Conclusions

We have demonstrated the constitutiveness, in the narrower sense, of the 2NW potential. We have shown further that it represents data on networks of varying cross-link densities adequately, with a G_N that is sensibly independent of the degree of cross-linking.

We have also examined the stress–strain properties of swollen networks. When the degree of swelling is not too high, parameters obtained from the dry network by the 2NW potential adequately describe the stress–strain behavior of swollen networks. This implies that, when a network is swollen, the topological environment around the network chains is not altered. The effect of the neighboring chains on a given network chain is diminished due to dilution only and is not changed in character. This observation casts doubt on the existence of trapped entanglements because, once swollen, their nature as well as their concentration would change.

References and Notes

(1) Eringen, A. C. "Mechanics of Continuous Media"; Wiley: New York, 1967; p 142.
(2) Flory, P. J. "Principles of Polymer Chemistry", Cornell University Press: Ithaca, NY 1953.
(3) James, H. M.; Guth, E. J. *J. Chem. Phys.* **1943**, *11*, 455.
(4) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(5) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(6) Rivlin, R. S. *Philos. Trans. R. Soc. London, Ser. A* **1948**, *240*, 459.
(7) Ariano, R. *Rend., Ist. Lomb. Sci.* **1930**, (2), *63*, 740.
(8) Mooney, M. *J. Appl. Phys.* **1940**, *10*, 485.
(9) Carmichael, A. J.; Holdaway, H. W. *J. Appl. Phys.* **1961**, *32*, 159.
(10) Mooney, M. *J. Appl. Phys.* **1940**, *11*, 582.
(11) Valanis, K. C.; Landel, R. F. *J. Appl. Phys.* **1967**, *38*, 2997.
(12) Kawabata, S.; Kawai, H. *Adv. Polym. Sci.* **1977**, *24*, 89.
(13) Seth, B. R. In "Second Order Effects in Elasticity, Plasticity, and Fluid Dynamics"; Reiner, M., Abir, D., Eds.; Macmillan: New York, 1973; p 162.
(14) Blatz, P.; Sharda, S.; Tschoegl, N. W. *Trans. Soc. Rheol.* **1974**, *18*, 145.
(15) Ogden, R. W. *Proc. R. Soc. London, Ser. A* **1975**, A*326*, 485.
(16) Rivlin, R. S.; Sawyers, K. N. *Trans. Soc. Rheol.* **1976**, *20*, 545.
(17) Tschoegl, N. W. *Polymer* **1979**, *20*, 1365.
(18) Gurer, C.; Tschoegl, N. W., to be submitted to *J. Polym. Sci, Polym. Phys. Ed.*
(19) Kawabata, S.; Matsuda, M.; Tei, K.; Kawai, H. *Macromolecules* **1981**, *14*, 154.
(20) Obata, Y.; Kawabata, S.; Kawai, H. *J. Polym. Sci. Part A-2*, **1970**, *8*, 903.
(21) Lorenz, O.; Parks, C. R. *J. Polym. Sci.* **1961**, *50*, 299.
(22) Allen, G.; Kirkham, M. J.; Padget, J.; Price, C. *Trans. Faraday Soc.* **1971**, *67*, 1278.
(23) Flory, P. J.; Tatara, Y. J. *J. Polym. Sci. Polym. Phys. Ed.* **1975**, *13*, 683.
(24) Yu, C. U.; Mark, J. E. *Macromolecules* **1974**, *7*, 229.
(25) Erman, B.; Flory, P. J. *Macromolecules* **1982**, *15*, 806.

Behavior of Elastomer Networks in Moderately Large Deformations. 2. Determination of the Parameters of the Elastic Potential from Measurements in Small Deformations

Cigdem Gurer and N. W. Tschoegl*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125.

Received March 8, 1984

ABSTRACT: The proposed elastic potential is completely determined by two moduli, G_X and G_N. Their sum is the equilibrium modulus, G, which can be obtained from stress relaxation measurements on the cross-linked material, in the linear region. It is shown that G_N is proportional to $G_N{}^0$, the plateau modulus of a high molecular weight un-cross-linked sample of the same polymer. The proportionality constant appears to be independent of the cross-link density and of the nature of the polymer. Its best current estimate is 0.354.

