Macromolecules 1981, *14*, 1071-1076

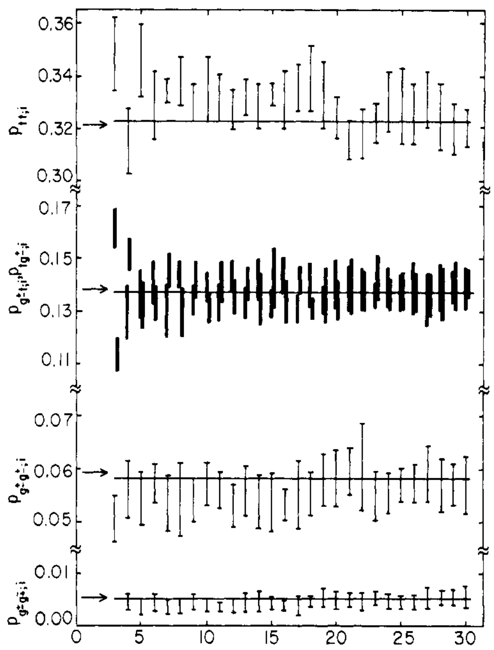

Figure 9. Second-order a priori probabilities for bonds 3–30 in an attached polymethylene chain of 300 bonds. Horizontal lines denote averages of $p_{\xi\eta;i}$ for bonds 3–299. Arrows denote $p_{\xi\eta}$ for a long unperturbed chain in free solution.

bonds 3–299 in the attached chains are essentially identical with the $p_{\xi\eta}$ reported by Jernigan and Flory[1] for long unperturbed polymethylene chains.

The general conclusion from Figures 8 and 9 and Table I is that end effects extend somewhat further into the chain when one end is attached to an impenetrable interface. However, the largest displacement of $p_{\eta;i}$ from p_η, or $p_{\xi;i}$ from $p_{\xi\eta}$, is of comparable size for free and attached chains. Furthermore, the end effects produced in a chain of 300 bonds by the impenetrable interface do not cause either p_η or $p_{\xi\eta}$ to differ from values obtained with the free unperturbed chain. It would seem appropriate, therefore, to categorize the end effects produced by the impenetrable interface as being "small".

One means of placing the size of the end effects discussed here in their proper perspective is to compare the largest $p_{\eta;i} - p_\eta$ and $p_{\xi\eta;i} - p_{\xi\eta}$ (Table I) with the largest perturbations produced in the main chain when a butyl group is attached to an atom in the interior of a long polymethylene chain. When a butyl group is present, $p_{t;i} - p_t$ and $p_{tt;i} - p_{tt}$ can be as negative as −0.20 and −0.22, respectively.[21] Perturbations produced by the butyl group are much larger than those arising from the end effects produced by the impenetrable interface.

Acknowledgment. This investivation was supported by National Science Foundation Research Grant PCM 78-22916. Part of this work was carried out while Professor Mattice was at the University of Sydney for a Cooperative Research Visit supported by the National Science Foundation and the Australian Department of Science and the Environment. Professor Mattice thanks Professors Moore and Napper for their generous hospitality while he was in Sydney.

References and Notes

(1) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4165.
(2) Smith, R. P. *J. Chem. Phys.* **1965**, *42*, 1162.
(3) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(4) Mattice, W. L.; Santiago, G. *Macromolecules* **1980**, *13*, 1560.
(5) Feigin, R. I.; Napper, D. H. *J. Colloid Interface Sci.* **1979**, *71*, 117.
(6) DiMarzio, E. A.; McCrackin, F. L. *J. Chem. Phys.* **1965**, *43*, 539.
(7) Yoon, D. Y.; Flory, P. J. *J. Chem. Phys.* **1974**, *61*, 5366.
(8) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(9) Patterson, G. D.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1098.
(10) Flory, P. J.; Yoon, D. Y. *J. Chem. Phys.* **1969**, *50*, 4178.
(11) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4178.
(12) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(13) Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756.
(14) Šolc, K. *J. Chem. Phys.* **1971**, *55*, 355.
(15) Kranbuehl, D. E.; Verdier, P. H. *J. Chem. Phys.* **1977**, *67*, 361.
(16) Mattice, W. L. *Macromolecules* **1979**, *12*, 944.
(17) Mattice, W. L. *J. Am. Chem. Soc.* **1980**, *102*, 2242.
(18) Mattice, W. L. *Macromolecules* **1980**, *13*, 506.
(19) Mattice, W. L. *Macromolecules* **1980**, *13*, 904.
(20) Mazur, J.; Guttman, C. M.; McCrackin, F. L. *Macromolecules* **1973**, *6*, 872.
(21) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.

Elasticity Theory. 5. Mean Field Solution of the Network Collapse Problem

B. E. Eichinger

Department of Chemistry, University of Washington, Seattle, Washington 98195.
Received December 23, 1980

ABSTRACT: The problem of network collapse is solved by combining the asymptotic form of the unperturbed distribution function of the radius of gyration with a mean field representation of the repulsive forces of volume exclusion. The theory gives well-behaved thermodynamic densities for elastomers.

