

Rubber Co. for kindly providing the polymers.

Registry No. PIP, 9003-31-0; PVE, 9003-17-2.

References and Notes

- (1) Roland, C. M. In *Handbook of Elastomers—New Developments and Technology*; Bhowmick, A. K., Stephens, H. L., Eds.; Marcel Dekker: New York, to be published 1987; in press.
- (2) Krause, S. J. *Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C7*, 251.
- (3) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (4) Garcia, D. J. *Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 107.
- (5) Farenholtz, S. R.; Kwei, T. K. *Macromolecules* **1981**, *14*, 1076.
- (6) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
- (7) Balazs, A. C.; Sanchez, I. C.; Epstein, I. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1985**, *18*, 2188.
- (8) Bates, F. S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev. Lett.* **1985**, *55*, 2425.
- (9) Bates, F. S.; Wignall, G. D. *Macromolecules* **1986**, *19*, 934.
- (10) Buckingham, A. D.; Hentschel, H. G. E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 853.
- (11) Tate, D. P.; Bethea, T. W. In *Encyclopedia of Polymer Science and Technology*; Mark, Bikales, Overberger, Manges, Eds.; Wiley: New York, 1985; Vol. 2, p 537.
- (12) Roland, C. M.; Bohm, G. G. A. *Macromolecules* **1985**, *18*, 1310.
- (13) Roland, C. M.; Bohm, G. G. A. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 79.
- (14) Skewis, J. D. *Rubber Chem. Technol.* **1966**, *39*, 217.
- (15) Kramer, E. J.; Green, P. F.; Palmstrom, C. J. *Polymer* **1984**, *25*, 473.
- (16) Green, P. F.; Doyle, B. L. *Phys. Rev. Lett.* **1986**, *57*, 2407.
- (17) Stockmayer, W. J. *Chem. Phys.* **1949**, *17*, 588.
- (18) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1966.
- (19) Ahmad, H.; Yaseen, M. *Polym. Eng. Sci.* **1979**, *19*, 858.
- (20) Cohen, R. E.; Wilfong, D. E. *Macromolecules* **1982**, *15*, 370.
- (21) Ueda, A.; Watanabe, H.; Akita, S. presented at the "International Rubber Conference"; Kyoto, Japan, Oct 1985.
- (22) Braun, H. G.; Rehage, G. *Angew. Macromol. Chem.* **1985**, *131*, 107.
- (23) Kaplan, D. S. *J. Appl. Polym. Sci.* **1976**, *20*, 2615.
- (24) Bauer, R. F.; Dudley, E. A. *Rubber Chem. Technol.* **1977**, *50*, 35.
- (25) Couchman, P. R. *Macromolecules* **1978**, *11*, 1156.
- (26) Plans, J.; MacKnight, W. J.; Karasz, F. E. *Macromolecules* **1984**, *17*, 810.
- (27) MacKnight, W. J.; Stoelting, J.; Karasz, F. E. *Adv. Chem. Ser.* **1971**, *99*, 29.
- (28) De Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.
- (29) Wendorff, J. H. J. *Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 439.
- (30) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1978**, *11*, 150.
- (31) Patterson, D. *Polym. Eng. Sci.* **1982**, *22*, 64.
- (32) Bates, F. S. *Macromolecules* **1985**, *18*, 525.
- (33) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
- (34) Rim, P. B.; Runt, J. P. *Macromolecules* **1984**, *17*, 1520.
- (35) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
- (36) Roberts, D. E.; Mandelkern, L. *J. Am. Chem. Soc.* **1955**, *77*, 781.
- (37) Runt, J. P.; Martynowicz, L. M. *Adv. Chem. Ser.* **1985**, *211*, 111.
- (38) Keith, H. D.; Padden, F. J. *J. Appl. Phys.* **1964**, *35*, 1286.
- (39) Burfield, D. R.; Kim, K.-L. *Macromolecules* **1983**, *16*, 1170.
- (40) Gotro, J. T.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2767.
- (41) Carella, J. M.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2775.

Solution-Cross-Linked Networks. 1. Swelling and Absorption Behavior of Natural Rubber Networks

Beng Teik Poh,[†] Keiichiro Adachi,* and Tadao Kotaka

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. Received February 9, 1987

ABSTRACT: Swelling and absorption behavior of bulk and solution cross-linked natural rubber (*Hevea Brasiliensis*) networks was examined. The networks were prepared by irradiation of a 2–40-Mrd dose of γ -rays to solutions of a natural rubber sample at cross-linking concentrations C_x of 0.1–1 (bulk). Swelling and absorption tests were carried out at 308 K against pure benzene and benzene solutions of anionically prepared high *cis*-polyisoprene (*cis*-PI) of concentration ϕ . Equilibrium volume fractions of the solvent, v_1 , the network, v_2 , and the guest, v_3 , were determined from the swelling ratio q ($=1/v_2$) and the absorption ratio $(v_2 + v_3)/v_2$ as functions of C_x and ϕ of the guest solution in which the network had been soaked. Results indicated that the solution-cross-linked networks swell/absorb more than the corresponding bulk-cross-linked networks having the same cross-link density. The classical Flory–Rehner theory has been modified by replacing the linear expansion coefficient α ($=q^{1/3}$) by α' defined as $\alpha C_x^{1/3}$ to explain the swelling/absorption behavior. The modified equation explains well the absorption/swelling behavior of the networks, although the agreement is only semiquantitative.