Introduction

In two previous communications,[1,2] we proposed an elastic potential of the form

$$W = \frac{G_X}{2}(\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3) + \frac{2G_N}{m^2}(\lambda_1{}^m + \lambda_2{}^m + \lambda_3{}^m - 3) \tag{1}$$

This potential was shown to be highly successful in describing arbitrary deformations (general biaxial tension) of rubberlike materials, if the deformations are moderately large, i.e., if they are restricted to the region below the upswing in a plot of the stress vs. the largest principal stretch ratio.

The potential contains three material parameters. Of these, the strain parameter m was originally left to be determined by experiment. Elsewhere,[2] however, we presented arguments which led to the adoption of a "universal" value of 0.34 for m. Of the remaining two parameters, G_X and G_N, the first represents the modulus ascribed to the presence of chemical cross-links in the network. The second expresses the contribution arising from topological constraints. The two moduli can be obtained from stress–strain experiments in simple tension for which eq 1 yields

$$\sigma_M = G_X + G_N\varphi_m(\lambda) \tag{2}$$

where

$$\sigma_M = \frac{\bar{\sigma}}{\lambda^2 - \lambda^{-1}} \tag{3}$$

$$\varphi_m(\lambda) = \frac{2(\lambda^m - \lambda^{-m/2})}{m(\lambda^2 - \lambda^{-2})} \qquad m = 0.34 \tag{4}$$

In these equations λ is the stretch ratio and $\bar{\sigma}$ is the true stress in the direction of the stretch. The two moduli are linked by the additivity relation

$$G_X + G_N = G \tag{5}$$

in which G is the shear modulus of the material. If any two of the moduli G, G_X, and G_N are known, the third can be obtained by using eq 5.

Table I
$\bar{G}_N$ and G_N^0 for Different Rubbers

rubber	$\bar{G}_N$, MPa	SD	N	G_N^0, MPa	ref
PEA	0.0612	0.0165	5	0.160	5
PDMS	0.0764	0.0241	11	0.119	6
IIR	0.108	0.0143	3	0.288	7
NR	0.185	0.0513	37	0.575	6, 8
SBR	0.244	0.0191	3	0.776	1
PBD	0.438	0.135	11	1.148	6, 9

We now examine the possibility of determining the parameters of the elastic potential for moderately large deformations of rubberlike materials from measurements in small (theoretically infinitesimal) deformations. Stress relaxation measurements in such deformations on the cross-linked polymer yield the (equilibrium) shear modulus, G. We have found that G_N is proportional to the plateau modulus, G_N^0, of a high molecular weight precursor of the network, i.e., that

$$G_N = \xi G_N^0 \tag{6}$$

G_N^0 can be obtained from stress relaxation measurements in small deformations on the un-cross-linked polymer. Thus, if eq 6 is valid, and ξ is known, G_X and G_N can both be obtained from measurements in small deformations.

Results

We have tested the hypothesis contained in eq 6 on several materials for which the necessary information could be found in the literature. These materials were butyl rubber (IIR), natural rubber (NR), styrene–butadiene rubber (SBR), cross-linked *cis*-1,4-polybutadiene (PBD), poly(ethyl acrylate) (PEA), and poly(dimethylsiloxane) (PDMS). The values of G_N^0 for these polymers were obtained from $J_N^0 = 1/G_N^0$ as given by Ferry,[3] except for PEA, which was taken from Janacek[4] et al. The values are listed in Table I, together with estimates of $\bar{G}_N$ which were secured in the following manner. For each material, values of G_X and G_N were obtained for several cross-link densities. If our hypothesis is correct, then G_N is independent of the latter. Hence, the values of G_N were averaged. These averages are shown in Table I as $\bar{G}_N$, together with their standard deviations (SD) and the number of observations on which the latter is based (N). For SBR we obtained G_X and G_N from eq 2 using our own data. For the other materials we used published values of the constants $2C_1$ and $2C_2$ of the Mooney–Rivlin equation

$$\sigma_M = 2C_1 + 2C_2/\lambda \tag{7}$$

References are listed in Table I. From ref 6, we selected only those sets which represent variations in cross-link density.