Introduction

Networks formed by cross-linking linear polymer chains have properties unlike those of the parent molecules. Linear chains in the bulk (or in certain dilute solutions) can be brought to a state where their configurations are unperturbed by the influence of neighboring molecules. In this state molecular dimensions are determined solely by the short-ranged intramolecular potential, the intermolecular influences having been nullified by fundamental cancellation with the nonbonded part of the intramolecular potential.[1] This ideal or Flory Θ state is firmly established; it is realized in practice[2] and it serves as the reference state for rigorous perturbation theory of the influence of nonbonded interactions upon molecular dimensions.[3] The decomposition of potentials into inter- and intramolecular components is not possible for networks, however. Upon cross-linking the collection of molecules into a single reticulated molecule, the forces that had been intermolecular

0024-9297/81/2214-1071$01.25/0

become intramolecular, and the basis for cancellation of the two effects no longer applies.

The consequences of this re-formation turn out to be remarkable. For example, it can be proved that a cubic lattice of uniform chains joined by hexavalent junctions has an unperturbed mean-square radius of gyration $\langle s^2 \rangle_0$ comparable to that of one of the chains which comprise it.[4,5] This result has long been known from the work of James and Guth;[6,7] it is furthermore true for any net with crystallographic symmetry, as may be inferred from general considerations based on space groups. Similarly, the expectation value of $\langle s^2 \rangle_0$ for a large network selected at random from the set of all regular nets seems to be very small.[8,9] Less rigorous, but corroborative results have been obtained by computer simulation of nets formed with constraints acting to limit connectivity to spatial neighborhoods of the junctions.[10] It is now quite clear that unperturbed, reticulated molecules having a fixed proportion of cross-links to chain elements collapse in the thermodynamic limit of large systems to unrealistic states of infinite density.[11] Because of this, the unperturbed state ceases to be a useful basis for a perturbation calculation of dimensions.

To circumvent this problem, one must incorporate molecular repulsion in the configuration integral.[11] It will be shown here that a mean field potential suffices for this purpose and that it has the added advantage of being imposed fairly late in otherwise intricate calculations of distribution functions of molecular dimensions. For the present it will be enough to show that the mean field sustains a spherical elastomer against collapse, and on this account only the radius of gyration need be considered.

The unperturbed distribution functions of the radius of gyration and of the gyration tensor are not simple, even for molecules with Gaussian bonds.[9] They may be rendered into the form of low-dimensionality integrals, but from that point on general results can only be obtained by piecewise analysis or by use of approximation methods.[9,12] Numerical integrations notwithstanding, the distribution function of the radius of gyration s may be evaluated for small s, for $s^2 \approx \langle s^2 \rangle_0$, and for the asymptotic region where $s^2 \gg \langle s^2 \rangle_0$. Near the asymptote this distribution function is principally determined by the minimum nonzero eigenvalue λ_1 of the Kirchhoff matrix $\mathbf{K}$ that specifies the connectivity of the molecule of interest and by the multiplicity of this eigenvalue.[12]

At this stage network collapse changes from disaster to benefit, since only the asymptotic unperturbed distribution function is relevant to reality. This function, together with the mean field, yields a proper thermodynamic density for elastomers, provided λ_1 has the correct dependence upon the number n of statistical units in the molecule.

It is necessary to assert that $\lambda_1 = O(n^{-2/3})$ to obtain all that is claimed above. This is exactly right for large crystallographic nets, as is readily proved. That it is correct for random nets is still open to question. McKay[13] has obtained the rigorous bounds $O(n^{-4/3}) \le \lambda_1 \le O(n^{-2/3})$ for random graphs with constraints on the vertex density and edge length. Computer simulations[10] of random nets containing up to 216 nodes gave $\lambda_1 = O(n^{-0.4})$. Edge effects likely had a significant impact on this result, but there can be no doubt that λ_1 was indeed inversely proportional to a power of n close to the value $^2/_3$ required here. In summary, the theory to follow demonstrates that $\lambda_1 = O(n^{-2/3})$ is the only n dependence consistent with the mean field and thermodynamic densities.

An additional assertion regarding the multiplicity ω_1 of λ_1 will also be required in the mild form $\omega_1 < O(n)$. There are several arguments that can be mustered to justify this assumption. In the first place, high multiplicities are associated with a high degree of redundant regularity in those molecules whose Kirchhoff matrices have known eigenvalue spectra. Second, all numerical computations[10,14] and theory[8] on random nets to date give spectra which appear to be dense on the interval $\lambda_1 \le \lambda \le \lambda_{\max}$, where $\lambda_{\max}$ is the maximum eigenvalue of $\mathbf{K}$, and $\lambda_{\max} = O(1)$ for nets with modest junction functionality. A substantial proportion of the eigenvalues are larger than the minimum. Third, the connection[9] between eigenvalue spectra and viscoelastic relaxation time spectra gives $\omega \approx O(\lambda^{-1})$ for small eigenvalues. It therefore appears from several lines of evidence that $\omega_1 < O(n)$. (Besides, $\omega_1 = 3$ for the simple cubic net, the case that can be invoked to justify all that follows.)

