of the manuscript. I thank Professor M. Gordon for bringing to my attention a number of useful references, and I am very much indebted to Professor I. Noda for sending me the original data underlying ref 28. A part of these data has been used in the analysis in connection with Figure 8.

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Computer Experiments on Branched-Chain Molecules

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ABSTRACT: Star-shaped chain molecules with 4, 6, and 8 branches were simulated on a 5-choice simple cubic lattice according to Metropolis' scheme where the nearest-neighbor interactions were taken into account. Approximately 100 000 samplings were made for each chain over the Φ range 0.275–0.750. Here Φ denotes $-\epsilon/k_BT$, with ϵ being the attractive energy between a pair of unbonded units on the adjacent lattice sites; $\Phi_\Theta = 0.275$ corresponds to the Θ point as estimated by McCrackin et al. The data scattered considerably owing to branch segregation observed below the Θ point, so it was not possible to estimate the Θ point exactly. Taking $\Phi_\Theta = 0.275$ for branched chains as well, chain collapse was found to follow the equation based on the tricritical conjecture regardless of the number of branches.

1. Introduction

The Flory temperature (Θ point) is defined[1] as a reference point for chain configuration in solution in analogy with the Boyle temperature of an imperfect gas, where the binary interaction term vanishes. A linear chain is known to behave quasi-ideally[2] at the Θ point though the higher (ternary etc.) interaction terms have still nonzero values to spoil the exactness of the Θ point.[3] A quasi-ideal configuration of a linear chain is characterized by the proportionality of the second moment of chain distribution (the mean-square radius of gyration) to the chain length. However, its higher moments are not necessarily proportional to the corresponding powers of the chain length because of the nonzero values in the higher interaction terms, so the chain distribution is not strictly Gaussian. The most comprehensive view on the chain configuration just above the Θ point is offered by two-parameter theory,[4] which is based on Gaussian statistics and a δ-function binary interaction. The experimental data on linear-chain solutions are discussed satisfactorily in terms of two-parameter theory where the Θ point is estimated from the condition that the second virial coefficient is zero. In practice, the two-parameter approximation is satisfied for the linear-chain system. The two-parameter approximation fails when the attractive interaction becomes serious (below the Θ point) and chain molecules collapse to a rather dense form.[5]

As compared to a linear chain, a branched chain expands faster and its virial coefficient grows slower with increasing quality of solvent when the two-parameter approximation is applied to a branched-chain structure.[6] Though qualitatively correct, the two-parameter approximation fails in detail for the branched-chain system[8,9] probably because of the higher interaction terms due to increased segment density by branching. A depression of the Θ point was noted by branching[9–11] though this apparent depression may be caused again by the higher interaction terms (the third virial coefficient etc.).[12]

The characteristic changes of the conformational properties due to branching is often concealed by the mostly very pronounced heterogeneity with respect to size and structure. Classic examples are the osmotic pressure of

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glycogen aqueous solution, obeying the van't Hoff law,[13] and the behavior of randomly branched polycondensates. For instance, the mean-square radius of gyration of critically branched products is proportional to the degree of polymerization, and its second virial coefficient is close to zero regardless of temperature[14] although apparently good solvents were used. The present work is motivated by the above-mentioned characteristics of branched-polymer solutions. Isolated star-like coupled chains of up to 1202 units are generated on a 5-choice simple cubic lattice where the chains are not allowed to self-intersect. The chains are made of 4, 6, or 8 branches of equal length. The simulation follows the Metropolis scheme[15] and the energy of each configuration is calculated by counting the nearest-neighbor interaction potentials $\Phi = -\epsilon/k_BT$, where ϵ is the attractive energy between a pair of unbonded units on the adjacent lattice sites, k_B is the Boltzmann constant, and T is the temperature. Approximately 100 000 samplings are made for each chain with a wide range of Φ according to the procedure described previously.[16] (A similar simulation procedure was applied to the linear-chain system to check the "thermal blob" theory.[17]) The present work complements the earlier work of Mazur and MaCrackin,[23b] which was confined to the temperature region above the Θ point, while here the temperature is extended below the Θ point.

