Table I
Experimental Values of ρ of Polystyrene in Cyclohexane (except for the Last Value) at the Θ Temperature

M	N	R_H, nm	R_G, nm	ρ	ref
4.1×10^6	4660	45.4	59.9	1.32	26
6.7×10^5	761	17.29	24.2	1.40	26
1.79×10^5	203	9.44	12.5	1.32	26
1.1×10^5	125	7.31	9.82	1.34	26
2.7×10^6	3068	36.28	48.6	1.34	24
6.7×10^5	761	18.36	24.2	1.32	24
2.0×10^5	227	9.99	13.2	1.32	24
1.1×10^5	125	7.26	9.82	1.35	24
2.1×10^4	24	3.41	4.29	1.26	24
1.79×10^5	203	9.11	13.0	1.43	25

be difficult to see in the presence of the $1/N^{1/2}$ approach to the asymptotic behavior. In particular, correction terms of order ln N, as de Gennes[17] found for $\langle R^2 \rangle$, or N^δ (for $\delta < {}^1/_2$) would be nearly impossible to detect by our Monte Carlo calculations. In the same vein, such weak N variations would be difficult to detect experimentally.

We should remark, however, that in our earlier work[10] we did notice that the partition function of the Monte Carlo generated chain did not go to the expected Gaussian value of 1 at the Θ temperature; rather, it reached 1 at a value of $\epsilon/RT = 0.250$, somewhat lower than the Θ temperature. This observation is consistent with theoretical results[17,18] that the third virial is finite for N approaching infinity at the Θ point (the temperature at which $R_G{}^2 \sim N$). However, we are unaware of any earlier arguments that any of the distance moments themselves show non-Gaussian behavior.

IV. Comparison with Experiment

The ρ_E factor was computed for polystyrene of various molecular weights in cyclohexane at the Θ temperature from values of R_G obtained from elastic light scattering and values of $1/R_H$ obtained from quasi-elastic light scattering using eq 1 and 2.

Recent experimental values[19-21] of the root-mean-square radius of gyration of polystyrene in cyclohexane at the Θ temperature were fit to the equation

$$R_G = 0.0296M^{1/2} \quad \text{(nm)} \tag{14}$$

This value of 0.0296 is slightly larger than that of 0.0290 used by Schmidt and Burchard[3] because we used only data for cyclohexane while they used data for several solvents. The values of R_H were measured for four polystyrene samples in cyclohexane at the Θ temperature by using the experimental method given in ref 22. These measurements and others from the literature with the calculated values of ρ_E are given in Table I.

The number of statistical steps in these polystyrene samples must be determined before their values of ρ_E may be compared to Monte Carlo and analytical Gaussian coil values. The number of monomers, n, in a polystyrene molecule is $M/104$ and the length, b, of the monomer for the molecule in the extended (trans) configuration is[23] 0.255 nm. Therefore

$$C_n = 8.41 \tag{15}$$

and

$$N = n/8.41 = M/874 \tag{16}$$

The number of statistical steps, N, of the polystyrene samples computed by eq 16 is given in Table I and the experimental values of ρ in Table I are plotted in Figure 2 vs. N. The previously computed values of ρ are also shown for the Gaussian coil and Monte Carlo models, each with values of h^* of 0.3 and 0.4, in Figure 2. It is clear the Monte Carlo model is in better agreement with the experimental values than the analytical Gaussian coil model.

As we have indicated earlier in this paper, the result reported here is only one possible explanation for the disagreement between the experimental ρ_E and the analytical Gaussian coil value of ρ. The Kirkwood theory with its many assumptions may be in error. Our model of the chain used for Monte Carlo simulation may not be realistic enough. Or the errors in extrapolation discussed in section IV may be important. Therefore our results should be viewed as tentative.