Asymptotic Unperturbed Distribution Function

The distribution function $P_0(s^2)\,\mathrm{d}s^2$ of the square of the radius of gyration s of an unperturbed Gaussian molecule of n beads is given by[9,15]

$$P_0(s^2)\,\mathrm{d}s^2 = (\mathrm{d}s^2/2\pi) \int_{-\infty}^{\infty} \exp(i\beta s^2) \prod_{k=1}^{n-1} (1 + i\beta/\gamma n \lambda_k)^{-3/2}\,\mathrm{d}\beta \quad (1)$$

where $\gamma = 3/2\langle l^2 \rangle_0$; $\langle l^2 \rangle_0$ is the mean-square displacement of a single equivalent bond. The λ_k are the eigenvalues of the Kirchhoff matrix of the graph describing the molecule. The moment-generating function $\langle \exp(-as^2) \rangle$ is related to the integrand of eq 1 by

$$\langle \exp(-as^2) \rangle = \prod_{k=1}^{n-1} (1 + a/\gamma n \lambda_k)^{-3/2} \quad (2)$$

which gives

$$\langle s^2 \rangle_0 / \langle l^2 \rangle_0 = n^{-1} \sum_{k=1}^{n-1} 1/\lambda_k \quad (3)$$

$$(\langle s^4 \rangle - \langle s^2 \rangle_0{}^2)/\langle l^2 \rangle_0{}^2 = (2/3n^2) \sum_{k=1}^{n-1} 1/\lambda_k{}^2 \quad (4)$$

and so on for the cumulants.

The evaluation of eq 1 in the domain $s^2 \gg \langle s^2 \rangle_0$ has already been achieved by a somewhat roundabout method.[12] A more straightforward estimate of the integral may be obtained by the method of the stationary phase, which has the added advantage of being applicable to the calculation of the distribution function of the gyration tensor. To make this work self-contained and to suggest future extensions of it, the integral in eq 1 will be estimated for the situation applicable to elastomers, i.e., $n > 10^{20}$ and $s^2 \gg \langle s^2 \rangle_0$.

The integral F to be considered is

$$F = \int_{-\infty}^{\infty} \exp[f(\tau)]\,\mathrm{d}\tau \quad (5)$$

where $\tau = \beta/\gamma n$ and

$$f(\tau) = i\gamma n s^2 \tau - (3/2) \sum_{k=1}^{n-1} \ln\,(1 + i\tau/\lambda_k) \quad (6)$$

The saddle point is located at τ_0, where

$$f'(\tau_0) = \mathrm{d}f(\tau)/\mathrm{d}\tau|_{\tau=\tau_0} = 0 \quad (7)$$

and the integral is given approximately by

$$F \approx [-2\pi/f''(\tau_0)]^{1/2} \exp[f(\tau_0)] \quad (8)$$

The first two derivatives are

$$f'(\tau) = i[\gamma n s^2 - (3/2) \sum_{l=1}^{n-1} (\lambda_l + i\tau)^{-1}] \quad (9)$$

$$f''(\tau) = -(3/2)\sum_{l=1}^{n-1}(\lambda_l + i\tau)^{-2} \qquad (10)$$

The saddle point must lie on the imaginary axis, since $f'(\tau_0) = 0$ if and only if the sum in eq 9 is real. Furthermore, since F is real $f''(\tau_0)$ must be real, excluding the unlikely and fortuitous cancellation of imaginary terms in $[f''(\tau_0)]^{-1/2}$ and $\exp[f(\tau_0)]$. The solution of the equation $f'(\tau_0) = 0$ behaves as follows: as s^2 increases from very small to very large values, $i\tau_0$ decreases from large values through zero to small negative values which approach λ_1. At $\tau = 0$, $s^2 = \langle s^2\rangle_0$ by eq 3 and 9, and at $i\tau = -\lambda_1$, the sum in eq 9 is singular.

Since our interest is in $s^2 \gg \langle s^2\rangle_0$, let $i\tau_0 = -\lambda_1 + \epsilon$, where ϵ is presumed to be smaller than λ_1; the multiplicity of λ_1 will be denoted by ω_1. Equation 9 yields

$$\gamma n s^2 - 3\omega_1/2\epsilon - (3/2)\textstyle\sum'(\lambda_l - \lambda_1 + \epsilon)^{-1} = 0 \qquad (11)$$

for the saddle point, where $\sum'$ is over all $\lambda_l > \lambda_1$. Having separated the important, potentially singular term of the characteristic function from the rest, we may now replace the sum by an integral for a large system on the assumption that the spectrum is not pathological. Let $g(\lambda)\,d\lambda$ be the proportion of eigenvalues of the Kirchhoff matrix lying between λ and $\lambda + d\lambda$. Equation 11 becomes

$$ns^2/\langle l^2\rangle_0 - \omega_1/\epsilon - (n - \omega_1)\int_{\lambda>\lambda_1} g(\lambda)(\lambda - \lambda_1 + \epsilon)^{-1}\,d\lambda = 0 \qquad (12)$$

with cancellation of a factor of $^3/_2$ via the definition of γ. The integral is more conveniently written with $g^+(\lambda) = g(\lambda + \lambda_1)$, whereupon

$$ns^2/\langle l^2\rangle_0 - \omega_1/\epsilon - (n - \omega_1)\int_{\lambda>0} g^+(\lambda)(\lambda + \epsilon)^{-1}\,d\lambda = 0 \qquad (13)$$

For $\epsilon = 0$, the integral over the spectrum is seen to differ from $\langle s^2\rangle_0/\langle l^2\rangle_0$ only by deletion of the contribution from the smallest eigenvalue, and certainly

$$\int_{\lambda>0} g^+(\lambda)(\lambda + \epsilon)^{-1}\,d\lambda < \int_{\lambda>0} g^+(\lambda)\lambda^{-1}\,d\lambda$$

for $\epsilon > 0$. The contribution from the integrated term is therefore of order no greater than $\langle s^2\rangle_0/\langle l^2\rangle_0$. Assume it negligible, to obtain

$$\epsilon = \omega_1\langle l^2\rangle_0/ns^2 \qquad (14)$$

If it is indeed true that $\lambda_1 = O(n^{-2/3})$ and $s^3 = O(n)$, then $\epsilon = O(\omega_1 n^{-5/3})$. This has to be much smaller than λ_1 since ω_1 cannot possibly be $O(n)$ as argued in the Introduction. The saddle point is therefore accurately located by

$$\tau_0 = i(\lambda_1 - \omega_1\langle l^2\rangle_0/ns^2) \qquad (15)$$

for $s^2 = O(n^{2/3}) \gg \langle s^2\rangle_0$.

