

Rubber Elasticity of Poly(*n*-butyl Acrylate) Networks Formed with Multifunctional Crosslinkers

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Synopsis

The rubber elasticity characteristics of poly(*n*-butyl acrylate) networks crosslinked with tetrafunctional (EGDM and TEGDM), hexafunctional (TMPTM), and octafunctional (PETMA) vinyl crosslinkers were investigated. Both gel-sol analyses and crosslinking efficiency theories were used to evaluate the chemical crosslink contribution ν_c and the entanglement contribution ν_p to the elastically effective network chains ν_e , and the effect of the crosslink junction functionality f on the front factor g . The front factors obtained were in the range of 0.50–0.92, depending upon the network system and the counting method for ν_c . The relationship of $g = [(f - 2)/f]/\langle r^2 \rangle / \langle r^2 \rangle_0$ seems reasonable in the case of the tetrafunctional and hexafunctional networks, but deviates in the case of the octafunctional network. It is also evident that the functionality scheme for the front factor could only be valid under the postulate of a high ν_p , which increases with increasing ν_c , especially in the high ν_c region near the Gaussian limit. The average energetic contribution to the retractive force of the present systems, expressed as F_e/F , is -0.30 ± 0.1 .

INTRODUCTION

While the theory of rubber elasticity is based mainly on entropic considerations, several other effects have been shown to be important. These include the crosslink junction functionality, the ratio of the chain end-to-end distance in the network to that of the corresponding free chain, and the energetic contribution to the retractive force. This paper analyzes each of these terms using modulus-temperature data obtained from poly(*n*-butyl acrylate) networks. A list of the terms employed herein is shown in Appendix A.

The kinetic theory of rubber elasticity indicates that the equilibrium shear modulus G of a Gaussian network is given by¹⁻⁴

$$G = g\nu_eRT \quad (1)$$

where ν_e is the concentration of elastically effective network chains, R the gas constant, T the absolute temperature, and g represents the so-called "front factor," which is still in dispute concerning its physical meaning and numerical value.^{2,4-7} It has been experimentally observed, however, that G in eq. (1) frequently yields greater values of ν_e than justified by the chemical crosslink contribution, depending on the assumptions employed in the derivation.^{2,8-12} It is argued that ν_e should be the sum of the chemical crosslink contribution ν_c and the trapped physical entanglement contribution ν_p , although it is still argued whether or not the quantities should be simply additive¹³:

$$\nu_e = \nu_c + \nu_p \quad (2)$$

If the crosslinking mechanism and kinetics are well known (hence the topological structure), eq. (2) could be reasonably applied to eq. (1).^{11,14} On the other hand,

it was recently suggested that deviation from the "phantom network" theory is due to the physical constraints on the crosslink junctions imposed by surrounding chains.^{15,16}

The front factor g should be expressed as¹⁷

$$g = g' \langle r^2 \rangle / \langle r^2 \rangle_0 \quad (3)$$

where $\langle r^2 \rangle / \langle r^2 \rangle_0$ is the ratio of the mean square end-to-end distance of the polymer chains in the relaxed network to that of the same chains in the uncrosslinked state. Combining eqs. (1), (2), and (3),

$$G = g'(\nu_c + \nu_p) \frac{\langle r^2 \rangle}{\langle r^2 \rangle_0} RT \quad (4)$$

Under the assumption of no contribution from trapped entanglements, eq. (4) simply reduces to

$$G = g' \nu_c \langle r^2 \rangle / \langle r^2 \rangle_0 RT \quad (5)$$

In most of the classical theories g' is unity, while some investigators argue that $g' = 0.5$ and others suggest values in between 0.5 and 1.0. Equation (5) with $g' = 1$ coincides with the classical theory of affine deformation, and is also coincident with Flory's modified theory,^{15,16} which indicates that constraints on the junctions make the junction fluctuation nearly affine, thus making g' approach to unity in real networks.

Duiser and Stavermann⁶ and Graessley⁷ have proposed that g' depends on the crosslink junction functionality f such that $g' = (f - 2)/f$. Hence, from eq. (4),

$$G = \left(\frac{f - 2}{f} \right) \frac{\langle r^2 \rangle}{\langle r^2 \rangle_0} (\nu_c + \nu_p) RT \quad (6)$$

In order to apply eqs. (4), (5), and (6) to practical systems, it should be preceded by an exact evaluation of ν_c . It is also true, however, that the counting procedure for calculating ν_c ¹⁸⁻²¹ remains in dispute. Two theories for evaluating ν_c will be examined.

The Flory criterion¹⁸ counts ν_c , according to Langley,¹¹ in the following way:

$$\nu_c = \sum_{f=3}^{\infty} (f - 2) C_f \quad (7)$$

where C_f is the concentration of crosslink junctions connected to the gel by f paths (junction functionality). Scanlan's criterion,¹⁹ on the other hand, gives

$$\nu_c = \sum_{f=3}^{\infty} \frac{f}{2} C_f \quad (8)$$

Experimentally, several methods of evaluation are available. The so-called "gel-sol probability" approach constitutes one way to evaluate ν_c and ν_p , which is based on the concept of a crosslinking index γ . For monodisperse primary chains, γ is expressed through the following relationship¹⁸:

$$1 - W_g = e^{-\gamma W_g} \quad (9)$$

where W_g is the gel fraction. Langley¹⁴ developed a relationship for calculating

ν_c using the gel-sol data via eq. (2). For tetrafunctionally crosslinked systems, the Flory criterion gives

$$\nu_e = \nu_0 \gamma W_g T_p^{1/2} + \nu_p T_p \quad (10)$$

where $\nu_0 = \nu_c/\gamma$ and T_p is the trapping factor which is expressed as

$$T_p = \left[2 - W_g - 2W_g \left(\ln \frac{1}{1 - W_g} \right)^{-1} \right]^2 \quad (11)$$

assuming a randomly crosslinked system of monodisperse primary chains.

