, but none of them provided a fully satisfactory picture of dynamics of the entangled polymer systems.[2,3] Among the theories proposed so far, the tube model proposed by de Gennes[4] and Doi and Edwards[5] appears to provide a most straightforward picture of the polymer dynamics and is most widely used.

In the tube model, it is assumed that a representative chain molecule is confined in a hypothetical tube. The diameter of the tube is assumed to be equal to the end-to-end distance of a chain having the molecular weight between entanglements M_e. When the chain diffuses out of the tube, the stress relaxes. However, in reality, since other chain molecules forming the tube also move, the tube itself may disintegrate gradually. The process was called tube renewal by Klein,[6] who modified the tube theory taking the effect of this process into account.

Obviously, networks swollen by guest polymer molecules have two advantages in studying the effect of entanglement. First of all, in the networks the constraint on the guest molecules should not change, since the network chains forming the tube do not diffuse away. Therefore, studies on the viscoelastic properties of network/guest polymer systems will provide information free from the complex effect of tube renewal. Second, in contrast to M_e which is a fixed parameter in undiluted polymers, we can prepare networks with varying molecular weight M_x between cross-links and test the mobility of guest polymers in the networks.

Several network/guest polymer systems have been studied by Ferry and his co-workers[7-12] and by Kraus and Rollmann.[13] The general conclusions from all these studies show that the guest polymer in the network relaxes slower than the same polymer in the uncross-linked environment. However, the relaxation time is found to be nearly independent of guest concentration in the networks.

Recently, de Gennes[14] proposed a schematic phase diagram to classify the network/guest systems in terms of mobility of the guest polymer molecules as a function of M_x, M_e, and molecular weight M of the guest molecules. Figure 1 shows the diagram for the systems containing a small amount of the guest polymer. Evidently, the crossover in actual systems occurs in a definite region, and therefore the boundary between the regimes is not so clear as to be represented by a line. He proposed that when $M_x > M_e$ (the regimes 1 and 2 in Figure 1), the tube diameter for the guest molecules is equal to that in the uncross-linked polymer. Thus, the relaxation time, τ_{mg}, of the guest molecule in regimes 1 and 2 is the same as the relaxation time τ_m in the uncross-linked polymer. On the other hand,

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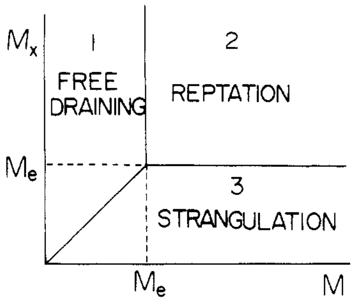

Figure 1. Phase diagram representing the mobility of guest polymer molecules in networks as a function of the molecular weight M_x between cross-link points, the molecular weight M of the guest, and the molecular weight M_e between entanglements.

Table I
Characteristics of *cis*-Polyisoprene

code	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n
PI-05		4.5	
PI-13	13.0		1.08
PI-14	14.4		1.05
PI-25	24.5		1.05
PI-31	31.2		1.09

when $M_x < M_e$ (regime 3), the tube diameter is equal to the end-to-end distance of network chains. In such a case, the motion of the guest molecules with $M > M_x$ in regime 3 is more severely restricted than those in the uncross-linked state. Then, the τ_{mg} is given by

$$\tau_{mg} = \tau_m(M_e/M_x) \qquad (1)$$

This situation was called "strangulation".[14] Viscoelastic data[7-13] reported so far for network/guest systems were not analyzed quantitatively from this viewpoint.

To understanding the dynamic behavior of guest molecules in the network, we have carried out measurement of dynamic Young's moduli on the NR/*cis*-PI systems. From the measurement we obtained mechanical relaxation spectra of the whole systems. Then, assuming an adequate blending law,[15] we separately evaluated the contribution of the guest polymers from the networks. In this study, we attempted to substantiate "de Gennes' phase diagram" by clarifying the effect of M_x and M_e on the mobility of *cis*-PI with molecular weight M absorbed in NR through viscoelastic spectroscopy.

Experimental Section

The samples of *cis*-PI were prepared by anionic polymerization. Table I shows the characteristics of *cis*-PI. The same natural rubber networks as used in the preceding paper (part 1)[1] were used. They were prepared by irradiation of γ-ray to toluene solutions of NR with various concentration C_x and coded NR(C_x in volume fraction: dose of γ-ray in Mrd). M_x was determined from the swelling ratio and Young's modulus. Details of preparation and characteristics of the networks were given in part 1.[1] The average values of M_x determined by the two methods are given in Table II for NR(0.4:30) and NR(1:40), and M_x from Young's modulus is given for NR(0.1:20).