Introduction

As is well-known, the swelling behavior of a polymer network can be described by a balance between mixing and elastic free energies,^{1,2} and usually, the entropy of mixing acts as the main driving force for swelling. If a network is placed in an undiluted linear polymer either of the same or different kind, it will barely swell because the entropy of mixing of the polymers is very small.^{3,4} Therefore, an ordinary bulk-cross-linked network can absorb a bulk polymer only when the enthalpy of mixing between the network and the guest polymer is negative. Unfortunately,

such polymer pairs are very rare.⁵ For this reason, only a few studies have been made on the swelling of networks by polymers or polymer solutions. However, the systems consisting of guest polymers absorbed in networks are an interesting subject of studies on dynamic,⁶ conformational,⁷ and viscoelastic⁸ properties of the entrapped guest polymers. The systems are somehow related to semiinterpenetrating polymer networks.⁹

Although the phantom network model has a defect, that the network should collapse to a point in the absence of external stresses, we take the model as a convenient starting point of analyzing the swelling behavior of a polymer network toward solvent and polymer solutions.^{1,2,10} Other more sophisticated models incorporating the excluded volumes among the network segments^{10–15} and/or

[†] Present address: School of Industrial Technology, Universiti Sains Malaysia, Minden, Penang, Malaysia.

topological interactions¹⁷ between the strands are too complex to be applied to an analysis of such a problem.

Generally, phantom network theories of swelling of a polymer network usually assume that network strands in the dry state are in the most probable conformation.¹ In case of a network cross-linked in a solution state, the average end-to-end distance of the strands in the dry state is expected to be shorter than those in the as-cross-linked state containing the solvent in which the strands may assume the most probable conformation.¹⁰ Thus, a solution-cross-linked network may have a self-driving force to be swollen even by polymers and polymer solutions as well as solvents. Thus, such a network may be referred to as a "high free energy network" or "hungry network".

Posthuma de Boer and Pennings¹⁶ showed that solution-cross-linked polyethylenes exhibited a higher degree of swelling than bulk-cross-linked ones. However, they did not study the swelling behavior in guest polymer solutions. In this paper, we describe the swelling and absorption behavior of high-free-energy networks prepared from natural rubber cross-linked by γ -rays in pure benzene and benzene solutions of anionically polymerized *cis*-polyisoprenes. Four major factors are expected to affect the swelling behavior: The concentration C_x of natural rubber in the cross-linking solution, the molecular weight M_x between cross-links, the molecular weight M , and the concentration ϕ of the guest *cis*-polyisoprene in the solutions in which the network is soaked. The purpose of this study is to investigate systematically the effect of these factors.

There is no theory developed so far to describe the swelling behavior of a solution-cross-linked rubber network in polymer solutions. In this paper, we attempt to describe the swelling and absorption behavior of such a high free energy network toward solutions of the free polymers of the same kind by slightly modifying the classical Flory-Rehner¹ equation.

Theory

Swelling of a network is governed by two free energy terms, i.e., the changes in the free energy of mixing ΔF_m and in the free energy of elastic deformation, ΔF_{el} :^{1,2}

$$\Delta F = \Delta F_m + \Delta F_{el} \quad (1)$$

According to the Flory-Huggins theory,¹ ΔF_m is given by

$$\Delta F_m = RT[\sum n_i \ln v_i + \chi_{12}(n_1 v_2 + n_1 v_3)] \quad (2)$$

where the subscripts 1, 2, and 3 denote the solvent, the network, and the guest molecules, respectively; n_i is the moles of the species i ; v_i is the volume fraction; and χ_{ij} is the interaction parameter. Here, we assumed the guest polymer and the network are the same species, say, *cis*-polyisoprene.

Several theories for ΔF_{el} are available.^{11-15,17} Except Iwata's theory,¹⁷ these are essentially based on the classical theory of rubber elasticity; i.e., ΔF_{el} is due to the conformational entropy change of the network strands. To avoid the defect of the phantom network model, Iwata¹⁷ proposed the idea that rubber elasticity is due to repulsive forces between strands which depend strongly on their topological configuration. The calculation of ΔF_{el} based on the sophisticated theories of Iwata,¹⁷ Flory,^{11,14} Edwards,¹⁵ and others^{12,13} are rather complex, and in some cases, computer simulation is needed. Therefore, in this study, we use the simplest phantom network model¹ to describe qualitatively the behavior of solution-cross-linked networks. It reads

$$\Delta F_{el} = (RT\nu_e/2)(3\alpha^2 - 3 - 3 \ln \alpha) \quad (3)$$

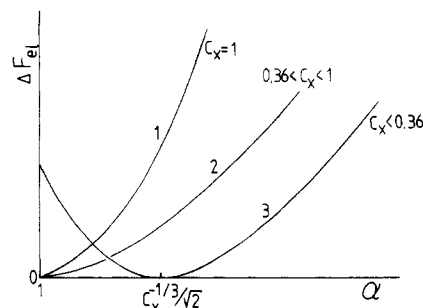


Figure 1. Schematic diagram representing the dependence of elastic free energy $\Delta F'_{el}$ on linear expansion coefficient α for networks cross-linked in a solution state with concentration C_x . Curves are drawn by adding a constant to eq 6 so that the minimum value of $\Delta F'_{el}$ becomes 0.

where ν_e is the moles of effective network chains and α , the linear expansion coefficient. According to Flory,¹⁰ α for a network cross-linked in a solution at concentration C_x should be replaced by a new expansion coefficient α' given by

$$\alpha'^3 = V/V_c \quad (4)$$

where V and V_c are the volume of the swollen network and that of the as-cross-linked state, respectively. If we define the volume of the dry network as V_0 , α^3 and C_x are equal to V/V_0 and V_0/V_c , respectively, and hence α' is given by

$$\alpha' = C_x^{-1/3} \alpha \quad (5)$$

Thus, for the solution-cross-linked network, eq 3 becomes

$$\Delta F'_{el} = (RT\nu_e/2)(3C_x^{2/3}\alpha'^2 - 3 - 3 \ln \alpha' - \ln C_x) \quad (6)$$