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References and Notes

(1) Kirwood, J. G. *J. Polym. Sci.* **1954,** *12,* 1.
(2) Zimm, B. H. *J. Chem. Phys.* **1956,** *24,* 269.
(3) Schmidt, M.; Burchard, W. *Macromolecules* **1981,** *14,* 211.
(4) Jones, G.; Caroline, D. *Chem. Phys.* **1979,** *40,* 153.
(5) Nose, T.; Chu, B. *Macromolecules* **1979,** *12,* 590.
(6) Schmidt, M. Doctoral Thesis, Freiburg, Feb 1980.
(7) Horta, A.; Fixman, M. *J. Am. Chem. Soc.* **1968,** *90,* 3048.
(8) Zimm, B. H. *Macromolecules* **1980,** *13,* 593.
(9) Benmouna, M.; Akcasu, A. Z. *Macromolecules* **1980,** *13,* 409.
(10) McCrackin, F. L.; Mazur, J.; Guttman, C. M. *Macromolecules* **1973,** *6,* 859.
(11) Wang, F. W. *J. Polym. Sci.* **1975,** *13,* 1215.
(12) Yamakawa, H. "Modern Theory of Polymer Solutions"; Wiley: New York, 1969; pp 917, 149, 329.
(13) Akcasu, A. Z.; Higgins, J. S. *J. Polym. Sci.* **1977,** *15,* 1745.
(14) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Harper and Row: New York, 1971.
(15) Osaki, K. *Macromolecules* **1972,** *5,* 141.
(16) Elias, H. G. "Macromolecules"; Plenum Press: New York, 1979; Vol. 1.
(17) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979. See also: *J. Phys. (Paris)* **1975,** *36,* L-55. *Ibid.* **1978,** *39,* L-299.
(18) Sanchez, I. C. *Macromolecules* **1979,** *12,* 980. See also: Oyama, T.; Oono, Y. *J. Phys. Soc. Jpn.* **1977,** *42,* 1348.
(19) Miyaki, Y.; Einaga, Y.; Fujita, H.; Fukuda, M. *Macromolecules* **1980,** *13,* 588.
(20) Yamamota, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971,** *2,* 799.
(21) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978,** *11,* 1180.
(22) Han, C. C.; McCrackin, F. L. *Polymer* **1979,** *20,* 427.
(23) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975,** *8,* 776.
(24) King, T. A.; Knox, A.; McAdam, J. D. G. *J. Polym. Sci., Polym. Symp.* **1974,** *No. 44,* 195.
(25) Nose, T.; Chu, B. *Macromolecules* **1979,** *12,* 590. The solvent was *trans*-decalin. Both $\langle S^2 \rangle^{1/2}$ and $\langle 1/R_H \rangle$ were experimentally determined.
(26) This work.

Conformational Analysis of Syndiotactic Polymer Chains in the Crystalline State: Polypropylene and 1,2-Poly(1,3-butadiene)

PAOLO CORRADINI, ROBERTO NAPOLITANO, VITTORIO PETRACCONE,* BENIAMINO PIROZZI, and ANGELA TUZI

Istituto Chimico, Università di Napoli, 80134 Napoli, Italy.
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Conformational energy maps for the isolated chain of syndiotactic polypropylene were calculated by Natta, Corradini, and Ganis[1] under the restriction of a periodic repetition. The calculations were performed under the approximation of constant valence angles; moreover, for the interactions between nonbonded atoms, the methyl and

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Table I
Nonequivalent Minimum-Energy Conformations of Syndiotactic Polypropylene according to Our Calculations

	conformation[a]	τ_{CH}, deg	τ_{CH_2}, deg	E, kJ (mol CRU)$^{-1}$	symmetry
a	...175.8°,175.8°,55.7°,55.7°...	110.9	114.4	0	s(M/N)2
b	...178.8°,178.8°,–179.1°,–179.1°...	108.0	115.5	2.7	s(M/N)2
c	...178.3°,178.3°,157.4°,157.4°...	111.2	113.8	5.0	s(M/N)2
d	...179.6°,179.2°,–179.6°,–179.2°...	112.6	113.9	9.0	*tc*

[a] Conformations a, b, and d have been obtained by imposing only the indicated symmetry. Conformation c has been obtained under the further restriction of having a unit height of 5.05 Å for two monomeric units.

methylenic groups were assumed as single units. The condition of a periodic repetition was considered for the two symmetries that are possible according to the equivalence postulate:[2] repetition through a glide plane (*tc* symmetry of the chain), corresponding to a succession of isoclined enantiomorphic units, and repetition through a helix, associated with twofold axes perpendicular to the chain (s(M/N)2 symmetry of the chain), corresponding to a succession of anticlined isomorphous units.[3] The results brought prediction of two possible nonequivalent conformations of minimum energy, both of them nearly corresponding to those existing in the two crystalline modifications experimentally observed.[4,5]