The networks were soaked in benzene solutions of *cis*-PI for a few days so that the guest content reached the 10–30% level, as listed in Table II. In part 1, it was confirmed that the networks soaked in *cis*-PI solutions reached equilibrium in 80 h. Therefore, the distribution of the guest molecules in the network is considered to be homogeneous. The swollen networks were then dried under vacuum at 50 °C until constant weight was attained. Thickness, width, and length of the samples were determined with an accuracy of ±0.01 mm and were about 1 × 5 × 10 mm^3, respectively.

Complex Young's moduli, E' and E'', were measured in the range from 0.01 to 110 Hz by a Rheovibron (type DDV-II-C, Toyo Baldwin Co., Japan). The temperature was varied from −110 to 70 °C.

Table II
Amount and the Logarithm of the Longest Relaxation Time τ_{mg} of the Guest *cis*-Polyisoprene Absorbed in Cross-Linked Natural Rubber[a]

system	M_x of network	content, wt %	log τ_{mg} from $H(\tau)$	log τ_{mg} from E''
NR(0.1:20)/PI-25	3000	25.4	−0.9	−1.0
NR(0.1:20)/PI-31		34.0	−0.7	−1.0
NR(0.4:30)/PI-13	5300	20.9	−2.6	−2.4
NR(0.4:30)/PI-31		13.4	−0.9	−1.4
NR(1:40)/PI-05	2200	20.8		
NR(1:40)/PI-13		19.1	−2.1	−1.6

[a] Determined at 273 K from the relaxation spectra $H(\tau)$ and from the E'' curves.

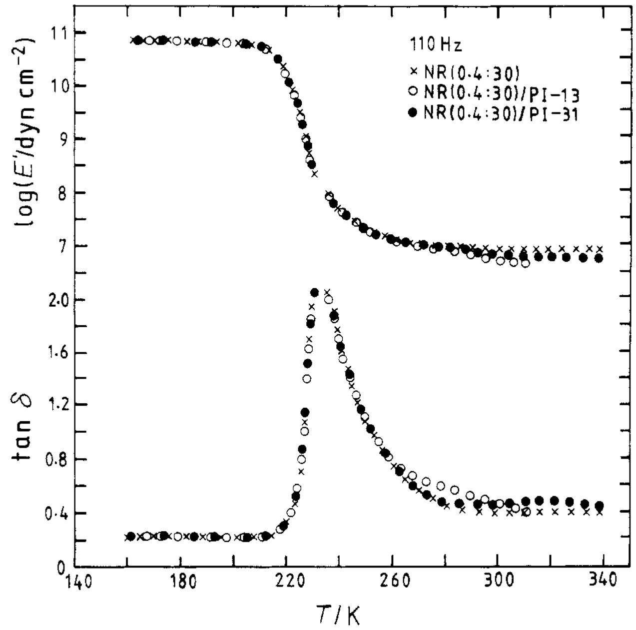

Figure 2. Temperature dependence of E' and tan δ for pure network NR(0.4:30) and NR(0.4:30) containing PI-13 (20.9%) and PI-31 (13.4%).

Results and Discussion

Temperature Dependence of E' and E''. Figure 2 shows the temperature dependence of E' and loss tangent (tan δ) at 110 Hz for pure NR(0.4:30) and the same network containing PI-13 and PI-31. Below 220 K, both the guest polymer and network were in the glassy state with a modulus of the order of 10^{11} dyn cm^{-2}. However, with increasing temperature, relaxation occurred at about 235 K. Obviously, this relaxation is associated with the glass transition. As is well-known, the glass transition process is almost independent of either M or M_x provided that M and M_x are not extremely low. Therefore, it is quite natural that all the curves become indistinguishable in this glass transition region.

In the range above 260 K, extra relaxation was observed only for the network containing guest molecules. Hence this was assigned to the relaxation of the guest molecules. It was also observed that the guest *cis*-PI with higher M relaxed at higher temperature, indicating that this relaxation is due to the rubber–liquid transition of the guest polymer.