To obtain G_X and G_N we first calculated pairs of values of σ_M and $1/\lambda$ in the interval $0.5 < 1/\lambda < 0.8$ at increments of $\Delta(1/\lambda) = 0.05$, using eq 7. We then used those pairs to obtain G_X and G_N from eq 2. A plot of σ_M calculated from eq 7 is not linear in $\varphi_m(\lambda)$. However, in the interval $0.5 < 1/\lambda < 0.8$ the departure from linearity is indistinguishable within the usual experimental error. Details of the calculations are tabulated elsewhere.[10]

A plot of $\bar{G}_N$ vs. G_N^0 is shown in Figure 1. The slope of the straight line gives ξ as 0.354. The line is the line of best fit to the natural rubber data. The error bars represent limits of ±1 standard deviation. The errors result from a number of sources such as differences in sample preparation, vagaries in the determination of the Mooney–Rivlin constants, differences in the times used to establish equilibrium, etc. Figure 1 suggests that, for the other five materials, ξ is the same as that for natural rubber within ±1 standard deviation.

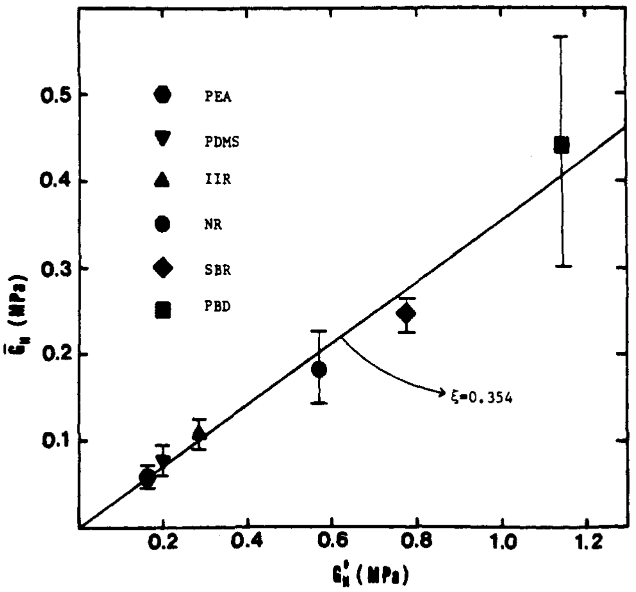


Figure 1. $\bar{G}_N$ as a function of G_N^0 for different rubbers.

Any cross-link density dependence of G_N, if it exists, would be hidden within the error bars in Figure 1. To determine if G_N is indeed independent of cross-link density, a plot of G_N as a function of the latter would be required. Since for most materials, the cross-linking reaction is not stoichiometric, we decided to use G_X as a measure of cross-link density instead of the amount of cross-linker. It is shown in another publication[2] that in cross-linked polymers G_X relaxes to its equilibrium value much faster than G_N. If any long-time relaxation processes persist, i.e., it is difficult to attain elastic equilibrium, the quantity that has not relaxed to equilibrium would be G_N. Since $G = G_X + G_N$, the ratio G_N/G can be expected to minimize any lack of equilibrium. Also, as shown in the next section, G_N depends more than G_N/G on network imperfections such as loose chain ends, and the presence of a sol fraction. We therefore attempted to reduce the scatter by employing the ratio $\bar{\nu}_N = G_N/G$, instead of G_N. The quantity $\bar{\nu}_N$ may be viewed as the mole fraction of "equivalent cross-links" modeling the effect of topological constraints.[11] Using eq 5 and 6 it becomes

$$\bar{\nu}_N = \frac{G_N}{G_X + G_N} = \frac{\xi G_N^0}{G_X + \xi G_N^0} \tag{8}$$

which may be rearranged to

$$\frac{1}{\bar{\nu}_N} = 1 + \xi^{-1}\frac{G_X}{G_N^0} \tag{9}$$

The latter form is convenient in assessing the effect of cross-link density, as reflected in G_X.

The plot according to eq 9 is shown in Figure 2. The solid line is the line of best fit to the natural rubber data, the slope yielding $\xi = 0.354$. A few of the natural rubber data were omitted from the plot for clarity of presentation.