A schematic plot of $\Delta F'_{el}$ vs. α is shown in Figure 1. It is seen that the solution-cross-linked network has lower $\Delta F'_{el}$ than that of a corresponding bulk-cross-linked network and exhibits a minimum at $\alpha = 2^{-1/2}C_x^{-1/3}$ in the case where C_x is lower than the critical concentration $C_x^* = 2^{-3/2}$ ($=0.36$). This predicts that the solution-cross-linked network may absorb a larger amount of the solvent and guest polymer than the bulk-cross-linked one, if ν_e is the same.

Calculation of Swelling and Absorption Ratios.

From eq 2, the excess chemical potentials ($\mu_j^s - \mu_j^0$) of the solvent ($j = 1$) and the guest polymer ($j = 3$) of the same kind as the network ($j = 2$) in the solution phase are given by

$$(\mu_1^s - \mu_1^0)/RT = \ln(1 - \phi) + \phi - \phi/\gamma + \chi_{13}\phi^2 \quad (7)$$

$$(\mu_3^s - \mu_3^0)/\gamma RT = - (1 - \phi) + \ln \phi/\gamma + (1 - \phi)/\gamma + \chi_{13}(1 - \phi)^2 \quad (8)$$

where the superscripts 0 and s denote the quantities in the pure state and in the solution phase, respectively; ϕ denotes the volume fraction of the guest polymer in the solution phase; γ is the degree of polymerization of the guest polymer; and χ_{13} is the polymer-solvent interaction parameter. On the other hand, from eq 2 and 6, the excess chemical potentials ($\mu_j^N - \mu_j^0$) in the network phase are

$$(\mu_1^N - \mu_1^0)/RT = (\rho V_s/M_x)(C_x^{2/3}v_2^{1/3} - v_2/2) + \ln v_1 + 1 - v_1 - v_3/\gamma + \chi_{12}v_2(1 - v_1) + \chi_{13}v_3(1 - v_1) - \chi_{23}v_2v_3 \quad (9)$$

$$(\mu_3^N - \mu_3^0)/\gamma RT = (\rho V_s/M_x)(C_x^{2/3}v_2^{1/3} - v_2/2) - v_1 + (1/\gamma) \ln v_3 + (1 - v_3)/\gamma - \chi_{12}v_1v_2 + \chi_{13}(1 - v_3)v_1 + \chi_{23}(1 - v_3)v_2 \quad (10)$$

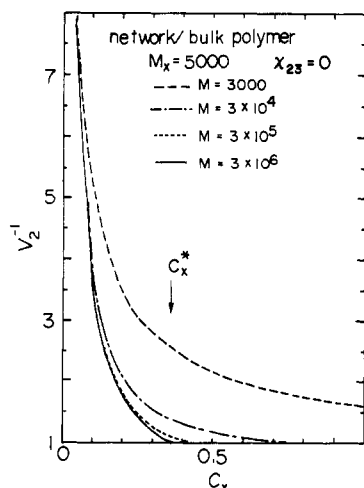


Figure 2. Theoretical prediction of the C_x dependence of $1/v_2$ for a network having $M_n = 5000$ when soaked in the undiluted polymers with molecular weight M from 3000 to 3×10^6 . Calculation was made based on eq 10 with the following conditions: $\chi_{23} = 0$; $\rho V_s = 81.9$; $y = M/68$.

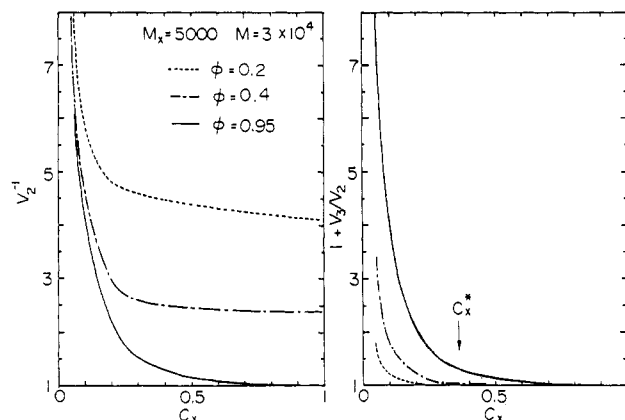


Figure 3. Theoretical swelling ratio $q = 1/v_2$ and absorption ratio $1 + v_3/v_2$ for a solution-cross-linked network in solutions of the same polymer with $M = 3 \times 10^4$. The concentration ϕ of the solutions are taken to be 0.2, 0.4, and 0.95. χ_{12} is assumed to be 0.21, and the other parameters are the same as in Figure 2.

where ρ is the density of the dry network; V_s , the molar volume of the solvent; and M_x , the molecular weight between cross-link points. Since the guest polymer and the network are of the same kind, $\chi_{23} = 0$ and $\chi_{12} = \chi_{13}$ in the present systems.

Since these equations cannot be solved analytically, we solved them numerically with a microcomputer. The method is based on two trial functions f_1 and f_3 : f_1 is equal to the right-hand side (rhs) of eq 9 subtracted by the rhs of eq 7, and similarly f_3 is given by eq 10 - eq 8. First, we assume an arbitrary value of v_3 and draw graphs of f_1 and f_3 against v_2 on the computer display. If the assumed value of v_3 is correct, f_1 and f_3 have a common intercept on the horizontal v_2 axis, because $f_1 = f_3 = 0$ for the true solutions. We determined the most appropriate solutions by extrapolating the trial values of v_3 to $f_1 = f_3 = 0$.