At the highest temperature, 340 K, tan δ for the three samples approached a common value, indicating that relaxation was over. Around 340 K, E' for the network containing guest molecules was lower than that for the pure network. This behavior can be explained as the effect of dilution by guest molecules of the network.

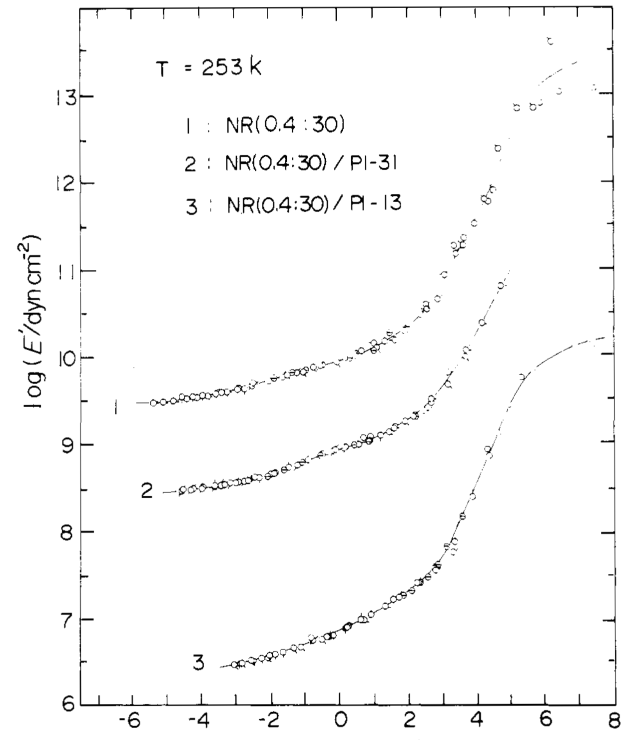

Figure 3. Master curve of E' vs. frequency at 253 K for pure network NR(0.4:30) and NR(0.4:30) containing PI-13 (20.9%) and PI-31 (13.4%). Curves 1 and 2 have been shifted upward by 3 and 2 decades, respectively.

Frequency Dependence of E' and E''. The master curves were constructed based on the time–temperature superposition principle.[2] The temperature dependence of the shift factor a_T for the pure networks and the same networks containing guest *cis*-PI agreed within the experimental error of ca. ±0.2 decades in the temperature range above 250 K. However, the values of a_T scattered ca. ±0.5 decades in the range below 250 K, probably due to the error in temperature measurements. No systematic difference between a_T's for the pure network and the networks containing the guest *cis*-PI was observed. The shift factors conformed approximately to the Williams–Landel–Ferry (WLF) equation[2] with a reference temperature of 273 K. The parameters C_1 and C_2 in this equation for NR(0.1:20), NR(0.4:30), and NR(1:40) were determined to be 5.69, 7.13, and 16.8, 110, 120, and 130, respectively.

In constructing these master curves, the temperature correction in the vertical direction was made but the effect of the density change was neglected. The same shifting factors were used to shift the E' and E'' curves to give the master curves. Typical master curves of E' and E'' are shown in Figures 3 and 4, respectively. Curves 1 and 2 in these figures were shifted upward by 3 and 2 decades, respectively, in order to separate the three curves.

In order to investigate the effect of guest molecules on the dynamic Young's moduli of the networks containing them, three curves are compared in the same graph, as shown in Figures 5–7. For the networks containing the guest polymers, a terminal relaxation process was observed similarly to the relaxation observed in the temperature-dependence curves (Figure 2). We see that the guest polymer with higher M relaxes at lower frequencies. In the frequency region where the wedge-shaped E'' curve was observed, all the curves converge since the dynamic behavior is independent of M or M_x.

In the higher frequency range, the slope of the E″ curve is close to $-^1/_2$. This behavior is in harmony with the Rouse theory.[16] In the low-frequency region, the loss modulus for the pure network is greater than that of the network containing guest molecules. This behavior is again explained as the dilution effect.