We have performed new calculations of the conformational energy of syndiotactic polypropylene according to recent developments of the methods of conformational analysis;[6] that is, we include the possible variation of all the valence angles ∠C–C–C along the main and lateral chains and of all the torsional angles, never considering a group of atoms as a single unit. The energetic parameters used are those of Flory et al.[7-9] Flory et al. have already performed conformational energy calculations for syndiotactic polypropylene,[7] but without the restriction of a periodic repetition, since they were interested in establishing the possible chain conformations in a Θ solvent. The method of calculation and minimization of the energy in respect to many parameters is that reported by us in a preceding paper.[10] We have performed the calculations on a piece of the chain corresponding to five monomeric units, both for the helical and the glide plane symmetry. The results for the helical symmetry are reported in Figure 1.

At variance with previous maps, the absolute minimum occurs for the $\sim$...TTG_+G_+... (≡...G_-G_-TT...) conformation experimentally observed for the most stable modification of syndiotactic polypropylene.[4] The other minimum occurs for a nearly ...TTTT... conformation. Conformations near to ...TTTT... are possible both for the *tc* and the s(M/N)2 symmetries of the chain.

The experimental X-ray data on the second crystalline modification of syndiotactic polypropylene gives a strong indication that the chain conformation must be highly extended and nearly zigzag planar, since the most intense reflections may be interpreted on the basis of an identity period $c = 5.05 \pm 0.10$ Å, comprising two monomeric units. Some faint reflections occurring in the most exposed X-ray photographs may be indicative, however, of a long-distance spiralization as originally pointed out by Natta et al.[5] and checked again by us.

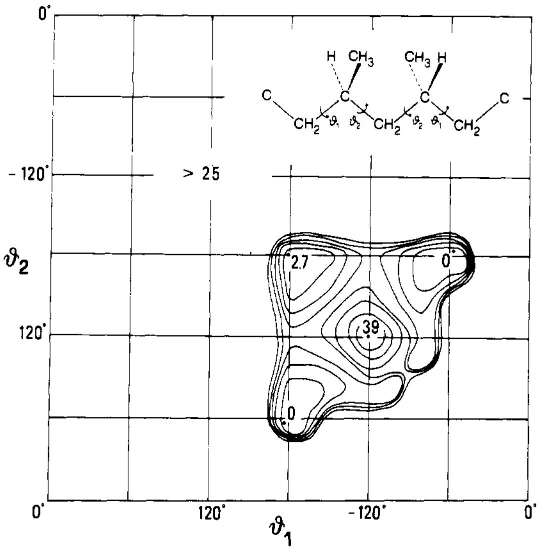

Figure 1. Internal energy map for helical conformations (...θ_1,θ_1,θ_2,θ_2...) of a syndiotactic polypropylene chain. The curves are reported at intervals of 5 kJ/(mol CRU). For each pair θ_1,θ_2 the values of the other parameters are those for which the energy assumes the minimum value.

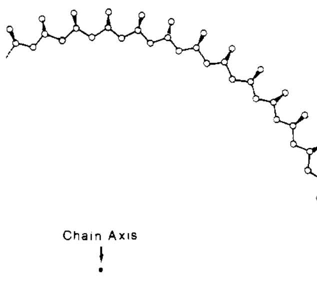

Figure 2. Projection along the chain axis of the minimum-energy conformation near ...TTTT... for a syndiotactic polypropylene chain (conformation b in Table I).

The minimum that corresponds in Figure 1 to the conformation $\sim$...TTTT... (s(M/N)2 symmetry) occurs for valence angles of 115.5° at the CH_2 and valence angles of 108.0° at the CH (Table I). The departure of these valence angles from equality leads to a conformation that corresponds to a large-radius helix with a very short unit height (0.21 Å). Such a conformation is only locally near to trans planar (Figure 2) and disagrees with the experimental data. A similar result has been discussed by Beck and Hägele[11] for the case of isotactic polystyrene. For a *tc* symmetry of the chain, the conformation of minimum energy, which is obtained by varying all possible internal parameters, has an identity period of 5.15 Å but the energy is 6.3 kJ/(mol CRU), higher than that at the minimum $\sim$...TTTT... of Figure 1. The higher energy of the *tc* conformation arises from the need of having nearly equal valence angles at the CH_2 and at the CH along the chain (see Table I). Therefore we have searched for helical conformations in the neighborhood of ...TTTT... satisfying the conditions of being extended (with a unit height as expected for an all-trans conformation) and of having an energy significantly lower than that corresponding to a *tc* symmetry.