Figures 2 and 3 show the theoretical swelling behavior of a network having $M_n = 5000$ in the bulk polymers of the same kind and in solutions of the polymer, respectively. These figures demonstrate clearly that the solution-cross-linked networks with C_x below C_x^* absorb polymers and solvents strongly.

Molecular Weight between Cross-Links. To determine v_e or M_x of a network, we usually use data of swelling ratio q ($=1/v_2$) and/or Young's modulus E . Hereafter, we distinguish the molecular weight between cross-links de-

Table I
Cross-Linking Concentration C_x (in Volume Fraction), Swelling Ratio q , Young's Modulus E in dyn cm^{-2} , and Molecular Weight between Cross-Links M_x^a

code	C_x	q	$10^{-6}E$	$10^{-3}M_{xs}$	$10^{-3}M_{xE}$
NR(0.1:10)	0.12	16.5			
NR(0.1:20)	0.11	13.9	5.4	3.2	3.0
NR(0.1:40)	0.11	20.0	4.4	6.4	3.7
NR(0.2:40)	0.21	18.8		10.0	
NR(0.3:40)	0.36	12.7		7.4	
NR(0.4:40)	0.42	10.7	8.8	6.0	4.5
NR(0.4:30)	0.42	11.7	12	7.2	3.3
NR(0.4:20)	0.42	12.5	10.3	8.1	3.8
NR(0.4:10)	0.42	13.8	11.5	9.7	3.4
NR(0.5:40)	0.51	11.1		7.6	
NR(0.7:40)	0.69	10.2		8.2	
NR(0.8:40)	0.81	7.7		5.4	
NR(0.9:40)	0.90	7.3		5.3	
NR(1:40)	1	5.3	55	3.0	1.3
NR(1:20)	1	5.2	67	2.9	1.1
NR(1:5)	1	6.7	16	4.8	4.4
NR(1:2)	1	10.3	5	11.0	14

^a Subscripts s and E represent that M_x was determined from the swelling ratio and Young's modulus, respectively.

termined from swelling ratio and Young's modulus by M_{xs} and M_{xE} , respectively.

For a network cross-linked at C_x , Flory¹⁰ proposed

$$-\ln(1 - v_2) - v_2 - \chi_{12}v_2^2 = (\rho V_s/M_{xs})(C_x^{2/3}v_2^{1/3} - v_2/2) \quad (11)$$

When the swelling ratio q is high, eq 11 is reduced to

$$q^{5/3} = (M_{xs}/\rho V_s)(1/2 - \chi_{12})C_x^{-2/3} \quad (12)$$

The theory of rubber elasticity predicts that the Young's modulus E of a phantom network is written as¹⁰

$$E = (3\rho RT/M_{xE})(\langle r_i^2 \rangle / \langle r_0^2 \rangle) \quad (13)$$

where $\langle r_i^2 \rangle$ and $\langle r_0^2 \rangle$ are the mean square end-to-end distance of the strands in the network and that in a θ solvent. For a bulk-cross-linked sample, $\langle r_i^2 \rangle / \langle r_0^2 \rangle$ is assumed to be unity but for a solution-cross-linked network, the ratio should be equal to $C_x^{2/3}$.

Experimental Section

Materials. Natural rubber (*Hevea Brasiliensis*) having molecular weight of ca. 10^6 was purified by precipitation from a benzene solution in methanol and dried at 50°C in vacuum until constant weight was reached. Solutions of the natural rubber in toluene were sealed in glass ampules under vacuum at liquid nitrogen temperature. To prepare films of natural rubber networks, the solutions were also sandwiched with an O-ring made of Teflon between glass plates. We estimated C_x (in volume fraction) assuming additivity of the volumes of toluene ($\rho = 0.87$) and the natural rubber ($\rho = 0.92$).

All the sample solutions sealed in glass ampules or between glass plates were irradiated by γ -rays from ^{60}Co at an ambient temperature. The dose of the irradiation was from 2 to 40 Mrd. No phase separation was observed for the irradiated samples in the C_x range 10–100%. After irradiation, all the samples were dried at 50°C under vacuum of ca. 0.1 Pa for a few days until constant weight was reached. It was found that the sol fraction in the networks was only 1–2% after extraction with benzene. The sample codes are identified as NR(C_x in volume fraction: dose in Mrd). Table I shows M_{xs} and M_{xE} characterized by eq 11 and 13, respectively, for the various networks used in this experiment.

In determining M_{xs} , we need the values of χ_{12} , V_s , and ρ . Hayes¹⁸ showed that χ_{12} should be taken as 0.21 in the Flory-Rehner equation for swelling of a cross-linked natural rubber in toluene. Since the solvent quality of benzene and toluene is similar, we used $\chi_{12} = 0.21$ instead of the commonly used value of ca. 0.4.¹⁹ It is known that χ_{12} varies with concentration.²⁰ However, the concentration dependence of χ_{12} in the natural