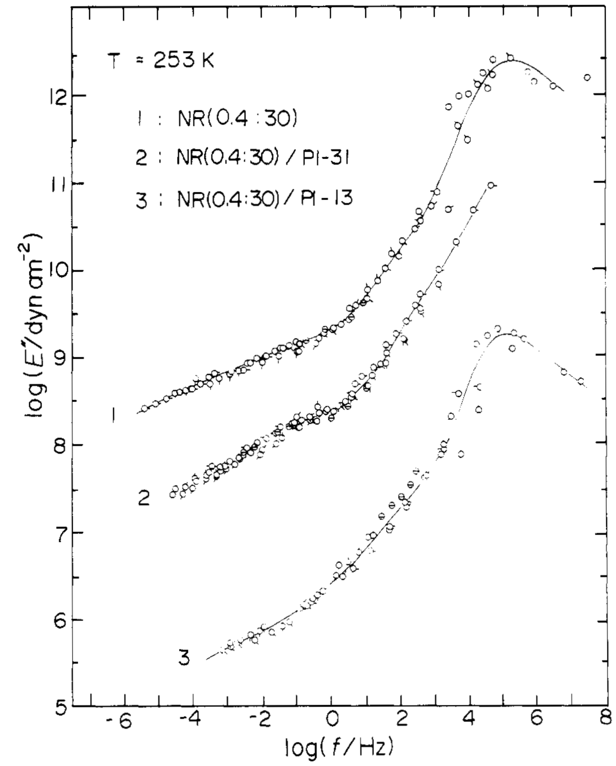

Figure 4. Master curves of E'' vs. frequency f at 253 K for the same samples as in Figure 3. Curves 1 and 2 have been shifted upward by 3 and 2 decades, respectively.

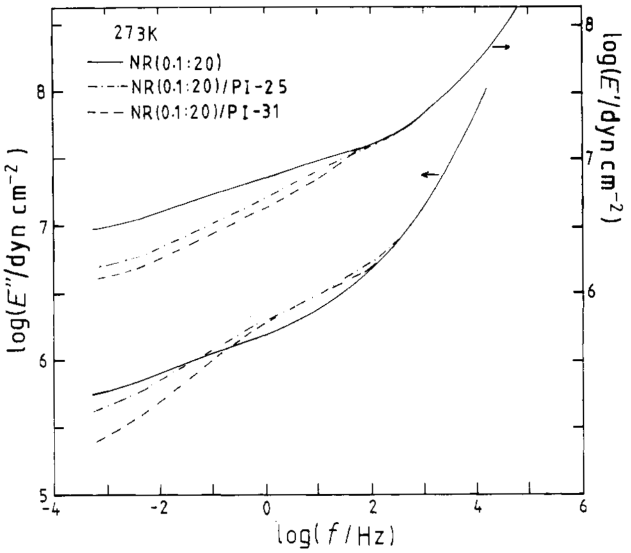

Figure 5. Comparison of E' and E'' curves among pure network NR(0.1:20) and NR(0.1:20) containing PI-25 (25.4%) and PI-31 (34.0%) at 273 K.

Relaxation Spectrum of the Guest Molecule. The relaxation spectrum $H(\tau)$ for the guest *cis*-PI was calculated from the contribution of the guest to the E'' curve of the whole system by assuming a simple additivity law for E' and E''. Thus, the contribution of the guest polymer toward the complex modulus E_g is given by

$$E^*_T = \phi E^*_g + (1 - \phi)E^*_N \qquad (2)$$

where ϕ is the volume fraction of the guest polymer and the subscripts T and N stand for the total system and pure network, respectively. In this calculation, E''_g for some

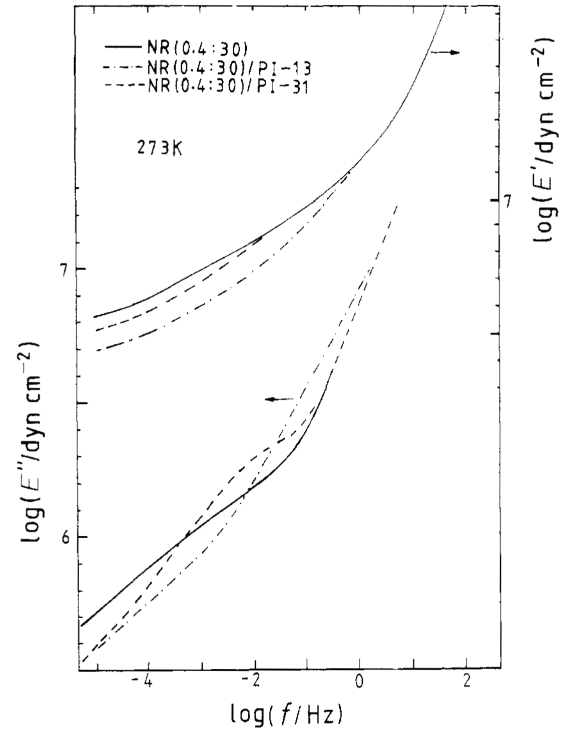

Figure 6. Comparison of E' and E'' curves among pure network NR(0.4:30) and NR(0.4:30) containing PI-13 (20.9%) and PI-31 (13.4%) at 273 K.