An integration along a contour of stationary phase which passes through the saddle point can be accomplished, since the real axis can be deformed into any contour passing below the singularity of $f(\tau)$ lying closest to the origin, without passing through any other singularity of the characteristic function. The second derivative is found to be

$$f''(\tau_0) = -3n^2s^4/2\omega_1\langle l^2\rangle_0{}^2 \qquad (16)$$

since the remaining contribution from the $\lambda_l > \lambda_1$ is negligible by the assertion that $s^4 \gg \langle s^4\rangle_0$. We also have

$$f(\tau_0) = -n\gamma\lambda_1 s^2 + (3\omega_1/2)\ln(e\lambda_1 ns^2/\omega_1\langle l^2\rangle_0) - (3/2)\textstyle\sum'\ln[1 - (\lambda_1 - \omega_1\langle l^2\rangle_0/ns^2)/\lambda_l] \qquad (17)$$

In the domain where $\lambda_1 \gg \omega_1\langle l^2\rangle_0/ns^2$, the sum in this equation gives only a constant contribution to $f(\tau_0)$. Thus we have the asymptotic result

$$P(s^2)\,ds^2 \sim (\text{const})s^{3\omega_1-1}\exp(-\gamma n\lambda_1 s^2)\,ds \qquad (18)$$

where factors of $s^{3\omega_1}$, s^{-2}, and s arise from $\exp[f(\tau_0)]$, $[-f''(\tau_0)]^{-1/2}$, and $ds^2 = 2s\,ds$, respectively. This agrees perfectly with the previous calculation.[12]

Mean Field Approximation

The interaction energy density in any fluid is determined by the local density of molecules. In an elastomer, the local density of segments in the vicinity of a cross-link is certain to be different from the mean. This is most vividly illustrated with telechelic polymers; significant perturbations of the local fluidlike structure must accompany the reorganizations required to link together chain ends to form junctions. It is therefore appropriate to use fluctuation theory for a first-order description of the effective potential of nonbonded forces in an elastomer.

Consider a small, open-volume element in the elastomer and let $a = a(T,\rho)$ be its free energy density at temperature T and segment number density ρ. No distinction will be made between chain segments and cross-links for the purpose of computing the number density; a junction is equivalent to one segment. One could relax this restriction, but the net result of what follows would not be materially altered. It follows from thermodynamics[16] that

$$da = -s\,dT + \mu\,d\rho \qquad (19)$$

where $\mu = (\partial a/\partial\rho)_T$ is the segment chemical potential. Now expand the local free energy density about the mean $\bar\rho$ to obtain

$$a(\rho) = a(\bar\rho) + \mu(\rho - \bar\rho) + (1/2\bar\kappa\bar\rho^2)(\rho - \bar\rho)^2 + \ldots \qquad (20)$$

where $\bar\kappa = -(\partial \ln V/\partial\rho)_T$ is the bulk compressibility evaluated at $\bar\rho$. The total free energy will be given by an integration over the volume V to obtain

$$\begin{aligned}\int \tilde a(\rho)\,d\mathbf{r} &= Va(\bar\rho) + (1/2\bar\kappa\bar\rho^2)\int(\rho^2 - \bar\rho^2)\,d\mathbf{r} \\ &= V(\tilde a - 1/2\bar\kappa) + (1/2\bar\kappa\bar\rho^2)\int\rho^2\,d\mathbf{r} \qquad (21)\end{aligned}$$

The linear term vanishes by definition of the mean, and that same relation has been used to simplify the quadratic term. Reasons for dropping higher order terms in the expansion have been amply discussed in the literature.[17,18]

The segment density at $\mathbf{r}$ depends upon the configuration, but for all it is given by

$$\rho(\mathbf{r}) = \sum_l \delta(\mathbf{r} - \mathbf{r}_l) \qquad (22)$$

where the sum extends over all n segments in the system. The distribution $\delta(\mathbf{x})$ may be approximated by a sharply peaked function, which is not an unreasonable device for smearing the centers of the multiatomic segments over small elements of volume so as to account for their imprecisely specified internal configurations. Hence set

$$\delta(\mathbf{x}) = (2b/\pi)^{3/2}\exp(-2b\mathbf{x}^2) \qquad (23)$$

where the range parameter b may be chosen as large as one likes. When this expression is substituted into eq 22 and it in turn is utilized in eq 21, the integration may be performed to yield

$$\begin{aligned}A &= V(\tilde a - 1/2\bar\kappa) + (\bar\kappa\bar\rho^2)^{-1}(b/\pi)^{3/2}\sum_{k<l}\exp[-b(\mathbf{r}_k - \mathbf{r}_l)^2] \\ &= V(\tilde a - 1/2\bar\kappa) + \sum_{k<l} v(r_{kl}) \qquad (24)\end{aligned}$$