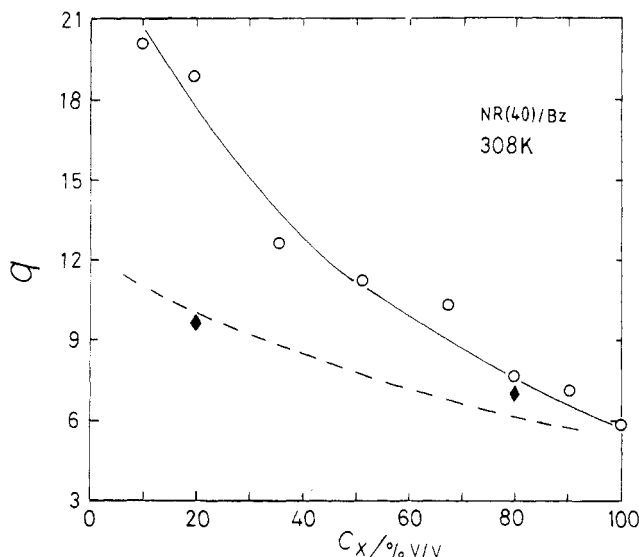


Figure 4. Plot of swelling ratio q ($=1/v_2$) in benzene against cross-linking concentration C_x for the natural rubbers cross-linked in the solution by γ -ray of 40 Mrd. The dashed line indicates the expected swelling ratio of bulk-cross-linked networks with the same cross-link density as the solution-cross-linked networks. The diamond symbols indicate q for NR(1:5) and NR(1:2) which have M_{xs} approximately the same as that of the solution-cross-linked networks with C_x of 0.8 and 0.2, respectively.

rubber/benzene system is reported to be relatively weak.²¹ Therefore, we neglected this effect for the sake of simplicity in the following analysis of the experimental results. We also assumed that for benzene $V_s = 89 \text{ cm}^3 \text{ mol}^{-1}$ and $\rho = 0.92 \text{ g cm}^{-3}$.

Guest polymers, *cis*-polyisoprene (*cis*-PI), were prepared by anionic polymerization in pentane with *sec*-butyllithium as the initiator. The contents of *cis*, *trans*, and vinyl linkages in the *cis*-PI samples were determined by ^{13}C NMR to be 79, 17, and 4%, respectively. Two *cis*-PI samples, PI-02 and PI-31, having molecular weight of 2.4×10^3 and 31.2×10^3 , respectively, were used as guest polymers. Their polydispersity index M_w/M_n was less than 1.09. Benzene of reagent grade was used without further purification as the swelling agent throughout the experiment. To determine the volume fraction of the polymer in the solutions and/or networks, we assumed again the additivity of density between *cis*-PI (0.92) and benzene (0.88).

Method. For the swelling experiment, rectangular network samples of the size of about $1 \times 3 \times 10 \text{ mm}^3$ were soaked at 308 K in benzene or in benzene solutions of the guest polymers for about 100 h until the length of the swollen specimen reached a constant. The swelling ratios of the networks were determined by measuring the swollen length quickly by using a traveling microscope. The absorption ratios defined as $1 + v_2/v_3$ was determined after benzene was thoroughly removed from the swollen network under vacuum. Young's modulus was measured at 3.5 Hz by a Rheovibron (Toyo-Baldwin, type DDV-II-C).

Results and Discussion

Swelling in Benzene. Figure 4 shows the C_x dependence of the swelling ratio q ($=1/v_2$) in pure benzene for networks NR(C_x :40) cross-linked at a 40-Mrd dose (see Table I). Since M_{xs} for these 40-Mrd samples varies from 5300 to 10000, Figure 4 does not represent the C_x dependence of q at constant M_x . However, eq 12 predicts that q varies by a factor of 1.46 due to the change in M_{xs} from 5300 to 10000. Since the observed variation of q is larger than this factor, Figure 4 represents approximately the C_x dependence of q at constant M_x , i.e., q ($=1/v_2$) vs. C_x in eq 11 (or 12) with constant M_{xs} .

Equation 12 predicts that the ratios of q for the solution-cross-linked network at C_x to q_0 for the bulk-cross-linked one ($C_x = 1$) is given by

$$q/q_0 = C_x^{-2/5} \quad (14)$$

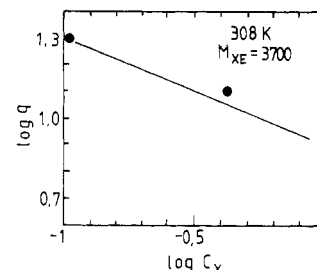


Figure 5. Double-logarithmic plot of swelling ratio q vs. C_x for the networks with $M_{xE} = 3700$. The solid line indicates the theoretical slope of 0.40.

provided that M_x is the same for these networks. The dashed line in Figure 4 shows the value of q_0 calculated by multiplying $C_x^{-2/5}$ by the smoothed value of q for the solution-cross-linked networks given by the solid line.

First, we tested this equation using the M_{xs} data. The diamond marks at $C_x = 0.2$ indicates the value of q_0 ($=9.7$) of a hypothetical bulk-cross-linked network having $M_{xs} = 10000$ interpolated from those of NR(1:5) and NR(1:2), and the other at $C_x = 0.8$ indicates q_0 ($=7.0$) estimated similarly for a bulk-cross-linked network with $M_{xs} = 5400$ from the data for NR(1:2) and NR(1:5). These two diamond symbols are located close to this theoretical expectation.

Strictly speaking, however, we cannot test the validity of eq 11 and 12 using M_{xs} , since M_{xs} is determined from these equations. We need the data of M_x determined by a method other than the swelling experiment. For this purpose, we used M_{xE} . Thus, we made a closer check by comparing the values of q for the actual and/or hypothetical networks having the same $M_{xE} = 3700$ but different C_x evaluated from the data listed in Table I. We see in Table I that M_{xE} of NR(0.4:20) and NR(0.1:40) is close to this value of 3700. We also estimated q_0 of a hypothetical bulk-cross-linked network with $M_{xE} = 3700$ to be 6.2.