The Scanlan criterion, likewise, counts ν_e for tetrafunctional crosslink junction systems as

$$\nu_e = \frac{1}{2} \nu_0 \gamma (3W_g - T_p^{1/2}) T_p^{1/2} + \nu_p T_p \quad (12)$$

Extending Langley's scheme to the hexa- and octafunctional crosslink junction systems (see Appendix B), the Flory criterion gives

$$\nu_e = \nu_0 \gamma [W_g (3T_p + T_p^{1/2}) - 2T_p^{3/2}] + \nu_p T_p \quad (13)$$

for hexafunctionally crosslinked systems and

$$\nu_e = \nu_0 \gamma [W_g (5T_p + 3T_p^{1/2} + 1) T_p^{1/2} - 2T_p^{3/2} (2T_p^{1/2} + 1)] + \nu_p T_p \quad (14)$$

for octafunctionally crosslinked systems.

Again, the Scanlan criterion gives

$$\nu_e = \frac{1}{2} \nu_0 \gamma [W_g T_p^{1/2} (5T_p^{1/2} + 3) - T_p (2T_p^{1/2} + 1)] + \nu_p T_p \quad (15)$$

for hexafunctional crosslink junction systems and

$$\nu_e = \frac{1}{2} \nu_0 \gamma [W_g T_p^{1/2} (7T_p + 5T_p^{1/2} + 3) - T_p (3T_p + 2T_p^{1/2} + 1)] + \nu_p T_p \quad (16)$$

for octafunctional crosslink junction systems. Therefore, combination of the data from equilibrium rubbery modulus measurements through eq. (4) and from gel-sol studies via eqs. (9)–(16) gives rise to the information about the g and ν_p of a given network.

The crosslinking efficiency ϵ is another way to evaluate ν_c , although restricted to the networks crosslinked with tetrafunctional vinyl monomers. According to Loshaek and Fox,²² ϵ is defined as the fraction of the tetrafunctional monomer reacted at both ends, but does not yield any information about intramolecular crosslinks (cyclized loops), and can be incorporated in the present theory as $G = g\epsilon\nu_c RT$. Experimentally, the calculation of ϵ is based on density data of both monomer mixtures and bulk network materials, considering the molar volume contraction. Nevertheless, the characteristics of rubber elasticity could be evaluated by combining ϵ and eqs. (4), (5), and (6).

Another problem concerning rubber elasticity is the elastic contribution originating from internal energy effects. The statistical kinetic theory of rubber elasticity presumes that the elastic retractive force F is entirely attributable to the conformational entropy of deformation, which is not quite true in real rubbers. In fact, deviations from ideal elasticity have been observed even in small deformations. The deviations can be ascribed to the energetic contribution to the retractive force F_e , whose contribution is usually represented as the relative energy contribution F_e/F .^{23,27} Shen and Blatz^{28,29} derived an equation which is independent of strain and easily measurable experimentally:

$$\frac{F_e}{F} = 1 - \frac{d \ln G}{d \ln T} - \frac{\alpha T}{3} \quad (17)$$

where α represents the thermal expansion coefficient.

In this paper, the rubber elasticity characteristics of poly(*n*-butyl acrylate) (PnBA) networks crosslinked with multifunctional crosslinkers are evaluated in terms of front factor, crosslink junction functionality, and internal energy contribution. The crosslinkers employed are tetrafunctional [ethylene glycol dimethacrylate (EGDM) and tetraethylene glycol dimethacrylate (TEGM)], hexafunctional [trimethylol propane trimethacrylate (TMPTM)], and octafunctional [pentaerythritol tetramethacrylate (PETMA)] vinyl crosslinkers.

Shear moduli in the rubbery state and gel-sol data are mainly used for the analysis. Also used are the crosslinking efficiency scheme and F_e/F data to supplement the analysis and to help evaluate the validity of the analysis.

EXPERIMENTAL

Materials and Synthesis

The *n*-butyl acrylate (nBA, Polysciences) monomer and EGDM (Polysciences) were washed with a 5% NaOH solution and deionized water, and then dried over CaSO₄ (Drierite). The dried monomer and EGDM were distilled under reduced pressure. The crosslinkers TEGDM (Polysciences), TMPTM (Polysciences), PETMA (Monomer-Polymer), and benzoin (Eastman) as photosensitizer were used as received.

Photopolymerization was carried out with UV lights. A solution of *n*-butyl acrylate monomer, containing crosslinker and benzoin, was purged for 2 min by bubbling N₂ gas and then transferred into glass plate molds sealed with a Viton O-ring cord. The concentration of benzoin for all materials was 0.074 g/100 mL of *n*-butyl acrylate. Photopolymerization was continued for 100 h at room temperature, followed by thermal further polymerized at 100°C for another 24 h. Finally, the networks were vacuum-dried at 100°C for 24 h to remove the unreacted monomers (less than 0.5% in weight). In the case of PnBA (PETMA) network formation, the crosslinker was not completely soluble in the monomer even after 24 h in the monomer solution. However, at low concentrations of PETMA, the polymerizing mass became clear right after the photopolymerization started. The thickness of the mold cavity was less than 0.25 in., to control shrinkage irregularities and thermal problems.