2. Fundamentals

The radius of gyration of star-shaped chains generated on the simple cubic lattice with a 5-choice random walk is given in the limit of $N \rightarrow \infty$ by[18]

$$\langle S^2 \rangle = \frac{3}{2}\left(\frac{1}{2f} - \frac{1}{3f^2}\right)N \tag{1}$$

where N denotes the number of chain units and f the number of branches. The proportionality factor is corrected for the lattice type employed.[19] In general, $\langle S^2 \rangle^{1/2}$ depends on the step length a, which is taken as unity here. When the intramolecular interaction is taken into account, the radius of gyration follows the well-known scaling law; i.e.

$$\langle S^2 \rangle = AN^\gamma \qquad (N \rightarrow \infty) \tag{2}$$

Here the exponent γ is a function of Φ, decreasing from $^6/_5$ (no attraction; $\Phi = 0$ in athermal solution) to $^2/_3$ (infinite attraction; $\Phi = +\infty$, corresponding to chain collapse).[2,20] The size of the condensed (collapsed) chain is solely determined by the number of chain units and does not depend on the chain structure, so the lower limit of the exponent γ $(={}^2/_3)$ should be the same for any chain structure and so should be the proportionality constant A in eq 2. The upper limit of the exponent γ $(={}^6/_5)$ is confirmed for very large linear chains in good solvent by various means[2] and would be expected to hold for any chain structure as far as for the corresponding random-flight chain $\gamma = 1$ is obtained.[21] However, $\gamma = {}^1/_2$ is obtained for the unperturbed dimensions of the monodisperse fractions from randomly cross-linked chains or polyfunctional polycondensates (no loops) before gelation takes place, and $\gamma = 1$ is predicted for its upper limit.[21] (The computer simulation on regular-comb model polymers suggests that γ is close to $^6/_5$.[22]) Thus for star molecules, γ becomes unity at some intermediate Φ (the Θ point) and the mean-square radius of gyration is then proportional to N as given by eq 1. The chain is, however, quasi-ideal at this range of Φ, and eq 1 may not hold strictly. Here A in eq 2 is not exactly equal to $(3/2)(1/2f - 1/3f^2)$ whereas $\gamma = 1$. The Θ point also depends slightly on the chain length as suggested by computer simulation of an isolated linear chain[23a,24] and is given as a fairly restricted region rather than a unique point.

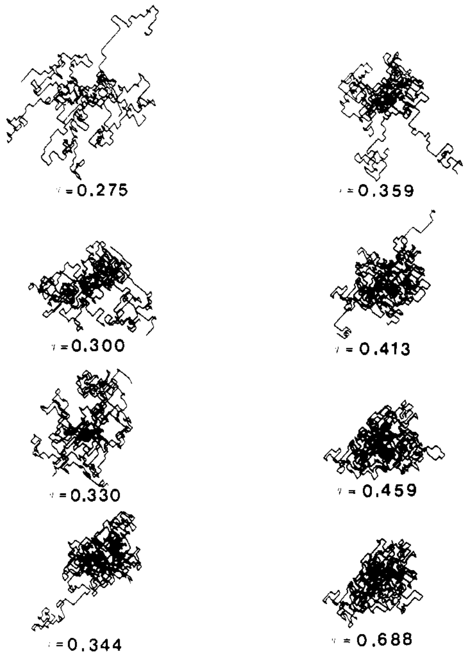

Figure 1. Simulated configurations of an 8-branch star-shaped chain molecule (N = 603) with various Φ values (as indicated in the figure).

Below the Θ point, the attractive intramolecular interactions dominate in the chain which would finally collapse to a compact globular form. (We treat here an isolated chain in solution.) This coil–globule transition may be related to a gas–liquid transition within the chain.[20] The tricritical analogy leads to the following relation in the collapse region:[2,25]

$$\langle S^2 \rangle \sim N^{2/3}(1 - \Phi_\Theta/\Phi)^{-2/3} \qquad (N \rightarrow \infty) \tag{3}$$

where the term $(1 - \Phi_\Theta/\Phi)^{-1}$ may be considered as a reduced temperature with respect to the Θ point. The exact same relation as eq 3 has been derived by considering the three-body interaction in addition to the pair interaction[26] in the conventional two-parameter theory. Equation 3 is expected to hold regardless of chain structure. (This statement is, of course, valid only for chains which are not hampered to form a close packing for steric or topological reasons.)