Figure 2 strongly supports the validity of eq 6. It also suggests that ξ is independent of the nature of the polymer. A closer examination of the data reveals, however, that although eq 9 is obeyed within experimental error by all polymers examined, the main premise underlying that equation, namely, $G_N = \xi G_N^0$, sometimes appears not to be valid. A plot of G_N vs. G_X for various natural rubber networks studied by Mullins et al.[12] is shown in Figure 3. The data indicate that G_N may be weakly dependent on cross-link density. However, we found this dependence

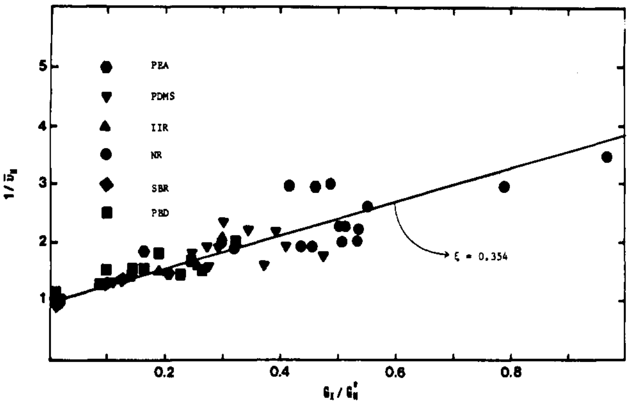


Figure 2. Mole fraction of cross-links as a function of cross-link density, for different rubbers.

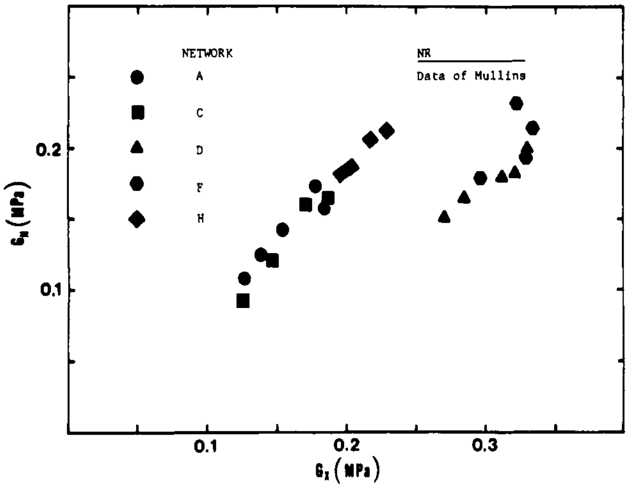


Figure 3. Data of Mullins showing G_N as a function of cross-link density.

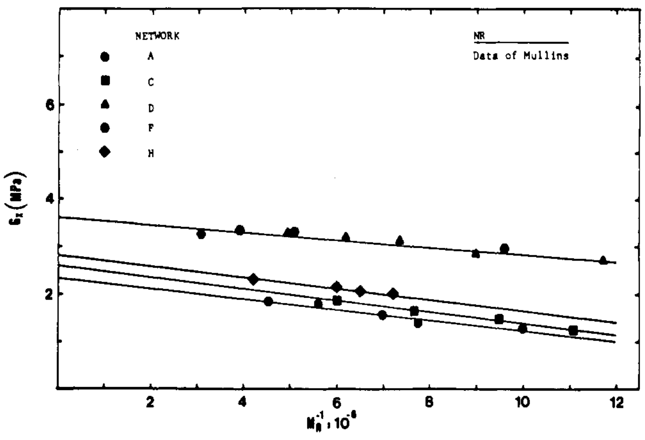


Figure 4. Dependence of G_X on the molecular weight of the precursor.

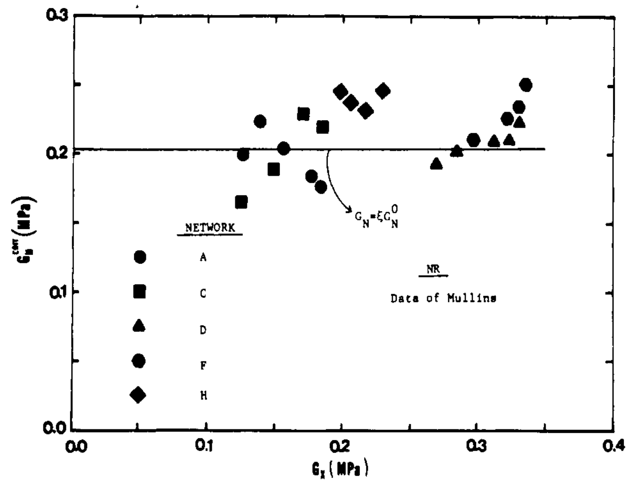


Figure 5. Data of Mullins corrected for loose ends.

to be due to the presence of loose chain ends in the network. As we will show in the next section, the cross-link density dependence of G_N disappears when this is accounted for.