Density and Gel Content Measurement

Density measurements were made with the use of a density gradient column for network materials and a pycnometer for monomer mixtures. Soxhlet extractors were used for sol extractions, by refluxing the THF. Each network was supported by a 100 mesh nickel screen thimble. The gel fraction was calculated from the limiting sample weight after at least 240 h of extraction or until no further weight reduction was observed. After extraction, each sample was dried at 90°C and 10 mm Hg for at least 150 h or was observed before weighing.

Shear Modulus

The shear modulus-temperature measurements were made on the samples with the use of a modified Gehman torsional tester.³⁰

RESULTS

For each of the four crosslinkers studied in this paper, a number of networks were prepared with the crosslinker concentration as the variable. Shear modulus data was obtained on each sample between 90°C and 160°C.

Figures 1 and 2 show the $\log 3G(10)$ -temperature behavior of PnBA(TEGDM) and PnBA(PETMA) networks, respectively, where $3G(10)$ represents three times the shear modulus at 10 s. While plots of $3G(10)$ vs. temperature were all linear, $\log 3G(10)$ plots are shown because of the wide distribution of moduli obtained. Other data were very similar in appearance.

Some of the lower crosslinker concentration data is not reported, however, because the incomplete network formed was thought to suggest incorrect conclusions in the following analysis.

Figure 3 illustrates the rubbery modulus-crosslinker concentration behavior of PnBA networks with multifunctional crosslinkers. One molar basis, the higher the crosslinker functionality, the higher the absolute value of the rubbery modulus.

Information about γ , W_g , and T_p are usually evaluated from the gelation mechanism of the system and its primary chain molecular weight distribution. All of the relationships used in this study are actually based on systems of randomly crosslinked monodisperse primary chains.

A required condition for the "sol-gel" analysis is that the network system have a considerable amount of sol fraction.

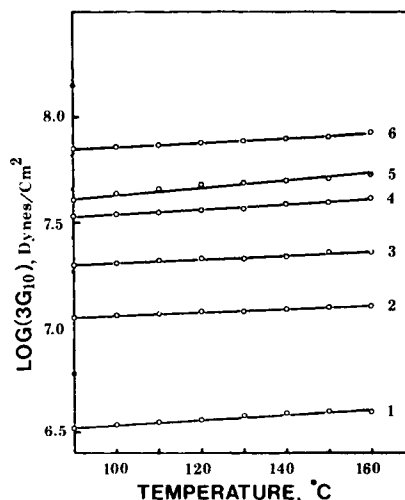


Fig. 1. Rubbery modulus, $3G(10)$, vs. temperature for PnBA(TEGDM) networks. Crosslinker concentration: Sample 1: 0.212×10^4 mol/cm³; Sample 2: 0.840×10^4 mol/cm³; Sample 3: 1.641×10^4 mol/cm³; Sample 4: 3.140×10^4 mol/cm³; Sample 5: 4.523×10^4 mol/cm³; Sample 6: 5.814×10^4 mol/cm³.

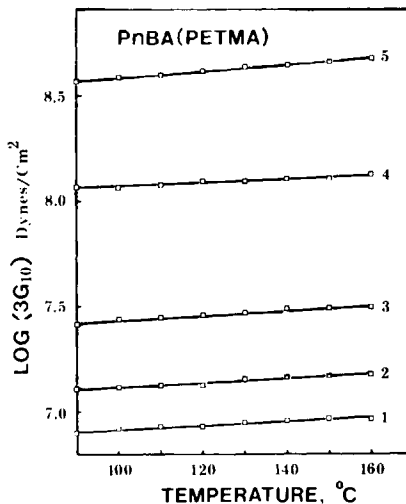


Fig. 2. Rubbery modulus, $3G(10)$, vs. temperature for PnBA(PETMA) networks. Crosslinker concentration: Sample 1: 0.420×10^4 mol/cm³; Sample 2: 0.830×10^4 mol/cm³; Sample 3: 1.623×10^4 mol/cm³; Sample 4: 3.095×10^4 mol/cm³; Sample 5: 4.448×10^4 mol/cm³.

Analysis

It is generally recognized that networks with G greater than 10^8 dynes/cm² no longer obey Gaussian statistics. As seen in Figure 8, the experimental values of $G(10)/RT$ increase rapidly with further increases in ν_c . Figure 3 indicates that the Gaussian upper limit corresponds to $c = 6.15 \times 10^{-4}$ mol/cm³ for PnBA(TMPTM) network and $c = 4.10 \times 10^{-4}$ mol/cm³ for PnBA(PETMA) network, respectively. All of the PnBA(EGDM) and PnBA(TEGDM) networks employed in this study (up to $\nu_c = 9.0 \times 10^{-4}$ mol/cm³) are within the Gaussian limit. It is also observed that the rubbery modulus increases with increasing c in the order of crosslinker functionality.