Figure 5 shows the double-logarithmic plot of the C_x dependence of q for this result. The slope of this plot is about -0.40 ± 0.05 . Within experimental error, this value coincides with the theoretical value of -0.4 predicted by eq 12. Since eq 12 holds only at high swelling ratio, one of the origins of the slight disagreement at $C_x = 1$ may be due to this approximation. These results indicate that eq 11 describes well the effect of solution cross-linking on the swelling behavior. Thus, we may conclude that the basic assumption, eq 5, describing the high free energy network is valid at least qualitatively.

Swelling Ratio in Guest Solution. To check the time needed to attain equilibrium swelling in solutions of guest *cis*-PI samples, we measured the time dependence of the absorption ratio $(v_2 + v_3)/v_2$ of the guest polymers in the networks. Figure 6 shows two examples for the NR(0.2:40) network soaked in benzene solutions of PI-31.

It was found that the equilibrium absorption ratio was reached after 100 h. On the other hand, a much shorter time was sufficient in the case of PI-02 solutions. For higher molecular weight *cis*-PI, we expect that it might take a much longer time to achieve equilibrium swelling, because the diffusion coefficient²² for entangled chain molecules is proportional to $M^{2.0}-M^{2.4}$. If we use *cis*-PI with $M = 10^5$ and a network having the size similar to this experimental value, it will take more than 1 month to attain equilibrium.

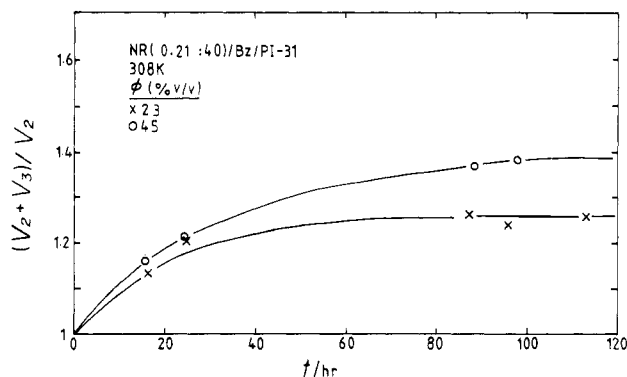


Figure 6. Time dependence of the absorption ratio ($=1 + v_2/v_3$) of PI-31 in NR(0.2:40) when soaked in PI-31 solutions with concentration of 23 (x) and 45% (o).

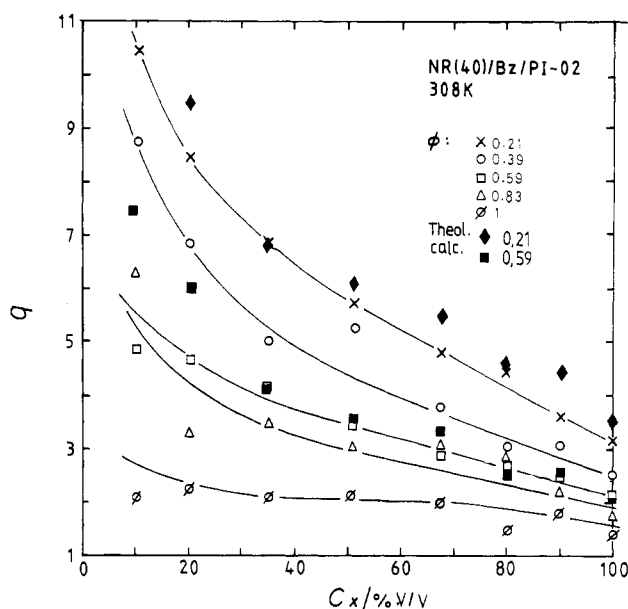


Figure 7. Cross-linking concentration C_x dependence of swelling ratio q in benzene solutions of PI-02. Concentration ϕ of the solutions is shown in the figure. The filled diamond and square symbols indicate the theoretical values calculated by eq 7-10 for $\phi = 0.21$ and 0.59 , respectively. The calculation was performed by using the M_{cs} data for the corresponding networks. The solid lines are a guide for the eyes.

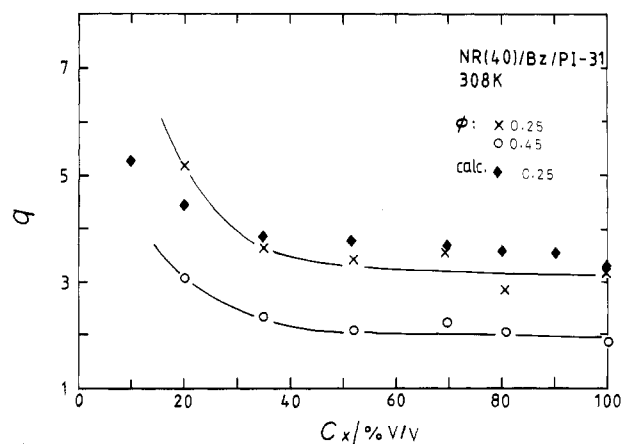


Figure 8. Cross-linking concentration C_x dependence of swelling ratio q in benzene solutions of PI-31. Concentration ϕ of the solutions is given in the figure. The filled diamond symbol indicates the theoretical values for $\phi = 0.25$ calculated similarly to that in Figure 7. The solid lines are a guide for the eyes.