Loose-End Correction

According to Flory,[13] the number of moles per unit volume of elastically active cross-links, ν_X, is given for tetrafunctionally cross-linked networks by

$$\nu_X = \nu_X^{chem}(1 - 2M_C/\bar{M}_n) \tag{10}$$

where ν_X^{chem} is the number of moles of chemical cross-links per unit volume put in, M_C is the molecular weight between cross-links, and $\bar{M}_n$ is the number average molecular weight of the polymer before cross-linking. The modulus due to the presence of chemical cross-links is then given by

$$G_X = \tfrac{1}{2}\nu_X RT \tag{11}$$

The volume fraction of loose ends, υ_L, is given by

$$\upsilon_L = M_c/(M_c + \bar{M}_n) \tag{12}$$

Therefore, if networks having the save ν_X^{chem} (and thus the same M_c) were prepared with differing $\bar{M}_n$, one would be able to determine the effect of loose chain ends on G_N. Mullins et al.[12] report stress-strain data on such networks.

As shown in a previous publication,[1] in a swollen network the true stress referred to the swollen, deformed area may be represented by

$$\tilde{\sigma} = G_X\upsilon_2^{1/3}(\lambda^2 - \lambda^{-1}) + (2G_N/m)\upsilon_2^{(-m+3)/3}(\lambda^m - \lambda^{-m/2}) \tag{13}$$

where υ_2 is the volume fraction of the polymer. For υ_2 close to unity, the dilution effect on G_X is minimal, while G_N varies linearly with the concentration of network chains. Since at equilibrium the loose ends would act like a diluent, G_N corrected for loose ends is given by

$$G_N^{cor} = G_N/(1 - \upsilon_L) \tag{14}$$

In Figure 4, Mullins' data are plotted according to eq 10 and 11. The straight lines represent the least-squares fit to the data. The intercept yields the quantity $G_X(\bar{M}_n = \infty) = {}^1/_2\nu_X RT$, and the slope divided by $G_X(\bar{M}_n = \infty)$ yields $2M_C$. Using eq 12 and 14, one can calculate the G_N values corrected for loose ends. Mullins' network designated by *B* was left out of our analysis because the data on this particular network were badly scattered.

G_N^{cor} vs. G_X plots are presented in Figure 5. As can be seen, there is no clear trend in the data, and G_N^{cor} appears to be indeed independent of cross-link density.

Conclusions

In this paper we have examined the validity of eq 6, which suggests that the modulus characterizing the topological constraints may be essentially independent of cross-link density and that all the information which differentiates the topological environment of a network may be obtainable from the un-cross-linked polymer. One important implication of the validity of eq 6 concerns the concept of trapped entanglements. If the nature of G_N were related to trapped entanglements, its cross-link density dependence would be more pronounced. Our analysis implies that the nature of G_N is related to a decrease in the configurations available to the network chains as compared to their phantom counterparts. This is implied by the fact that the topological environment of the un-cross-linked polymer is carried over to the cross-linked counterpart.

Although in form the preceding theory appears to be similar to the theory of Langley,[14] it is in fact quite different. The latter theory has been discussed at length by Queslel and Mark.[15] In the Langley theory, one has no way of separating the effect of topological constraints from the phantom network, because the strain dependence of the constraint network is unspecified. Therefore, the conclusions one would draw from the Langley theory are dependent on the assumption made about the relation of the chemical composition of the network to the modulus due to chemical cross-links. In our theory, no such assumption is necessary, because we obtain both moduli from experimental data.

We would like to point out that the conclusions we have drawn are not expected to be valid near the gel point. We have also based all of our conclusions on data on randomly cross-linked, tetrafunctional networks. Major differences are not expected for end-linked networks. The value of ξ would probably depend on network functionality. Most of the available data on networks that are not tetrafunctional are on PDMS. Unfortunately, PDMS has a very low G_N^0 so that the values of G_N would be relatively small. This fact precludes a study of the functionality dependence of ξ.

Registry No. PEA (homopolymer), 9003-32-1.