The spurious squared or self-interaction term that arises on squaring the density has been suppressed so as to make the transition from the continuous to the discrete representation. The effective pairwise additive intersegmental potential $\upsilon(r)$ is given by

$$\upsilon(r) = (\tilde{\kappa}\tilde{\rho}^2)^{-1}(b/\pi)^{3/2} \exp(-br^2) \qquad (25)$$

Before formulating the configuration integral, it is necessary to define $\tilde{a} = a(\tilde{\rho})$ more precisely. The free energy density within a volume element is sensitive to the local structure, not the long-range structure. Local connectivity is implicit in $a(\rho)$ but the long-range elastic forces are not. If the elastomer being discussed is devoid of chain ends, $a(\tilde{\rho})$ is the free energy density of the corresponding virtually infinite linear chain which has been packed into a box with mean density $\tilde{\rho}$, less the free energy density attributable to the long-range connectivity. With neglect of surface effects and in the Gaussian approximation, this latter contribution is just $-kT \ln (\pi/\gamma)^{3(n-1)/2}$, so that the total free energy of the hypothetical linear chain having mean density everywhere is

$$\tilde{A} = V[a(\tilde{\rho}) + (3kT\tilde{\rho}/2) \ln (\gamma/\pi)] \qquad (26)$$

This is the free energy of a high molecular weight prepolymer to within a small term depending upon the fluctuations.

The effective total potential for the elastomer is thus determined relative to a reference system and in the Gaussian approximation is given by

$$\sum_{k<l} \upsilon(r_{kl}) + kT\gamma \sum_{i-j} (\mathbf{r}_i - \mathbf{r}_j)^2 \qquad (27)$$

The first sum is most simply taken over all segment pairs, whereas the last is over bonded pairs only. The matrix of the quadratic form in the second term is the Kirchhoff matrix of the graph which describes the molecular connectivity of the elastomer.

It is now convenient to make a Fourier analysis of the nonbonded terms. Define

$$\phi(\mathbf{q}) = (2\pi)^{-3} \int \upsilon(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r})\, d\mathbf{r} \qquad (28a)$$

$$\phi(\mathbf{q}) = (8\pi^3\tilde{\kappa}\tilde{\rho}^2)^{-1} \exp(-q^2/4b) \qquad (28b)$$

so that

$$\sum_{k<l} \upsilon(r_{kl}) = \int \phi(\mathbf{q}) \sum_{k<l} \exp[i\mathbf{q}\cdot(\mathbf{r}_l - \mathbf{r}_k)]\, d\mathbf{q} \qquad (29)$$

The distribution of mass in the elastomer is assumed to be spherically symmetric, so that the complex exponential may be averaged over angles to give

$$\sum_{k<l} \upsilon(r_{kl}) = 4\pi \int_0^\infty q^2 \phi(q) \sum_{k<l} \frac{\sin q|r_k - r_l|}{q|r_k - r_l|}\, dq \qquad (30)$$

The Fourier–Debye kernel is now expanded in its Maclaurin series to give

$$\sum_{k<l} \frac{\sin q|r_k - r_l|}{q|r_k - r_l|} = n(n-1)/2 - (n^2/3!)\boldsymbol{s}_2 q^2 + (n^2/5!)\boldsymbol{s}_4 q^4 - (n^2/7!)\boldsymbol{s}_6 q^6 + \ldots \qquad (31)$$

where

$$\boldsymbol{s}_{2m} = n^{-2} \sum_{k<l} |\mathbf{r}_k - \mathbf{r}_l|^{2m} \qquad (32)$$

and $\boldsymbol{s}_2 = s^2$ by Lagrange's theorem.[19]

The function $(n^2/2) \exp(-s^2q^2/3)$ may now be extracted from the right-hand side of eq 31 to give

$$\sum_{k<l} \frac{\sin q|r_k - r_l|}{q|r_k - r_l|} = (n^2/2) \exp(-s^2q^2/3)[1 - (1 - 3\boldsymbol{s}^4/10s^4)(s^4q^4/18) + \ldots] \qquad (33)$$

In the limit $b \rightarrow \infty$, eq 30, with use of eq 33, integrates to

$$\sum_{k<l} \upsilon(r_{kl}) = [(n^2/s^3)(3/\pi)^{3/2}/16\tilde{\kappa}\tilde{\rho}^2][1 - (15/8)(1 - 3\boldsymbol{s}_4/10s^4) + \ldots] \qquad (34)$$

For a sphere of uniform density the integral in eq 30 may be computed in closed form to give

$$\sum_{k<l} \upsilon(r_{kl}) = (3/\pi)(3/20)^{3/2} n^2/\tilde{\kappa}\tilde{\rho}^2 s^3$$

and for a uniform cube, one finds

$$\sum_{k<l} \upsilon(r_{kl}) = n^2/8\tilde{\kappa}\tilde{\rho}^2 s^3$$

In general then, the mean field potential is given by

$$\sum_{k<l} \upsilon(r_{kl}) = Cn^2/\tilde{\kappa}\tilde{\rho}^2 s^3 \qquad (35)$$

where $C = O(10^{-1})$ is a constant. In the nonuniform case the constant depends upon the configuration, but if one assumes that the mass distribution in the elastomer is reasonably smooth and spherically symmetric, this dependence will not be strong.