Figures 7 and 8 show the C_x dependence of q in solutions of PI-02 and PI-31, respectively, for the networks cross-

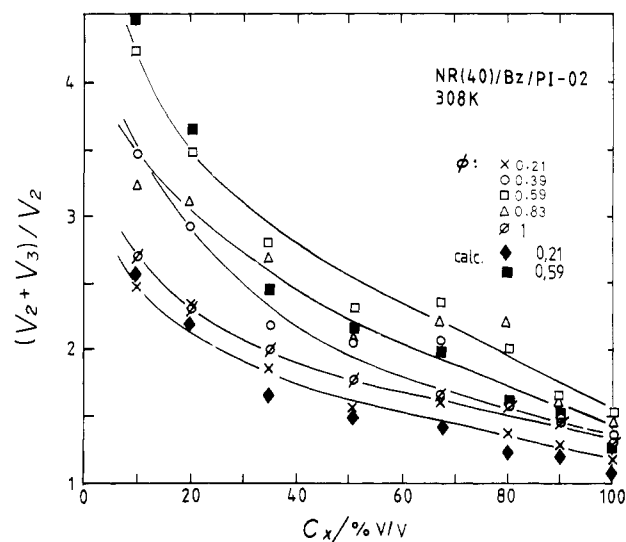


Figure 9. Cross-linking concentration C_x dependence of absorption ratio ($1 + v_3/v_2$) in benzene solutions of PI-02 with concentration ϕ . The filled diamond and square symbols indicate the theoretical values calculated with M_{cs} data for $\phi = 0.21$ and 0.59 , respectively. The solid lines are a guide for the eyes.

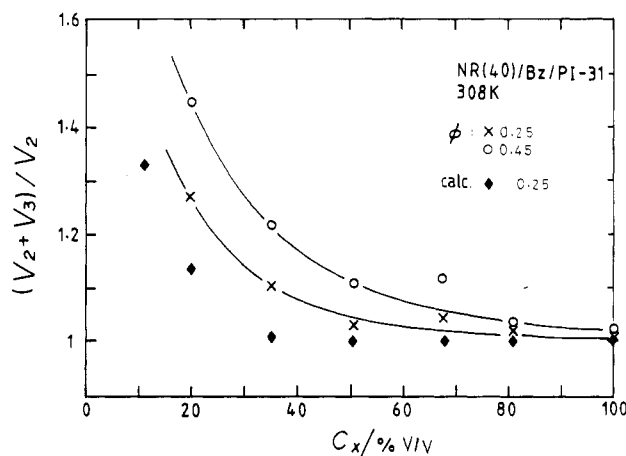


Figure 10. Cross-linking concentration C_x dependence of absorption ratio ($1 + v_3/v_2$) in benzene solutions of PI-31 with concentration ϕ . The filled diamond symbol indicates the theoretical values for $\phi = 0.25$ calculated by eq 7-10 with M_{cs} data listed in Table I. The solid lines are a guide for the eyes.

linked by 40-Mrd irradiation. The concentration ϕ of the guest solutions was changed from 20 to 100% (bulk) for PI-02 but only 25 and 45% for PI-31, because of the high viscosity and difficulty in handling the latter. We see that q increases with decreasing C_x similarly to the extent of swelling in pure benzene. However, the value of q is smaller in PI-02 solutions and much smaller in PI-31 solutions than that in the pure solvent. Clearly, this tendency is ascribed to the effect of mixing entropy of guest *cis*-PI molecules.

We now compare these results with the theoretical prediction given by eq 7-10. Calculation was made by using the value of M_{cs} for the corresponding network at 308 K. The results are shown in Figures 7 and 8. Theoretical q values are in agreement with the experimental data within ca. 30% indicating that eq 7-10 describe semiquantitatively the swelling behavior of the solution-cross-linked networks in solutions of the same or similar polymers.

Absorption Ratio of Guest Molecules. Figures 9 and 10 show the C_x dependence of the absorption ratio $(v_2 + v_3)/v_2$ for the 40-Mrd networks soaked in solutions of PI-02

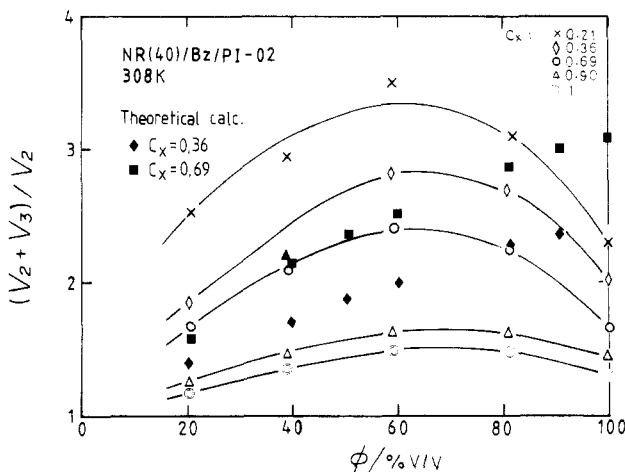


Figure 11. Absorption ratio $(1 + v_3/v_2)$ vs. concentration ϕ of the guest PI-02 solution in which the network was soaked. The filled diamond and square symbols show the theoretical values for C_x of 0.36 and 0.69, respectively. The C_x values are given in the figure. The solid lines are a guide for the eyes.

and PI-31, respectively. The absorption ratio is relatively high in PI-02 solutions even for the bulk-cross-linked network NR(1:40) as compared to that in PI-31 solutions. This is attributed to the relatively large mixing entropy of the former. As expected, the absorption of PI-31 in the bulk-cross-linked network is practically zero within experimental accuracy.

In contrast to the bulk-cross-linked network, the solution-cross-linked networks, especially the one cross-linked at low C_x , absorb a substantial amount of PI-31. We expect that the solution-cross-linked networks may absorb guest molecules of M even higher than that of PI-31 to the same extent shown in Figure 2. However, the time required to reach equilibrium becomes longer for higher molecular weight guest PI.