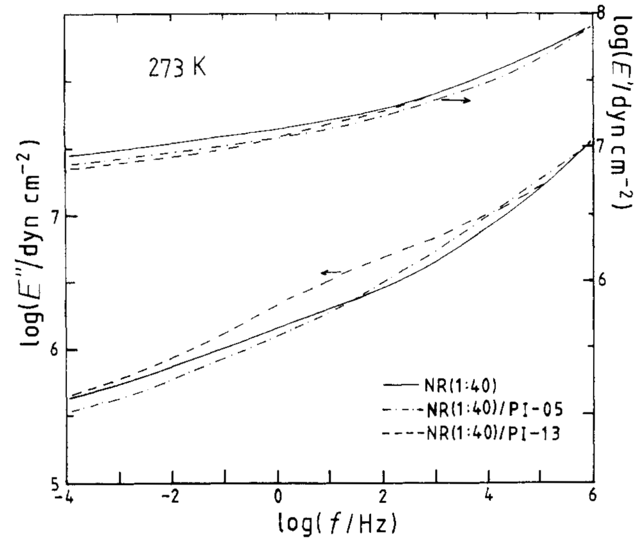

Figure 7. Comparison of E' and E'' curves among pure network NR(1:40) and NR(1:40) containing PI-05 (20.8%) and PI-13 (19.1%) at 273 K.

systems became negative in the frequency range below 10^{-3} Hz where the difference between E''_T and E''_N became small. We ascribed this to experimental errors.

Obviously, the E^*_g curves are dependent on the choice of the blending law. Ferry and his co-workers tested various blending laws in the studies on similar network/guest systems.[7-12] For example, in the ref 7-10, the blending law used was

$$E^*_T = \phi E^*_g + E^*_N \quad (3)$$

However, in other cases,[12] they assumed that the contribution of the network to the modulus is proportional to $(1 - \phi)^2$ similarly to the plateau modulus of an uncross-linked polymer including diluent. At the moment, the accuracy of this experiment is not enough to judge the validity of these blending laws.

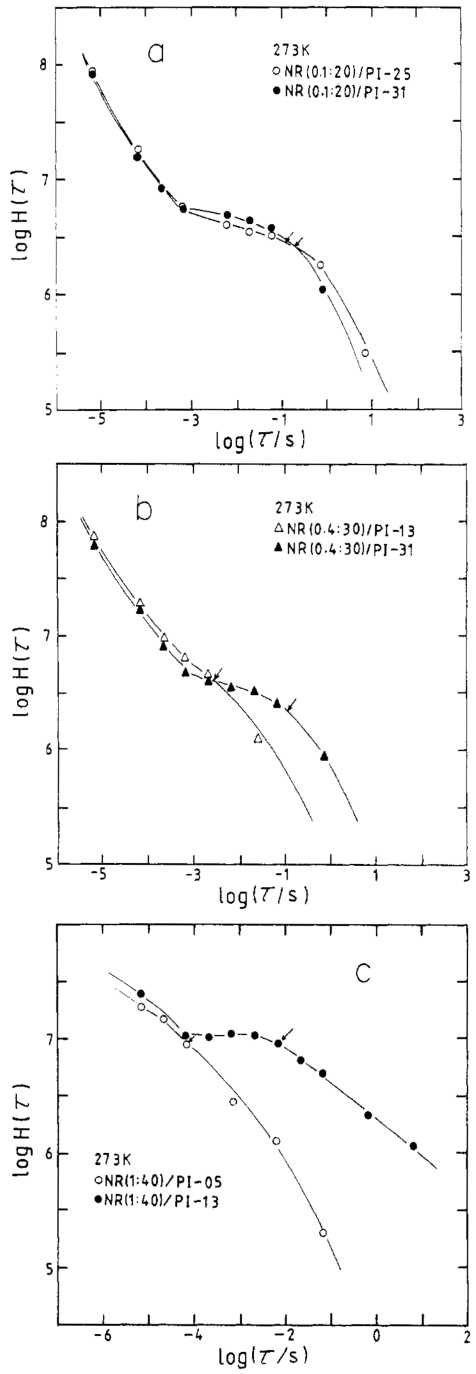

Figure 8. (a) Relaxation spectra of PI-25 (25.4%) and PI-31 (34.0%) in NR(0.1:20) at 273 K. (b) Relaxation spectra of PI-13 (20.9%) and PI-31 (13.4%) in NR(0.4:30) at 273 K. (c) Relaxation spectra of PI-05 (20.8%) and PI-13 (19.1%) in NR(1:40) at 273 K.