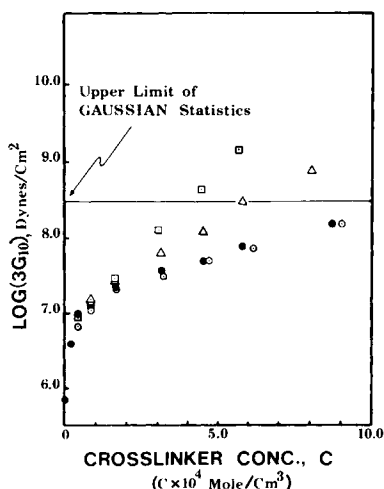


Fig. 3. Rubbery modulus $3G(10)$ (at 120°C) vs. crosslinker concentration C of PnBA networks crosslinked with various crosslinkers. Limit of Gaussian network is based on $G = 10^8$ dynes/cm². (○) PnBA(EGDM); (●) PnBA(TEGDM); (Δ) PnBA(TMPTM); (□) PnBA(PETMA).

Combining eqs. (1), (4), and (9)–(16) yields the following relationships for g and ν_p . For tetrafunctional networks,

$$(G/RT)/T_p = g\nu_0\gamma W_g T_p^{-1/2} + \nu_p \quad (18)$$

by the Flory criterion and

$$(G/RT)/T_p = (g\nu_0\gamma/2)(3W_g - T_p^{1/2})T_p^{-1/2} + \nu_p \quad (19)$$

by the Scanlan criterion.

For hexafunctional networks,

$$(G/RT)/T_p = g\nu_0\gamma[W_g(3T_p^{1/2} + 1) - 2T_p]T_p^{-1/2} + \nu_p \quad (20)$$

by the Flory criterion and

$$(G/RT)/T_p = (g\nu_0\gamma/2)[W_g(5T_p^{1/2} + 3)T_p^{-1/2} - 2T_p - 1] + \nu_p \quad (21)$$

by the Scanlan criterion.

For octafunctional networks,

$$(G/RT)T_p = g\nu_0\gamma[W_g(5T_p + 3T_p^{1/2} + 1)T_p^{-1/2} - 2T_p - T_p^{1/2}] + \nu_p \quad (22)$$

by the Flory criterion and

$$(G/RT)/T_p = (g\nu_0\gamma/2)[W_g(7T_p + 5T_p^{1/2} + 3)T_p^{-1/2} - 3T_p - 2T_p^{1/2} - 1] + \nu_p \quad (23)$$

by the Scanlan criterion.

Results for eqs. (18) and (19) are plotted in Figures 4 and 5; eqs. (20) and (21) in Figure 6; and eqs. (22) and (23) in Figure 7. The quantity g was taken from the slope and the trapped entanglements contribution ν_p from the intercept. Values for g and ν_p , from Figures 4–7, are shown in Table I. In the following, $\langle r^2 \rangle / \langle r^2 \rangle_0$ is assumed to be unity. Both PnBA(EGDM) and PnBA(TEGDM) networks display front factor values between 0.5 and 1.0, although the latter is slightly higher, possibly due to the longer chain between two vinyl groups.

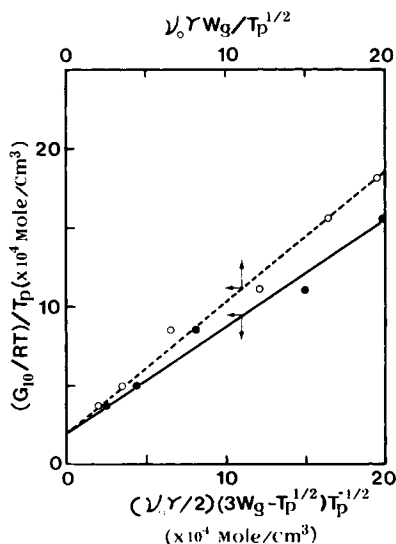


Fig. 4. Plot from eqs. (18) and (19) of PnBA(EGDM) networks to obtain g and ν_p . (O) Flory; (●) Scanlan.

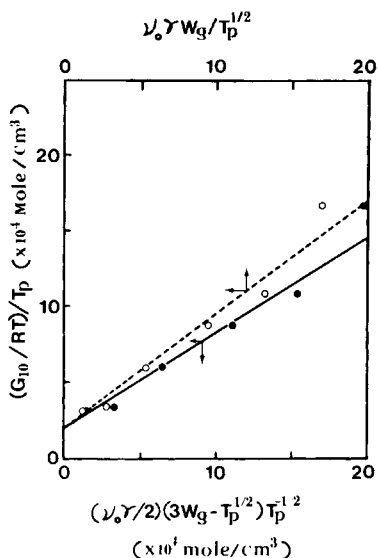


Fig. 5. Plot of eqs. (18) and (19) of PnBA(TEGDM) networks to obtain g and ν_p . (○) Flory; (●) Scanlan.

The front factor value of PnBA(TMPTM) is higher than those of PnBA(EGDM) and PnBA(TEGDM), which is consistent with the relationship $g = [(f - 2)/f] \langle r^2 \rangle / \langle r^2 \rangle_0$, see eq. (6). However, in the case of PnBA(PETMA) network, the front factor value is very low, close to 0.5, which is contradictory to theory.