For this purpose we have calculated a map that gives the unit height per two monomeric units in the case of the helical repetition, associated with twofold axes perpendicular to the chain axis (...$\theta_1\theta_1\theta_2\theta_2$...), which is shown in Figure 3. The superposition of this map with that of

Table II
Nonequivalent Minimum-Energy Conformations of Syndiotactic 1,2-Poly(1,3-butadiene) according to Our Calculations

conformation	τ_{CH}, deg	τ_{CH_2}, deg	E, kJ (mol CRU)$^{-1}$	symmetry
...–162.4°,–162.4°,77.5°,77.5°...	110.5	112.1	4.2	s(M/N)2
...–175.2°,–175.2°,174.8°,174.8°...	109.7	113.1	0	s(M/N)2
...–173.5°,–175.4°,173.5°,175.4°...	113.2	113.5	2.8	t*c*

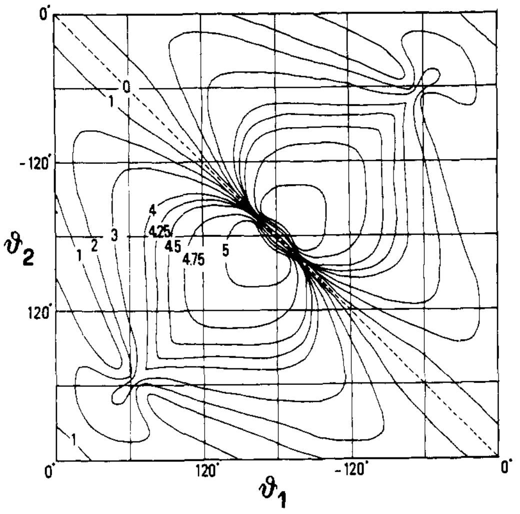

Figure 3. Map of the unit heights (h/Å) for two monomeric units of a hydrocarbon chain for the s(M/N)2 symmetry (...$\theta_1,\theta_1,\theta_2,\theta_2$...) with l_{C-C} = 1.53 Å and bond angles alternately 111° and 113°.

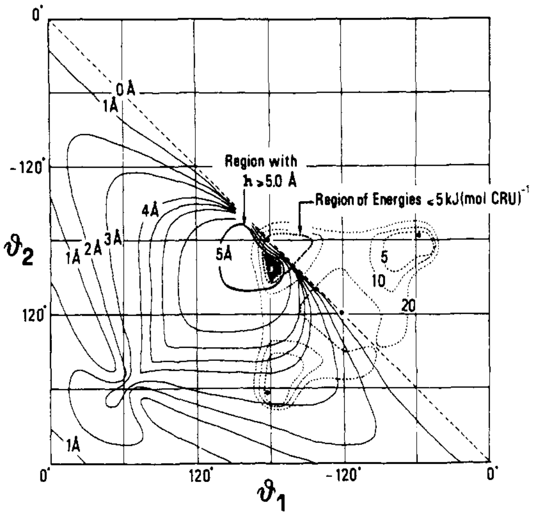

Figure 4. Superposition of some portions of the maps of Figures 1 and 3. The point at θ_1 = 178.3°, θ_2 = 157.4° indicates the torsion angle corresponding to the minimum c of Table I.

Figure 1 is shown in Figure 4. It is seen that the region of conformations having $h \geq 5.0$ Å overlaps with the region of energies ≤5 kJ/(mol CRU) for values in the neighborhood of θ_1 = 180°, θ_2 = 160° (or θ_1 = –160°, θ_2 = 180°; this last equivalent minimum is omitted in the figure for clarity). We have minimized the energy around this point, having as our only restriction a unit height h = 5.05 Å. As a result we have obtained a highly extended-chain model having θ_1 = 178.3°, θ_2 = 157.4°, τ_{CH} = 111.2°, τ_{CH_2} = 113.8°, and energy 5.0 kJ/(mol CRU) (see Table I). This value of energy is definitely lower than that corresponding to the t*c* symmetry (9.0 kJ/(mol CRU)) and it is nearer that of the minimum of the map of Figure 1 (2.7 kJ/(mol CRU)) in the region of the ...TTTT... conformation.