References and Notes

(1) Tschoegl, N. W.; Gurer, C. *Macromolecules*, preceding article in this issue.
(2) Gurer, C.; Tschoegl, N. W., to be submitted to *J. Polym. Sci., Polym. Phys. Ed.*
(3) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1980; p 374.
(4) Janacek, J.; Hrouz, J. *J. Polym. Sci., Polym. Symp.* **1975**, *53*, 203.
(5) Mark, J. E.; Kato, M.; Ko, J. H. *J. Polym. Sci., Polym. Symp.* **1976**, *54*, 217.
(6) Mark, J. E. *Rubber Chem. Technol.* **1975**, *48*, 495.
(7) Kato, M.; Mark, J. E. *Rubber Chem. Technol.* **1976**, *49*, 85.
(8) Mullins, L. *J. Appl. Polym. Sci.* **1959**, *2*, 257.
(9) Van der Hoff, B. M. E.; Buckler, E. J. *J. Macromol. Sci., Part A* **1967**, *1*, 747.
(10) Gurer, C. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1984.
(11) Tschoegl, N. W. *Polymer* **1979**, *20*, 1365.
(12) Mullins, L. *J. Appl. Polym. Sci.* **1959**, *2*, 1.
(13) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; p 463.
(14) Langley, R. N. *Macromolecules* **1968**, *1*, 348.
(15) Queslel, J. P.; Mark, J. E. *Adv. Polym. Sci.* **1984**, *65*, 135.

Stereochemical Kinetics of Anionic Vinyl Polymerization. 2. ^{13}C NMR Analysis of Poly(2-vinylpyridine) and Poly(4-vinylpyridine) Terminated with Labeled End Groups

Alain H. Soum and Thieo E. Hogen-Esch*

Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611.

Received July 13, 1984

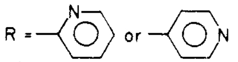
ABSTRACT: Carbon-13 NMR spectra of the ^{13}C-labeled methyl end group of poly(2-vinylpyridine) (P-2-VP), poly(4-vinylpyridine) (P-4-VP), and poly(2-isopropenylpyridine) (P-2-IP) were stereochemically assigned on the basis of known model compounds. It was found that in the case of P-2-VP the chain-end stereochemistry differed appreciably from that of the chain itself. For P-4-VP and P-2-IP, these stereochemistries are nearly identical. These results are shown to reveal consistency with a Bernoullian process for P-4-VP and P-2-IP and consistency with a second- or higher-order Markoff process in the case of P-2-VP. The results suggest that stereochemical comparison of end group and chain may be a valuable new method for analyzing the statistics of vinyl polymers prepared by anionic polymerization.

Introduction

We have recently reported the trapping of lithium salts of stereoisomeric "living" poly(2-vinylpyridine) anions by reaction with ^{13}C-labeled CH_3I followed by ^{13}C NMR analysis of the labeled end group[1] (eq 1). It was shown that the stereoisomeric composition fo the dyad flanking the carbanion differed from that of the chain itself as determined by ^{13}C NMR of the quaternary pyridine carbon. Such a pattern was previously shown to be consistent with the occurrence of a Markoff-type process in which the stereoisomeric composition of the chain end affects its rate of tactic monomer addition.[2-4] Such a process is not inconceivable for the anionic polymerization of 2-vinylpyridine in media of low polarity and in the presence of small counterions. Thus, in the case of Li or Na ion in THF, a strong coordination of the counterion with the nitrogen lone pair of the penultimate 2-pyridine ring has been demonstrated for both short-chain and longer chain living poly(2-vinylpyridine).[5,6] Inspection of CPK models shows that, in the case of tetramers and longer chains, the chelation tends to position the third asymmetric center in close proximity to the carbanion. As a result, a Markoff-type process is not implausible. The detection of Markoffian statistics in vinyl polymers from determination

$$I_n^-M^+ + (n+1)CH_2{=\!=}CRR' \longrightarrow \underset{\mathbf{1\text{-}5}}{I_n[CH_2CRR']_nCH_2CR'^-RM^+} \xrightarrow[(^{13}CH_3I)]{CH_3I} \underset{\mathbf{6\text{-}10}}{I_n[CH_2CRR']_nCH_2CR'RCH_3(^{13}CH_3)} \quad (1)$$

I_n = CH_3CHR, CH_2R, or living polyrene
M = Li, Rb, $MgCH_2Ph$



R' = H or CH_3
1, 6, n = 1; **2**, **7**, n = 2; **3**, **8**, n = 3; **4**, **9**, n = 4; **5**, 10, n = 20–100

0024-9297/85/2218-0690$01.50/0