This unexpectedly low front factor value for the PnBA(PETMA) network might be due to a low crosslinking efficiency, but the exact reason is not clear. It should be noted again at this point that the PETMA (in powder form) is not

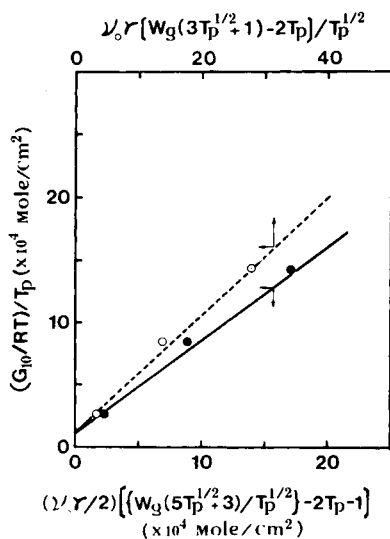


Fig. 6. Plot from eqs. (20) and (21) of PnBA(TMPTM) networks to obtain g and ν_p . (○) Flory; (●) Scanlan.

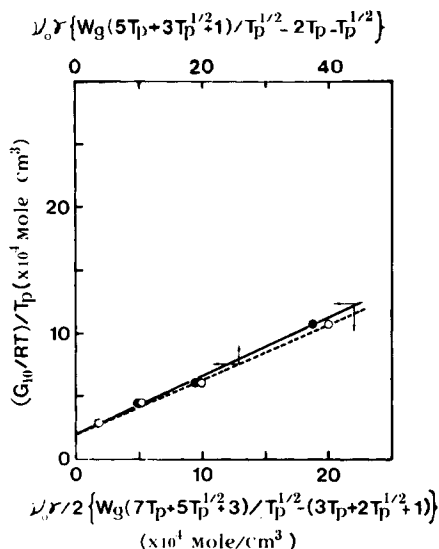


Fig. 7. Plot from eqs. (22) and (23) of PnBA(PETMA) network to obtain g and ν_p . (○) Flory; (●) Scanlan.

completely soluble upon mixing, but did dissolve once the polymerization proceeded to some extent (at a very early stage). Typically, the material became clear within 30 min. Since the gel point for such polymerizations is of the order of 2–6 h, local high concentrations of the crosslinker were deemed minimal, but could explain the discrepancy. Also, for this crosslinker, the probability of incomplete reaction is highest because of physical restraints. It should be noted that the lines for the Scanlan and Flory theories are inverted in Figure 7 relative to Figures 4, 5, and 6.

The crosslinking efficiency scheme can also be used to evaluate g and ν_p in a rudimentary way. The relationships of ν_c vs. $G/RT = \nu_e$ are plotted in Figure 8. The crosslinking reaction is assumed to be stoichiometrically complete. As pointed out earlier, the Loshaek and Fox ϵ calculated on some samples (Table II) help estimate the cyclized loop fraction such that the true crosslinking efficiency should be much lower.^{33,34} If the Loshaek and Fox ϵ is about 75–80% as indicated in Table II, irrespective of network species and crosslinker concentration (however, at $c = 0.5 \times 10^4$ mol/cm³ or below, ϵ approaches 100%), the true ϵ should be around 60%, considering the portion of loop formation reported in literature,^{33,34} which is designated as dotted line in Figure 8. In the above, c represents the concentration of crosslinker added to the network. This analysis was not carried to the hexa- and octafunctional crosslinked materials.

TABLE I
Front Factor g and Entanglement Contribution ν_p , Obtained by Gel-Sol Analysis

PnBA networks	Front factor g			ν_p ($\times 10^4$ mol/cm ³)
	Flory criterion	Scanlan criterion	$(f-2)/f$	
PnBA(EGDM)	0.78	0.64	0.50	2.0
PnBA(TEGDM)	0.80	0.71	0.50	1.9
PnBA(TMPTM)	0.92	0.76	0.67	1.7
PnBA(PETMA)	0.50	0.55	0.75	1.7

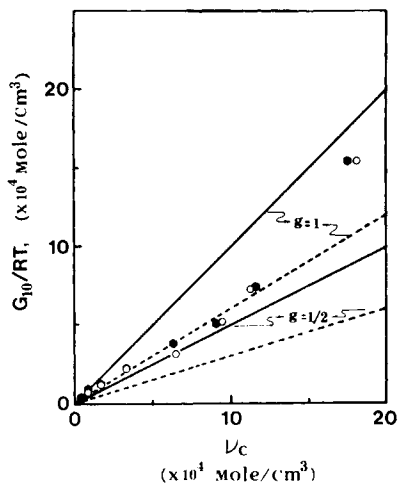


Fig. 8. Stoichiometric ν_c (according to eqs. (7) and (8)) vs. G/RT of PnBA(EGDM) and PnBA(TEGDM) networks to evaluate g and ν_p from the standpoint of crosslinking efficiency, ϵ . (O) PnBA(EGDM); (●) PnBA(TEGDM).

The results of F_e/F calculated by eq. (17) are represented in Table III. Values of F_e/F , though somewhat variable, do not indicate any specific trend depending upon either the crosslinker functionality or the crosslinker concentration. An overall average of $F_e/F = -0.30 \pm 0.1$ is obtained at 120°C.

It is interesting to compare the present F_e/F values to the results of Cirlin and Shen.³⁵ For the PnBA system, they reported -0.68 at 120°C and -0.35 at 30°C from uniaxial elongation experiments³⁵ and -0.36 at 30°C from simple shear measurements.³⁶

Theoretically, the front factor is related to the internal energy effect, hence to F_e/F .³⁷ The Gaussian theory of rubber elasticity, in fact, presumes the free energy additivity principle, which indicates that only intrachain interactions are affected by deformation. Hence the energetic effects in rubber elasticity must come from only the intrachain interactions of the network chains. An explicit representation of this relationship is expressed as³⁸

$$\frac{F_e}{F} = \frac{d \ln \langle r^2 \rangle_0}{d \ln T} = \frac{\epsilon'}{R} \quad (24)$$

where ϵ' represents the transgauche energy difference, or similar effects in rotating the chain. Recalling that the front factor is $g = g' \langle r^2 \rangle / \langle r^2 \rangle_0$, it is evident that F_e/F could be implicitly related to the front factor. However, there are few explicit expressions between F_e/F and $\langle r^2 \rangle / \langle r^2 \rangle_0$.