For uncross-linked polymers, it is well-known that entanglement effects are observed in the range of M higher than the characteristic molecular weight M_c ($\simeq 2M_e$).[2,3] With regard to the characteristic molecular weight M'_c for a guest molecule in networks with $M_x < M_e$, we may expect two possibilities: One is $M'_c = 2M_x$ and the other is $M'_c = M_x$ as proposed by de Gennes.[14]

To check these possibilities, the relaxation spectra $H(\tau)$ for the guest *cis*-PI were calculated from E''_g by the Tschoegl's second approximation.[2] The results are shown in Figure 8. The effect of M and M_x on the relaxation behavior is clearly seen in the relaxation spectra. Comparing parts b and c of Figure 8, we see that PI-13 in NR(1:40) exhibits a more enhanced box-type spectrum than that in NR(0.4:30) in which a box type spectrum is

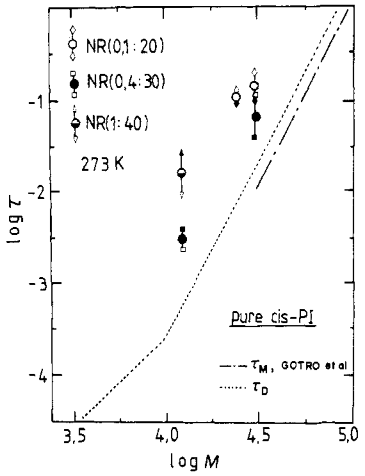

Figure 9. Molecular weight dependence of τ_{mg} for guest polymer. The open symbols showing the limit of the error bars indicate τ_{mg} determined from the relaxation spectra, and the closed ones indicate those from the E'' curves. The circles indicate average values of τ_{mg} determined from the $H(\tau)$ and E'' curves. The dash–dot line indicates the mechanical longest relaxation time τ_m for uncross-linked *cis*-PI reported by Gotro and Graessley.[19] The dotted line indicates the dielectric relaxation time τ_D for the normal-mode process.[20]

only seen as a shoulder. We also note that PI-05 in NR(1:40) does not exhibit a box-type spectrum. Here, we recall that M_x's reported in Part 1 for NR(0.4:30) and NR(1:40) are 5300 and 2200, respectively. Since M_e of *cis*-PI is 5000, we may conclude from these results that $M'_c = 2M_x$.

From these relaxation spectra, the longest relaxation time τ_{mg} for the guest polymer was estimated as shown by the arrow in each figure. We also estimated τ_{mg} from the maxima of the E''_g curves. The results are listed in Table II. The error in determination of τ_{mg} is estimated to be ±0.5 decade since a slight error in measurement of E'' causes a big error in determination of E''_g.

Molecular Weight Dependence of the Relaxation Time. In Figure 9, the τ_{mg} at 273 K is plotted against M of the guest polymer on the double-logarithmic scale. Nemoto et al[17,18] and Gotro and Graessley[19] reported the viscoelastic data for undiluted *cis*-PI at 243 and 298 K, respectively. For *cis*-PI, we reported the "dieletric normal mode process" due to fluctuation of the end-to-end vector.[20] According to a tube model, the dielectric relaxation time τ_D coincides with the mechanical longest relaxation time.[4,5] For the sake of comparison, τ_m was evaluated from the maxima of the G'' curve reported by Gotro and Graessley and shifted to 273 K by using the shift factor reported by themselves. The results are also plotted in Figure 9. Since Gotro and Graessley reported the data for *cis*-PI with $M > 10^5$, the data were extrapolated parallel to the τ_D vs. M curve toward the lower molecular weight region. It was found that τ_m reported by Nemoto et al.[17,18] was ca. 0.8 decade longer than the τ_m reported by Gotro and Graessley, presumably due to an error in determination of the shift factor.