We believe that conformations of this kind, corresponding to complex helices having a subperiodicity of nearly 5 Å for two monomeric units, may be present in the second modification of syndiotactic polypropylene.

The need of a slight spiralization in respect to an all-trans conformation arises mainly from the interaction between the lateral CH_3 group with the CH hydrogen atoms of the adjacent monomeric units.

It is reasonable to predict that in the case of polymers such as syndiotactic 1,2-poly(1,3-butadiene), for which the lateral group is planar, such kind of interaction should not occur and the main chain can keep an almost perfectly trans low-energy conformation. To this end we have performed analogous calculations for the above-indicated polymer. The results are collected in Table II. First of all, in this case, for the helical symmetry (Figure 5) the minimum in the region ...TTTT... becomes the absolute minimum, while the ...TTGG... minimum has an energy 4.2 kJ/(mol CRU) higher. Moreover, for the t*c* symmetry, which corresponds to the crystallographic symmetry of the polymer, the energy is only 2.8 kJ/(mol CRU) higher than the absolute minimum, which again corresponds to a large-radius, difficult-to-pack helix (and 1.4 kJ/(mol CRU) lower than the ...TTGG... minimum). Such a symmetry corresponds very nearly to the experimentally observed conformation,[12] reconfirming the deviation of the internal rotation angles from a completely trans conformation.

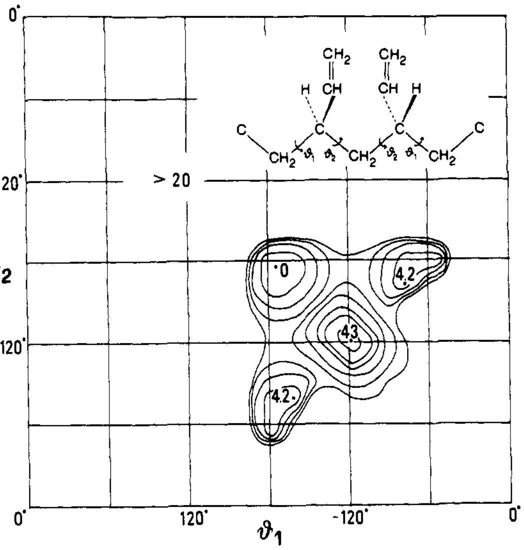

Figure 5. Internal energy map for helical conformations (...$\theta_1,\theta_1,\theta_2,\theta_2$...) of a syndiotactic 1,2-poly(1,3-butadiene) chain. The curves are reported at intervals of 5 kJ/(mol CRU). For each pair θ_1,θ_2 the values of the other parameters are those for which the energy assumes the minimum value.

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References and Notes

(1) Natta, G.; Corradini, P.; Ganis, P. *Makromol. Chem.* **1960**, *39*, 238.
(2) Corradini, P. *Atti Accad. Naz. Lincei, Rend.* **1960**, *28*, 1.
(3) The chain symmetries and conformations are denoted according to: IUPAC Commission on Macromolecular Nomencla-

ture. *Pure Appl. Chem.* **1979**, *51*, 1101.
(4) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C* **1967**, *16*, 2477.
(5) Natta, G.; Peraldo, M.; Allegra, G. *Makromol. Chem.* **1964**, *75*, 215.
(6) Corradini, P.; Petraccone, V.; Pirozzi, B. *Eur. Polym. J.* **1976**, *12*, 831.
(7) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(8) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(9) Yoon, D. Y.; Suter, U. W.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 784.
(10) Corradini, P.; Napolitano, R.; Petraccone, V.; Pirozzi, B.; Tuzi, A. *Eur. Polym. J.* **1981**, *17*, 1217.
(11) Beck, L.; Hägele, P. C. *Colloid Polym. Sci.* **1976**, *254*, 228.
(12) Natta, G.; Corradini, P. *J. Polym. Sci.* **1956**, *20*, 251.