DISCUSSION

The crosslinking mechanism of chain-type copolymerization is so complex that it is difficult to envisage the topological structure of the networks formed. Crosslinking processes between vinyl monomers and divinyl crosslinkers have been extensively studied,^{22,30-34,39-47} while those between vinyl monomers and crosslinkers containing three or more vinyls have been rarely investigated. The actual crosslinking reactions by copolymerization of vinyl monomer and multi-

TABLE II
Specification and Experimental Data of PnBA Networks Crosslinked with Tetrafunctional, Hexafunctional, and Octafunctional Crosslinkers

Networks	$C' \times 10^4$ ^a (mol/cm ³)	$C \times 10^4$ ^b (mol/cm ³)	Density @ 25° C (g/cm ³)	Gel content W_g (%)	Crosslinking ^a efficiency (ϵ)	G @ 120°C ($\times 10^7$ dyne/cm ²)
PnBA(EGDM)	0.776	0.844	1.044	97.0		0.366
	1.530	1.662	1.046	97.6		0.696
	2.974	3.233	1.052	98.1		1.007
	4.339	4.732	1.059	98.9		1.671
	5.632	6.181	1.071	99.5	0.75	2.360
	8.022	9.061	1.111	99.8	0.78	5.045
PnBA(TEGDM)	0.195	0.212	1.048	92.0		0.121
	0.769	0.840	1.052	99.3		0.401
	1.503	1.641	1.056	99.3		0.713
	2.874	3.140	1.066	99.7		1.239
	4.130	4.523	1.070	99.9	0.72	1.640
	5.285	5.814	1.089	99.8	0.77	2.529
	7.955	8.750	1.090	99.9	0.75	5.045
PnBA(TMPTM)	2.864	3.122	1.062	95.0		2.103
	4.109	4.503	1.075	98.0		4.008
	5.248	5.804	1.092	98.2		10.067
	7.264	8.054	1.110	98.5		25.287
PnBA(PETMA)	0.391	0.420	1.039	96.8		0.290
	0.776	0.830	1.045	97.5		0.505
	1.530	1.623	1.054	98.2		0.984
	2.974	3.095	1.075	98.5		4.197
	4.341 ^c	4.448	1.094	98.9		14.220
	5.631 ^c	5.675	1.110	99.0		47.087

^a Crosslinker concentration in monomer mixture at 120°C.

^b Crosslinker concentration in bulk network at 120°C, corrected from C' by considering (coefficient of volume expansion) = $6.9 \times 10^{-4} \text{ m}^3/\text{°C}$.³⁹

^c Specimens were so brittle that G values were obtained by discontinuous measurements.

^d At low level of crosslinker concentration, the Loshaek and Fox method was not applicable.

vinyl crosslinkers involve both intermolecular and intramolecular reactions (loop formation by cyclization). Pendant vinyl groups also remain to a greater or lesser extent.^{22,31-34,39-47} While most loops and dangling chains are recognized not to be elastically effective, some special loops are argued to be elastically effective.^{48,49} In the case of networks made of vinyl and divinyl monomers, a junction point with a dangling vinyl end does not provide an elastically effective network chain, and it is rather simple to classify the network chains into elastically effective ones, ineffective loops, and pendant chains, respectively.

Some experimental methods for characterizing the crosslinking efficiency before and at gel point have been proposed.^{33,43,45,46} However, once the reaction goes well past the gel point, it becomes quite complex experimentally to determine ϵ . One of the few methods available is that of Loshaek and Fox.²² However, this method is unable to differentiate the network chains into intermolecular and intramolecular species or to determine ϵ at low levels of divinyl crosslinkers.⁴¹ Hence, ϵ values shown in Table II should be taken as an indication of the fraction of double bonds consumed in the reaction.

As indicated earlier, the rubbery shear modulus in eq. (1) and related equations is an equilibrium modulus at low deformations. The 10-s moduli are not equi-

TABLE III
 Thermoelastic Data of PnBA Networks^a

PnBA networks	$C \times 10^4$ (mol/cm ³)	F_e/F (120°C)	
		From eq. (17) ^b	Average
PnBA(EGDM)	1.662	-0.49	
	3.233	-0.34	
	4.732	-0.52	-0.39
	6.181	-0.25	
	9.061	-0.34	
PnBA(TEGDM)	0.212	-0.27	
	1.641	-0.09	
	3.140	-0.52	-0.28
	4.523	-0.46	
	5.814	-0.18	
PnBA(TMPTM)	8.750	-0.15	
	3.122	-0.26	
	4.503	-0.15	-0.20
PnBA(PETMA)	5.804	-0.20	
	0.420	-0.52	
	0.830	-0.21	
	1.623	-0.29	-0.33
	3.095	-0.29	
	4.448	-0.34	

^a Reference temperature: 120°C.