We first discuss the τ_{mg} in NR(0.4:30) which was M_x similar to M_e. As seen in Figure 9, τ_{mg} in this network is longer than τ_m and τ_D by ca 0.8 decade even if M_x is similar to M_e. This slightly longer τ_{mg} is not in agreement with de Gennes' prediction and might reflect the relaxation time in the system without the tube renewal effect, while τ_m obviously reflects the relaxation time under the influence of tube renewal.

Since M_x of NR(0.1:20) and NR(1:40) are 3100 ± 100 and 2100 ± 900, respectively, eq 1 predicts that the τ_{mg} for the former and latter networks are 0.2 and 0.4 decade longer than τ_m, respectively. As seen in Figure 9, the τ_{mg}'s in the NR(0.1:20) and NR(1:40) systems are 1.3 and 1.5 decades longer than the τ_m, respectively. This result might be caused by the combination of the strangulation and tube renewal effects.

Kan et al.[12] reported that guest polybutadiene entrapped in a styrene–butadiene–styrene block copolymer has τ_{mg} longer than τ_m by 0.5 decade. Granick et al.[11] found that poly(dimethylsiloxane) relaxes 1–2 orders of magnitude slower in a network of the same polymer than in the uncross-linked polymer. These results are similar to the present result. Unfortunately, these authors did not evaluate M_x for their networks and hence we cannot compare their data quantitatively with the present result.

Finally, we comment on the slope of the log τ_{mg} vs. log M plot. As is well-known, the tube model[4,5] predicts a slope of 3.0, but most uncross-linked polymers exhibit a slope of ca. 3.5.[1,2] In terms of the tube model, one of the origins of this discrepancy may be due to the tube renewal effect.[6] If so, the slope for guest molecules in a network is expected to be smaller than 3.5. As shown in Figure 9, the slope for the guest *cis*-PI in NR(0.4:30) was 3.3 ± 0.5. It appears that the slope in the network/guest systems is still higher than 3.0 of the tube model. Kramer et al.[7] observed a slope of 3.0 for guest polyisobutylene in a butyl rubber network. However, Kramer et al.[8] also observed a slope of 3.5 for ethylene–propylene copolymer entrapped in a network of the same polymer. Obviously more accurate measurement is needed to derive a definite conclusion to this problem.

Conclusions

(1) Viscoelastic relaxation due to the motion of the guest molecules was observed both in the temperature- and frequency-dependence curves of dynamic Young's moduli for cross-linked natural rubbers containing guest *cis*-polyisoprene (*cis*-PI).

(2) The mechanical longest relaxation time τ_{mg} of the guest polymer in the network appears to be governed by the molecular weight M_e between entangelements and the molecular weight M_x between cross-links.

When M_x is smaller than molecular weight M_e between entanglements, τ_{mg} is appreciably longer than the relaxation time τ_m in the uncross-linked polymer. The nature of the constraint is attributed to the strangulation effect. However, in the network with $M_x \simeq M_e$, τ_{mg} is the same or only slightly longer than τ_m within the experimental error.

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Registry No. Polyisoprene, 9003-31-0.

References and Notes

(1) Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules*, preceding paper in this issue.
(2) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1961.
(3) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(4) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(5) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(6) Klein, J. *Macromolecules* **1978**, *11*, 852.
(7) Kramer, O.; Greco, R.; Neira, R.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2361.
(8) Kramer, O.; Greco, R.; Ferry, J. D.; McDonel, E. T. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1675.

(9) Greco, R.; Taylor, C. R.; Kramer, O.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1687.
(10) Nelb, G. W.; Pedersen, S.; Taylor, C. R.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 645.
(11) Granick, S.; Pedersen, S.; Nelb, G. W.; Ferry, J. D.; Macosko, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1745.
(12) Kan, H. C.; Ferry, J. D.; Fetters, L. J. *Macromolecules* **1980**, *13*, 1571.
(13) Kraus, G.; Rollmann, K. W. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 385.
(14) de Gennes, P. G. *Macromolecules* **1986**, *19*, 1245.
(15) Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1975.
(16) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(17) Nemoto, N.; Moriwaki, M.; Odani, H.; Kurata, M. *Macromolecules* **1971**, *4*, 215.
(18) Nemoto, N.; Odani, H.; Kurata, M. *Macromolecules* **1972**, *5*, 531.
(19) Gotro, J. T.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2767.
(20) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.