The incorporation of volume occupancy by way of the mean field expressed in eq 35 will soon be shown to yield a thermodynamic density. Several years ago Boggs[20] found that by appending fluid equation-of-state terms to the elastic free energy he could prevent collapse. His treatment is very much like the one expressed here, the essential difference being that a hard-core volume term working in opposition to an attractive van der Waals term sustains the net in Boggs's theory. Here the term in $1/s^3$ is repulsive; other fluid terms have already been factored into $A(\tilde{\rho})$. In approximate theories such as these, the stage at which one chooses to factor out the fluid contributions to the total free energy is somewhat arbitrary and depends more upon convenience than upon rigor.

Perturbed Distribution Function

The results of the previous two sections may now be joined by appeal to the Flory–Fisk theory.[21] The integration over all coordinates but s of the Boltzmann factor with the potential in eq 27, where the nonbonded term is immediately replaced by the mean field, gives

$$A = V[\tilde{a} - 1/2\tilde{\kappa} + (3kT\tilde{\rho}/2) \ln (\gamma/\pi)] - kT \ln W(s) \qquad (36)$$

where

$$W(s) = (\text{const}) s^{3\omega_1 - 1} \exp(-\gamma n \lambda_1 s^2 - Bn^2/s^3) \qquad (37)$$

is the perturbed distribution function of s and $B = C/kT\tilde{\kappa}\tilde{\rho}^2$. All terms but the last in eq 36 may be suppressed for the purposes to follow.

The mth moment of s is given by

$$\langle s^m \rangle = \frac{\int_0^\infty s^{3\omega_1 + m - 1} \exp(-\gamma n \lambda_1 s^2 - Bn^2/s^3)\, ds}{\int_0^\infty s^{3\omega_1 - 1} \exp(-\gamma n \lambda_1 s^2 - Bn^2/s^3)\, ds} \qquad (38)$$

which may be estimated by the method of Hermans and Overbeek.[22] Alternatively, another steepest descents calculation may be made. Let s_e locate the maximum of $s^\alpha \exp(-\gamma n \lambda_1 s^2 - Bn^2/s^3)$, where $\alpha = 3\omega_1 + m - 1$. One finds

$$s_e^5 - (\alpha/2\gamma n \lambda_1) s_e^3 = B\langle l^2 \rangle_0 n/\lambda_1 \qquad (39)$$

Suppose now that the term s_e^5 dominates the left-hand side and that $\lambda_1 = O(n^{-2/3})$. Then $s_e^5 = O(n^{5/3})$ and the density $n/s^3 \rightarrow$ constant as $n \rightarrow \infty$. The cubic term on the left-hand side is then of $O(\alpha n^{2/3})$, which is comparable to s_e^5

only if $\alpha \geq O(n)$. Since m is presumed to be a small number, $\alpha \geq O(n)$ only if $\omega_1 \geq O(n)$. But this possibility has already been excluded. Stated otherwise, $\alpha/2\gamma n\lambda_1 < s_e^2$ is a reality condition; if this is all that is asserted the left-hand side is $(\mathrm{const})s_e^5$, and such a case is encompassed even though the questionable term is discarded with the arguments presented. In any event, to within a constant

$$s_e^5 = B\langle l^2\rangle_0 n/\lambda_1 \tag{40}$$

locates the maximum, and

$$\langle s^m\rangle = (B\langle l^2\rangle_0 n/\lambda_1)^{m/5} \tag{41}$$

since the curvature at the maximum is independent of s_e, as is easy to show. Hence, $\langle s^m\rangle = O(n^{m/3})$ as required for thermodynamic stability.

The mean field will prevent the catastrophic collapse of the network if the minimum nonzero eigenvalue of the Kirchhoff matrix is of $O(n^{-2/3})$. The minimum eigenvalue for the cubic lattice is exactly $4 \sin^2 \pi/2n^{1/3}$, and in this case there is nothing wanting in the rigor of the result. There are signs that a graph theoretic proof of $\lambda_1 = O(n^{-2/3})$ will be found,[13] but in the meantime the calculation presented here is an indirect proof that this is the correct behavior for all physically realizable networks.

Discussion

There is an immediately interesting question that is now subject to analysis: What is the compressibility of the elastomer relative to that of the prepolymer? From eq 36 and 37 we have

$$\langle A\rangle = \tilde{A} + kT(\gamma n\langle\lambda_1\rangle s^2 + \langle B'\rangle n^2/s^3) \tag{42}$$

on dropping the incommensurate term proportional to ln s. Here $\tilde{A}$ is given by eq 26 and angle brackets denote network ensemble averages. In eq 42 the quantity B' is given by

$$B' = B - Vs^3/2kT\tilde{\kappa}n^2 = \epsilon B$$

which results from joining the two terms in $1/\tilde{\kappa}$ from eq 24 and 35. The constant ϵ depends upon the magnitude of the fluctuations and can be expected to be small, as it is proportional to $\int(\rho^2 - \bar{\rho}^2)\,\mathrm{d}\mathbf{r}$.