As shown in Figures 9 and 10, the absorption ratio computed from theory is in rough agreement with experimental data. Thus, the data shown in Figure 10 are a clear evidence of the hungriness of the solution-cross-linked networks.

Figure 11 indicates the dependence of the absorption ratio on the concentration ϕ of the PI-02 solutions. As is seen from the figure, the experimental absorption ratio exhibits a maximum around $\phi = 50\%$, but the theoretical value does not. We consider the origin of this discrepancy as due to the neglect of χ_{23} between the network with a 100% *cis*-1,4 structure and the guest *cis*-PI with ca. 79% *cis*-1,4 structure. We will demonstrate in our succeeding paper (part 3 of this series)²³ that the mean-square end-to-end distance of the guest *cis*-PI in the natural rubber is slightly smaller than in the Θ state due to weak repulsive interactions. Probably, nonzero χ_{23} resulted in the smaller absorption ratio in the *cis*-PI/NR system than the theoretical value calculated with $\chi_{23} = 0$. We see that in the range of ϕ below ca. 60%, the experimental results agree roughly with the theory, but in the higher ϕ range the discrepancy between them increases. Obviously this is due to the increase of the effect of χ_{23} with increasing ϕ .

The networks soaked in solutions of $\phi = \text{ca. } 50\%$ and then dried contain more guest molecules than those that reached equilibrium absorption in bulk PI-02 ($\phi = 1$). Therefore, the former network should be in a nonequilibrium state and should eventually deswell. However, we could not observe elimination of the excess guest molecules from such a nonequilibrium network during the period of the experiment. At the moment, it is not clear whether the network is actually in a nonequilibrium state or it

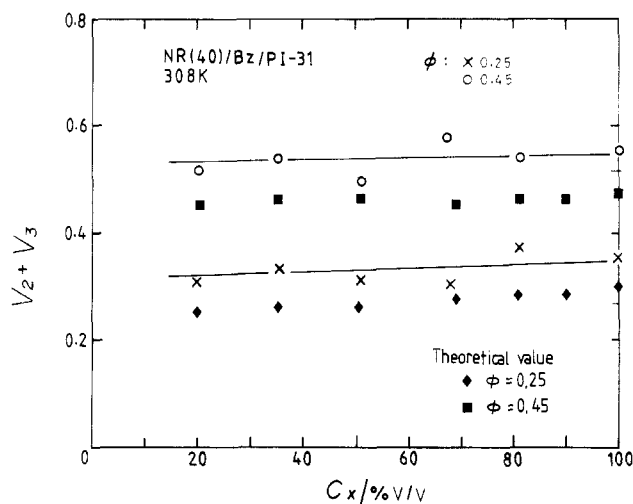


Figure 12. Cross-linking concentration C_x dependence of total concentration of polymer in solution of PI-31 in benzene. The diamond and square symbols indicate the theoretical values for ϕ .

exhibits microphase separation inside the network.

Figure 12 shows that the C_x dependence of the total polymer concentration $v_2 + v_3$ ($= 1 - v_1$) in the swollen networks. As is seen in the figure, $v_2 + v_3$ is almost independent of C_x and approximately equal to ϕ . This experimental result is in close agreement with the theory, indicating again the theory is semiquantitatively valid. It is recognized that theoretical $v_2 + v_3$ coincides approximately with ϕ in the range $\phi > 0.1$ for the model network of $M_x = 5000$ and $C_x = 0.05-1$. However, in the range $\phi < 0.05$, the total concentration in the network is no longer equal to the concentration of the outside solution.

Conclusions

From this study, we can draw the following conclusions: (1) The solution-cross-linked networks swell/absorb the solvent and guest molecules more than the bulk-cross-linked networks. The former have higher free energy than the latter. (2) Swelling and absorption ratios of the networks increase with decreasing cross-linking concentration C_x . The driving power for swelling can be assessed by $C_x^{-2/5}$. (3) The swelling and absorption behavior of the networks can be described semiquantitatively by the modified Flory-Rehner theory in which the expansion coefficient α based on the dry network in the original theory is replaced by $C_x^{1/3}\alpha$. (4) Swelling and absorption ratios of the networks decrease with increasing molecular weight of the guest molecules.

Acknowledgment. B. T. Poh thanks the Japan Society for the Promotion of Science for granting a fellowship to him to carry out this work.

Registry No. Polyisoprene, 9003-31-0.

References and Notes

- (1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
- (2) Flory, P. J.; Rehner, J., Jr. *J. Chem. Phys.* **1943**, *11*, 521.
- (3) Sakurada, I.; Nakajima, A.; Aoki, H. *J. Polym. Sci.* **1959**, *35*, 507.
- (4) Bastide, J.; Candau, S.; Leibler, L. *Macromolecules* **1981**, *14*, 719.
- (5) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979.
- (6) de Gennes, P.-G. *Macromolecules* **1986**, *19*, 1245.
- (7) Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, 505.
- (8) For example: Granick, S.; Pedersen, S.; Nelb, G. W.; Ferry, J. D.; Macosko, C. W. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1745.

- (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. Faraday 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

Beng Teik Poh,[†] Keiichiro Adachi,* and Tadao Kotaka

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. Received February 6, 1987

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 afterward 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 Gennes⁴ and Doi and Edwards⁵ 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-workers⁷⁻¹² 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 Gennes¹⁴ 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,

[†] Present address: School of Industrial Technology, Universiti Sains Malaysia, Minden, Penang, Malaysia.