Solution-Cross-Linked Networks. 3. Dielectric Normal Mode Process of Guest Polyisoprene in Natural Rubber Networks

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ABSTRACT: The "normal-mode process" of dielectric relaxation due to fluctuation of the end-to-end polarization vector was investigated on *cis*-polyisoprene (*cis*-PI) absorbed in cross-linked natural rubbers (NR) and a synthetic isoprene rubber (IR). When the network has the molecular weight between cross-links M_x higher than the molecular weight between entanglements M_e the dielectric relaxation times τ_{ng} of the guest *cis*-PI were ca. 0.4 decade higher than those in pure *cis*-PI. In terms of the tube theory of polymer dynamics, this enhancement of τ_{ng} of the guest molecules with molecular weight $M > M_e$ in the networks with $M_x \geq M_e$ was explained by the absence of the tube renewal effect in the networks. On the other hand, the τ_{ng}s of the guest molecules (with $M > M_e$) in the networks with $M_x < M_e$ were much longer than those in the pure state due to the "strangulation" effect as pointed out by de Gennes. The τ_{ng} in the strangulation state increased with M of the guest *cis*-PI with the power of 4.0 ± 0.5. The mean-square end-to-end distance $\langle r^2 \rangle$ of the guest *cis*-PI in the networks was calculated from the contribution of the guest *cis*-PI to the dielectric relaxation strength for the normal-mode process. In NR networks, the $\langle r^2 \rangle$s of the guest *cis*-PI were slightly smaller than the value $\langle r^2 \rangle_0$ in the unperturbed state presumably due to repulsive interactions caused by the difference in the microstructure between the *cis*-PI molecules and the NR networks, while that in the IR network was the same as $\langle r^2 \rangle_0$.

Introduction

In the first paper of this series,[1] we reported the swelling and absorption behavior of solution-cross-linked natural rubber (NR) toward benzene solutions of guest *cis*-polyisoprene (*cis*-PI). It was found that since the solution-cross-linked NRs have higher free energy than bulk-cross-linked networks, they exhibit high swellability toward polymers. Using this property, we studied the contribution of the guest *cis*-PI molecules entrapped in the NR networks to their viscoelastic properties and reported the results in part 2 of this series.[2] Particularly in the latter,[2] we demonstrated that the networks containing guest molecules are an interesting model system for investigating the dynamic behavior of entrapped polymer chains.

For the dynamics of polymer chains entrapped in a network, de Gennes[3] proposed a "phase diagram" (see Figure 1 of the part 2 of this series) that classifies schematically the behavior into three regions depending on the molecular weight M of the guest polymer (which we assume to be chemically identical with that of the network polymer), that between cross-links M_x, and that between entanglements M_e:[4] In the region where $M < M_e < M_x$, the free-draining Rouse model[5] prevails; in the region where $M_e < M$ and M_x, the reptation modes of the tube model[6,7] are dominant; in the region of $M > M_e > M_x$ called the "strangulation"[3] region, the entrapped guest molecules suffer from stronger confinement due to the network rather than that due to entanglement.

Although viscoelastic spectroscopy of the network/guest polymer systems provided interesting information on the dynamics of the entrapped guest molecules, the method has two difficulties: In the first place, to extract the contribution of the guest molecules, we need to employ an adequate rule of mixtures,[8] and second, such a contribution is often obscured by the network especially when the amount of entrapped guest chains is small.

Previously, we demonstrated that *cis*-PI has a component of the dipole moment aligned parallel along the chain contour, exhibiting the "dielectric normal mode" process arising from fluctuation of such an end-to-end polarization vector.[9,10] Thus, we can determine from this study not only the dynamic behavior including the relaxation times and their distribution, but also the conformational characteristics, particularly the mean-square end-to-end distance $\langle r^2 \rangle$ of *cis*-PI in solutions of infinite dilution to the bulk state.[11]

Obviously, the "dielectric normal-mode" spectroscopy is applicable to the network/guest *cis*-PI systems as well. Moreover, this method has an additional advantage that the contribution of guest *cis*-PI is easily extracted since closed loops of network strands in the natural rubber network should not, in principle, exhibit the dielectric normal-mode process.

In this study, taking the advantages of the dielectric method over the mechanical spectroscopy, we attempted to clarify the dynamic and conformational properties of

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