Computation of $(\partial^2\langle A\rangle/\partial V^2)_T$ from eq 36 gives the compressibility as

$$\kappa^{-1} = \tilde{\kappa}^{-1} + \kappa_N^{-1} \tag{43}$$

where

$$\kappa_N^{-1} = (kT\sigma n\langle\lambda_1\rangle/3\langle l^2\rangle_0 s_e)(6\epsilon - 1) \tag{44}$$

Here $\sigma = s^3/V$ is a geometrical parameter, and κ_N is the intensive network contribution to the compressibility. The pressure p that must be applied to the elastomer so as to make its volume equal to that of the prepolymer at pressure $\tilde{p}$ is given by

$$p = \tilde{p} - (kT\sigma n\langle\lambda_1\rangle/\langle l^2\rangle_0 s_e)(1 - \epsilon) \tag{45}$$

There is relatively little compressibility data with which to compare eq 44. Measurements of Wood and Martin[23] on natural rubber generally give κ less than $\tilde{\kappa}$ by about 1%, with the exception of the low-temperature and -pressure data. Furthermore, they noticed an increase in density upon curing with dicumyl peroxide. The decrease in pressure at constant density given by eq 45 is compatible with an increase of density at constant pressure. Thus, it seems that ϵ must be in the range $1/6 \leq \epsilon < 1$ to account for the volumetric behavior of natural rubber. It would be advantageous to have differential compressibility data to thoroughly test this prediction of the mean field theory.

An approximate stress–strain relation may be extracted from eq 42, with the understanding that the necessary departure from spherical symmetry that attends the strain is not represented by s^2 alone. The distribution function of the gyration tensor is required for a thorough treatment of elasticity. This disclaimer aside, the tension τ may be obtained from an equation derived previously,[24] i.e.

$$\tau = (2s_0^2V^{1/3}/3V_0^{4/3})(\partial\langle A\rangle/\partial s^2)_T(\alpha - 1/\alpha^2) \tag{46}$$

where α is the dilation-corrected uniaxial extension ratio. If one now assumes that $V = V_0$, where V_0 is the undeformed volume, and hence that the mean field energy can be ignored in differentiating, one obtains

$$\tau = (nkT\langle\lambda_1\rangle s_0^2/\langle l^2\rangle_0 V_0)(\alpha - 1/\alpha^2) \tag{47}$$

The modulus is seen to be intensive and to depend upon the ensemble average network structure through $\langle\lambda_1\rangle$.

Conclusions

The mean field approximation may be effectively exploited to restrain the theoretical collapse of networks. The elastic restoring forces in a network act to pull the junctions to the center of the elastic body, but they are prevented from doing so by the incompressibility of the atoms.

The collapse of unconstrained or phantom networks turns out to be a boon rather than a problem. This is the case because it is relatively easy to calculate the distribution function of the phantom or unperturbed network in the asymptotic limit where the dimensions greatly exceed those of the most probable state. The form of the distribution function in this limit is found to give satisfactory results for (1) the thermodynamic density, (2) the increase of density with cure, (3) the decrease of compressibility with cure, and (4) the stress–strain relation in first approximation.

The critical network parameters that govern all elastic behavior are the minimum nonzero eigenvalue λ_1 of the Kirchhoff matrix of the gel component and its multiplicity ω_1. There is as yet no simple translation of these parameters into more familiar terms except for that provided by computer simulations.[10] The evaluation of λ_1 and ω_1, or better yet the entire spectrum of the Kirchhoff matrix, is the crucial graph theoretic problem that remains to be solved to obtain an elastic equation of state of practical value.

Note Added in Proof. McKay[13] has recently found a graph theoretic proof that $\lambda_1 = O(n^{-2/3})$ for all nets that have resonable constraints on their densities.

Acknowledgment. The author is indebted to Professor W. H. Stockmayer for drawing his attention to the work of F. W. Boggs.

References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953; p 602.
(2) For a recent review, see: Higgins, J. S.; Stein, R. S. *J. Appl. Crystallogr.* **1978**, *11*, 346.
(3) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656.
(4) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4104.
(5) Eichinger, B. E. *J. Chem. Phys.* **1976**, *65*, 2041.
(6) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(7) James, H. M.; Guth, E. *J. Chem. Phys.* **1943**, *11*, 455. *Ibid.* **1947**, *15*, 669. *J. Polym. Sci.* **1949**, *4*, 153.
(8) McKay, B. D., manuscript in press.
(9) Eichinger, B. E. *Macromolecules* **1980**, *13*, 1.
(10) Eichinger, B. E. *J. Chem. Phys.*, in press.
(11) Ball, R. C.; Edwards, S. F. *Macromolecules* **1980**, *13*, 748.
(12) Eichinger, B. E. *Macromolecules* **1977**, *10*, 671.
(13) McKay, B. D., unpublished.
(14) Martin, J. E.; Eichinger, B. E. *Macromolecules* **1980**, *13*, 626.

(15) Fixman, M. *J. Chem. Phys.* **1962**, *36*, 306.
(16) Katchalsky, A.; Curran, P. F. "Nonequilibrium Thermodynamics in Biophysics"; Harvard: Cambridge, 1967; Chapter 7.
(17) Fixman, M. *J. Chem. Phys.* **1961**, *35*, 889.
(18) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.
(19) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; Chapter 9, Appendix A.
(20) Boggs, F. W. *J. Chem. Phys.* **1952**, *20*, 632.
(21) Flory, P. J.; Fisk, S. *J. Chem. Phys.* **1966**, *44*, 2243.
(22) Hermans, J. J.; Overbeek, J. Th. G. *Recl. Trav. Chim. Pays-Bas* **1948**, *67*, 761.
(23) Wood, L. A.; Martin, G. M. *J. Res. Natl. Bur. Stand., Sect. A* **1964**, *68*, 259.
(24) Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 59.