^b $\alpha = 6.9 \times 10^{-4}/^\circ\text{C}$.

librium values in a strict sense but could be regarded as close to equilibrium, considering the temperature of measurement (120°) in terms of the time-temperature superposition principle.⁵⁰

While the reactivity ratios of butyl acrylate with the methacrylic crosslinkers employed are not known, Brandrup and Immergut⁵¹ list butyl acrylate (M_1) and methyl methacrylate (M_2) as having $r_1 = 0.20$ – 0.37 and $r_2 = 1.74$ – 1.8 . This indicates that the crosslinker would tend to enter the network earlier than random. However, the second, third, and fourth vinyls have reduced reactivities because of steric effects, counterbalancing the above, but to unknown extents.

CONCLUSIONS

An accurate determination of ν_c is indispensable in evaluating the front factor as well as the entanglements contribution ν_p . The gel–sol analysis as well as the crosslinking efficiency concept was used to attain this objective. Both schemes, however, turned out to have some limitations in being applied to our systems: The former requires a relatively high sol content and knowledge about the primary chain molecular weight distribution, and the latter requires the true crosslinking efficiency in terms of a distribution function. In fact, these limitations can be overcome only when the network topological structure is correctly understood.

By making appropriate assumptions, the gel–sol analysis gave rise to front factor values of 0.65–0.8 for the PnBA(EGDM) and PnBA(TEgDM) tetrafunctional networks; 0.76–0.92 for the hexafunctional PnBA(TMPTM) network; and 0.50–0.55 for the octafunctional PnBA (PETMA) network. As such, the front factor dependency upon the crosslink junction functionality, $g = [(f - 2)/f]/$

$\langle r^2 \rangle / \langle r^2 \rangle_0$, holds better in the cases of tetrafunctional networks than in the case of the octafunctional PnBA(PETMA), see Table I. The discrepancy in this last case could be explained in terms of the low crosslinking efficiency ϵ , or in terms of failure of the theories themselves. Unfortunately, the true ϵ could not be determined, at present, either theoretically or experimentally. However, it seems probable that ϵ decreases as the functionality of the crosslinker increases.

In all of the cases, the postulates of Duiser–Staverman and Graessley are reasonable only under the presumption of a significant contribution from ν_p .

A particular point of interest is that the same rubbery modulus-temperature data can yield, on the one hand, values for front factor in terms of the crosslink junction functionality and on the other hand the energetic contribution to the retractive stress F_e/F . To extract both pieces of information from the same data appears not to be contradictory, yet the literature shows analysis for only one or the other from individual papers.

It is unfortunate that F_e/F *per se* cannot be made to yield values of $\langle r^2 \rangle / \langle r^2 \rangle_0$, the remaining term in the front factor. In all of the above experiments, $\langle r^2 \rangle / \langle r^2 \rangle_0$, was assumed to be unity.

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APPENDIX A: NOMENCLATURE

C	crosslinker concentration in the bulk network at 120°C (mol/cm ³)
C'	crosslinker concentration as added to the monomer mixture at 120°C (mol/cm ³)
C_f	concentration of crosslink junctions connected to the gel by f paths (junction functionality) (mol/cm ³)
EGDM	ethylene glycol dimethylacrylate
F	elastic force (retractive) (kg/cm ²)
F_e	elastic stress contributed by the energy effect
f	crosslink junction functionality
G	equilibrium rubbery shear modulus (kg/cm ²)
g	front factor, $g = g' \langle r^2 \rangle / \langle r^2 \rangle_0$
g'	front factor, $g' = (f - 2)/f$
P	probability that a f -functional junction is anchored to the network
P_i	probability that a random crosslink junction unit in the system is connected separately by i strand(s)
PETMA	pentaerythritol tetramethacrylate
PnBA	poly(n -butyl acrylate)
R	gas constant (cal°K ⁻¹ ·mol ⁻¹)
$\langle r^2 \rangle$	mean square end-to-end distance of the polymer chains in the undeformed network (Å)
$\langle r^2 \rangle_0$	mean square end-to-end distance of the equivalent free chains (Å)
T	absolute temperature (°K)
T_p	trapping factor as defined in eq. (11)
TEGDM	tetraethylene glycol dimethacrylate
TMPTM	tetramethylol propane trimethacrylate
W_g	weight fraction of gel content
α	thermal expansion coefficient (°K ⁻¹)
γ	crosslinking index as defined in eq. (9)
ϵ	Crosslinking efficiency
ϵ'	Intrachain rotational energy
ν_c	chemical crosslink contribution to the elastically effective network chains (mol/cm ³)

ν_e	elastically effective network chains (mol/cm ³)
ν_0	$\nu_0 \equiv \nu_c/\gamma$ (mol/cm ³)
ν_p	entanglement contribution to the elastically effective network chains (mol/cm ³)

APPENDIX B

Recall eqs. (7) and (8) as analyzed by Langley¹¹ according to Flory criterion:

$$\nu_c = \sum_{f=3}^{\infty} (f-2)C_f \quad (7)$$

and according to Scanlan criterion,

$$\nu_e = \sum_{f=3}^{\infty} \frac{f}{2} C_f. \quad (8)$$

Also following Langley's definition,^{11,14} note

$$T_p^{1/2} = p_2 \quad (A-1)$$

and

$$W_g = p_1 + p_2 \quad (A-2)$$

where p_1 and p_2 are the probability that a random crosslink junction unit in the system is connected separately to the network by one strand or two strands, respectively. Hence,

$$C_f = CP \quad (A-3)$$

where C is the total crosslink junction (or crosslinker) concentration added and P is the probability of the way that an f -functional junction can be anchored to the network.