Communications to the Editor

Percolation Transition and Elastic Properties of Block Copolymers[†]

Recent advances in percolation theory have provided a new conceptual framework for a better understanding of composite materials and their properties, which are known for their complexity and intractability.[1] The central question in the original formulation of percolation theory, in which sites (or bonds) of a lattice can be occupied randomly with a certain probability p, concerns the conditions under which there would be a macroscopic association of occupied sites (or bonds) that pervades the whole lattice. In addition to this size information, modern percolation theory also addresses the question whether there is any singular behavior in relevant physical quantities when the average size of connected cluster of one component diverges, since the occupied and empty sites (or bonds) may possess contrasting physical properties. For example, they may represent, respectively, conductor and insulator, absorbing and transparent materials, or rubbery and brittle components. Although recent theoretical and experimental work on composite properties in conductivity,[1–5] dielectric constant,[6,7] Hall effect and magnetoresistance,[8] optical transmissivity and reflectivity,[9] and magnetism[10] has established several interesting correlations with the underlying percolation transition, analogous studies on mechanical properties have not been reported. We show here that elastic properties also undergo a rapid change near the percolation threshold. Our strategy is to first formulate an effective medium theory[11] for the elastic moduli and interpret out results by using concepts from percolation theory.[1] By analogy to the conductivity problem and applying scaling arguments,[12] we have identified the relevant critical exponents and their values. We then apply our results to block copolymers of styrene and butadiene[13] between the two glass transitions. The computed shear modulus with *no* adjustable parameter agrees very well with the torsion pendulum data. The same theory has also successfully accounted for the tensile properties of wet perfluorinated ionomers.[14] We conclude with a brief comparison of the present theory and interpretation with the previous attempts.

We consider in the following an ideal composite system in which spherical particulates of one material are randomly dispersed in the matrix of another. For simplicity each component is assumed to be macroscopically homogeneous and isotropic and thus can be characterized by the values of any two of the elastic modulii, say the bulk modulus K and the shear modulus G. The problem is to evaluate the effective moduli K_{eff} and G_{eff} in terms of the component values K_1, G_1 and K_2, G_2. For the case of glass particles, e.g., polystyrene below its glass transition temperature T_g (~100 °C), embedded in a rubber, say polybutadiene above T_g (~0 °C), a rubber-to-glass transition is expected. Qualitatively, this arises as follows. At low polystyrene contents, the hard styrene segments form separated domains that cannot react cooperatively, and the composite is controlled by the continuous, rubbery, polybutadiene phase. In the opposite extreme the glassy phase forms an extended network that pervades the entire system and collectively dominates the elastic properties. Somewhere between these limits a critical level of styrene loading exists at which the solid domains start interacting coherently—this is the percolation threshold. Around this composition the shear modulus would change rapidly.

This phenomenon can be established more rigorously by using the effective medium theory.[11] In this approach we imagine replacing the composite system by a homogeneous effective medium that has the same macroscopic properties (the bulk modulus K_{eff} and the shear modulus G_{eff}) as the composite system. The changes in the stresses and strains in the medium are calculated when a small portion of the effective medium is replaced by one of the components that make up the composite material. To ensure self-consistency we require the average change in these quantities to be zero when the particles are dispersed randomly.[15] These procedures are basically similar to those employed in the studies of transport,[16,17] optical,[18] and acoustic[19] properties. When states of pure shear and compression are considered, the following pair of equations emerge:

$$\frac{c(1 - K_1/K_{\text{eff}})}{3K_1 + 4G_{\text{eff}}} + \frac{(1 - c)(1 - K_2/K_{\text{eff}})}{3K_2 + 4G_{\text{eff}}} = 0 \qquad \text{(1a)}$$

$$\frac{c(1 - G_1/G_{\text{eff}})}{\alpha G_1 + G_{\text{eff}}} + \frac{(1 - c)(1 - G_2/G_{\text{eff}})}{\alpha G_2 + G_{\text{eff}}} = 0 \qquad \text{(1b)}$$

where $\alpha = (8 - 10\nu_{\text{eff}})/(7 - 5\nu_{\text{eff}})$, c is the volume fraction of component 1, and ν_{eff} is the effective Poisson ratio for the composite. Eliminating K_{eff}, we obtain

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