Compatibility of Polymer Mixtures Containing Novolac Resins

S. R. Fahrenholtz* and T. K. Kwei*,†

Bell Laboratories, Murray Hill, New Jersey 07974. *Received November 3, 1980*

ABSTRACT: Certain novolac resins were found to be compatible with poly(ethyl acrylate), poly(ethyl methacrylate), poly(methyl methacrylate), poly(vinyl acetate), poly(styrene-*co*-acrylonitrile), poly(2-methyl-1-pentene sulfone), polycarbonate, and poly(vinyl methyl ether). However, poly(4-vinylphenol) was found to be incompatible with poly(methyl methacrylate) or poly(styrene-*co*-acrylonitrile). Chemical interaction between the novolac resins and either poly(ethyl methacrylate), poly(ethyl acrylate), poly(vinyl acetate), poly(methyl methacrylate), or polycarbonate was manifested by a shift of ~20 cm^{-1} in the infrared stretching frequency of the carbonyl group. Large positive deviations of the experimentally observed glass transition temperatures from the calculated weight-average values were noted in mixtures containing poly(vinyl methyl ether) or poly(ethyl acrylate). The compatibility of these systems is discussed in terms of increased specific interactions between unlike polymers and decreased specific interactions between like polymers.

Introduction

Although novolac resins are used widely as ingredients in coatings and adhesives,[1] their miscibility with high molecular weight polymers has not been extensively documented.[2] We wish to report the results of a preliminary study in which the miscibilities of four novolac resins with polystyrene (PS), poly(styrene-co-acrylonitrile) (PSAN), poly(ethyl acrylate) (PEA), poly(vinyl acetate) (PVA), poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA), poly(2-methyl-1-pentene sulfone) (PMPS), bisphenol-A polycarbonate, and poly(vinyl methyl ether) (PVME) were investigated by calorimetry.

In order to help to understand the reasons for the miscibilities, the specific polymer–polymer interactions were investigated by infrared (IR) spectroscopy. In contrast to previous IR studies on different polymer–polymer systems,[3-6] we observed interactions that gave relatively large shifts in the infrared stretching frequencies of the carbonyl groups.

Experimental Section

1. **Materials.** PS, PSAN containing 25% by weight of acrylonitrile, PVME, PEMA, and poly(4-vinylphenol) were purchased from Polysciences, Inc. PMMA and PEA were obtained from Cellomer Associates, Inc. PMPS, an alternating copolymer of 2-methyl-1-pentene and sulfur dioxide, was prepared in this laboratory by a procedure which has been reported previously.[7] Bisphenol-A polycarbonate was a stabilizer-free sample obtained through the courtesy of General Electric Co. PVA was supplied by Aldrich Chemical Co. All polymers were dried in a vacuum oven at 100 °C overnight prior to use.

The novolacs were made by condensing formaldehyde with mixtures of substituted phenols. The published method for unsubstituted novolacs[8] was modified by allowing the reaction to proceed for 18 h at reflux before water and unreacted phenols were removed by vacuum distillation. Novolac 1 was synthesized here, novolac 2 at Polychrome, and novolacs 5 and 8 at Mead Chemical Co. according to our specifications (see Table I).

The blend samples for calorimetric studies were prepared by mixing appropriate amounts of the constituents in 2-butanone and allowing the solvent to evaporate slowly at room temperature. In the case of the polycarbonate mixture, methylene chloride was used as the solvent and the temperature of solvent evaporation was maintained at about 45 °C to increase the solubility of the novolac resin. The samples were again vacuum dried at 100 °C overnight.

Infrared studies were made by casting films from solution on salt plates, using concentrations adjusted to give about 20% transmittance through the dried film in the region of interest. The solvent was a mixture of 10% tetrahydrofuran–90% methylene chloride. The concentrations were as follows:

Blends for IR Studies

studies on carbonyl region	studies on hydroxyl region
95% novolac	2–4% novolac
5% carbonyl compound	98–96% carbonyl compound

The solvent was allowed to evaporate at room temperature followed by vacuum drying for 2–5 h at 85 °C. In one case when the film was used without this final drying the wavelengths absorbed were the same but the spectrum was not as well resolved.

2. **Calorimetry.** A Du Pont Model 990 differential scanning calorimeter was used for glass transition temperature measurements. The transition temperature was taken as the onset (extrapolated) of the abrupt increase in the specific heat of the specimen. Specimens were first heated at 10 °C/min to 100 °C in the calorimeter and then quenched by liquid nitrogen to an appropriately low temperature, after which heating was resumed. The experiment was repeated at least twice for each specimen and the reproducibility of the T_g value was about ±0.7 °C unless otherwise stated.

3. **Infrared Spectroscopy.** A Perkin-Elmer Model 597 infrared spectrometer was used for the IR studies. One sample was checked on a Digilab Fourier transform infrared spectrometer but gave qualitatively the same spectrum. All spectra were run on salt plates. To check that the shifts were not caused by changes in the index of refraction of the different polymers, a polished silicone plate was also used as the substrate in one experiment.[9] No difference in the wavelength of absorption was observed whether salt or silicone was used.

Results

Novolac 1 was incompatible with PS. The mixture was cloudy and two distinct T_g's were found in the thermogram. All the mixtures listed in Table II were compatible with each mixture, showing one T_g, which, except in the case of novolac 1 with PVME and with PEA, was either equal to or lower than the calculated weight-average value

---

[†] Now at Industrial Technology Research Institute, Taiwan.

0024-9297/81/2214-1076$01.25/0