Then for C_3

$$P = p_1 p_2 + p_2 p_1 \quad (A-4)$$

and, for C_4 ,

$$P = p_2^2 \quad (A-5)$$

Thus Langley got ν_c for the tetrafunctional crosslink junction,¹¹ as illustrated in eqs. (A-1)–(A-5).

Equations for higher functionality are lacking in the literature. Extending the above analysis to functionalities higher than four, i.e.,

for C_5 ,

$$P = p_1 p_2^2 + p_2^2 p_1 \quad (A-6)$$

for C_6 ,

$$P = p_2^3 \quad (A-7)$$

for C_7 ,

$$P = p_1 p_2^3 + p_2^3 p_1 \quad (A-8)$$

for C_8 ,

$$P = p_2^4 \quad (A-9)$$

Combining the equations above, and assuming monodisperse primary chains such that $C = \frac{1}{2} \nu_0 \gamma$, eqs. (10) and (11) (ν_c) are obtained as follows.

(1) In the case of

(i) Flory criterion [eq. (10)]:

$$\begin{aligned} \nu_c &= C_3 + 2C_4 \\ \nu_c &= \frac{1}{2} \nu_0 \gamma (p_1 p_2 + p_2 p_1 + 2p_2^2) \\ \nu_c &= \nu_0 \gamma W_g T_p^{1/2} \end{aligned} \quad (A-10)$$

(ii) Scanlan criterion [eq. (11)]:

$$\begin{aligned}\nu_c &= 1.5C_3 + 2C_4 \\ \nu_c &= \frac{1}{2} \nu_0 \gamma [1.5(p_1 p_2 + p_2 p_1) + 2p_2^2] \\ \nu_c &= \frac{1}{2} \nu_0 \gamma (3W_g - T_p^{1/2}) T_p^{1/2}\end{aligned}\quad (\text{A-11})$$

Equations (A-10) and (A-11) are Langley's result given in eqs. (10) and (12), respectively.

(2) In the case of $f = 6$

(i) Flory criterion:

$$\nu_c = C_3 + 2C_4 + 3C_5 + 4C_6$$

then

$$C_3 + 2C_4 = \nu_0 \gamma W_g T_p^{1/2} \quad (\text{A-10})$$

and

$$\begin{aligned}-3C_5 + 4C_6 &= 3(p_1 p_2^2 + p_2^2 p_1) + 4p_2^3 \\ &= 6p_2^2 p_1 + 4p_2^3 \\ &= (6W_g T_p - 2T_p^{3/2}) \nu_0 \gamma / 2\end{aligned}$$

Therefore

$$\nu_c = \nu_0 \gamma [W_g (3T_p + T_p^{1/2}) - T_p^{3/2}] \quad (\text{A-12})$$

which is depicted in eq. (13).

(iii) Scanlan criterion:

$$\nu_c = 1.5C_3 + 2C_4 + 2.5C_5 + 3C_6;$$

then

$$1.5C_3 + 2C_4 = \frac{1}{2} \nu_0 \gamma (3W_g - T_p^{1/2}) T_p^{1/2}$$

and

$$\begin{aligned}2.5C_5 + 3C_6 &= 2.5(p_1 p_2^2 + p_2^2 p_1) + 3p_2^3 \\ &= \frac{1}{2} \nu_0 \gamma (5W_g T_p - 2T_p^{3/2})\end{aligned}$$

Therefore,

$$\nu_c = \frac{1}{2} \nu_0 \gamma [W_g T_p^{1/2} + 3] - T_p (2T_p^{1/2} + 1) \quad (\text{A-13})$$

which is shown in eq. (15).

(3) In the case of $f = 8$

(i) Flory criterion:

$$\nu_c = C_3 + 2C_4 + 3C_5 + 4C_6 + 5C_7 + 6C_8$$

then

$$C_3 + 2C_4 + 3C_5 + 4C_6 = \nu_0 \gamma [W_g (3T_p + T_p^{1/2}) - T_p^{3/2}] \quad (\text{A-14})$$

and

$$\begin{aligned}5C_7 + 6C_8 &= 5(p_1 p_2^3 + p_2^3 p_1) + 6p_2^4 \\ &= \nu_0 \gamma (5W_g T_p^{3/2} - 2T_p^2)\end{aligned}$$

Therefore,

$$\nu_c = \nu_0 \gamma [W_g T_p^{1/2} (5T_p + 3T_p^{1/2} + 1) - T_p^{3/2} (1 + 2T_p^{1/2})] \quad (\text{A-15})$$

which is shown in eq. (14).

(ii) Scanlan criterion:

$$\nu_c = 1.5C_3 + 2C_4 + 2.5C_5 + 3C_6 + 3.5C_7 + 4C_8$$

then

$$1.5C_3 + 2C_4 + 2.5C_5 + 3C_6 = \nu_c$$

in eq. (A-13) and

$$3.5C_7 + 4C_8 = 3.5(p_1p_2^3 + p_2^3p_1) + 4p_2^4 \\ = \frac{1}{2} \nu_0 \gamma [7T_p^{3/2} (W_g - T_p^{1/2}) + 4T_p^2]$$

Therefore

$$\nu_c = \frac{1}{2} \nu_0 \gamma [W_g T_p^{1/2} (7T_p + 5T_p^{1/2} + 3) - T_p (3T_p + 2T_p^{1/2} + 1)] \quad (\text{A-16})$$

which is given in eq. (16).

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