Another transition is predicted approximately at $\Theta/2$ K ($\Phi \simeq 0.55$), corresponding to a liquid–solid transition.[27]

3. Results and Discussion

3.1. Position of the Θ Point. The simulations were made with FACOM 230/48 and FACOM M180-AD computers at the Computer Center, Institute for Chemical Research, Kyoto University, Kyoto, Japan. The nearest-neighbor interaction potential Φ varies from 0.275 to 0.750, where $\Phi_\Theta = 0.275$ corresponds to the Θ point as estimated by McCrackin et al.[23] for linear chains as well as for star-shaped chains on the simple cubic lattice. $\Phi_\Theta = 0.269$ was estimated by Janssens and Bellemans[28] from the calculation of the osmotic second virial coefficient of nonathermal polymer solutions, simulated on the simple cubic lattice. Figure 1 illustrates one of the simulated configurations of an 8-branch star-shaped molecule (N = 603) at respective Φ values. Segregation of one or two branches is observed at higher Φ values (lower temperatures) till the chain completely collapses; this segregation causes strong data fluctuations in spite of the large sam-

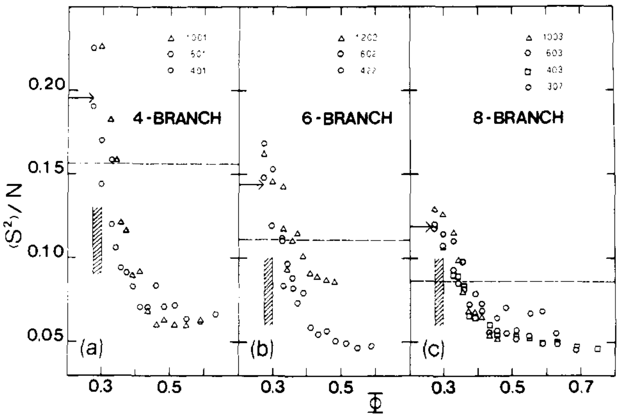

Figure 2. Mean-square radii of gyration of (a) 4-branch, (b) 6-branch, and (c) 8-branch star-shaped molecules plotted vs. Φ. The numbers in the figure indicate the correspondence of the respective symbols to the number of chain units. The horizontal broken lines represent the predicted mean-square radii of gyration for the random-flight model according to eq 1, and the shadowed areas show the Θ region (see text). The arrows show the mean-square radii of gyration of the respective star-shaped molecules ($N \to \infty$) at the Θ point as estimated by Mazur and McCrackin.[23b]

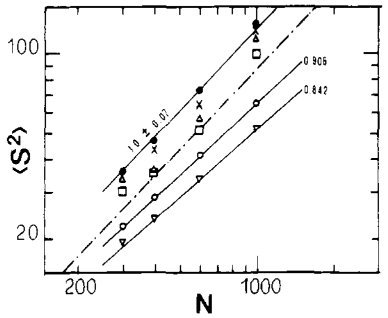

Figure 3. Radius of gyration of an 8-branch star-shaped chain molecule plotted vs. the number of chain units N for various Φ values on a double-logarithmic scale. Here the radii of gyration are shown for Φ values of 0.275 (●), 0.300 (×), 0.330 (△), 0.344 (□), 0.413 (○), and 0.459 (▽). The chained line represents the predicted radius of gyration for the random-flight model according to eq 1. The numbers in the figure denote the respective slopes.

pling applied in this computer work (no segregation is observed with linear chains). The mean-square radii of gyration (normalized by N) are plotted against Φ in Figure 2. The data scatter considerably due to the mentioned branch segregation. The horizontal lines in Figure 2 indicate the unperturbed dimensions for random-flight chains according to eq 1. These dimensions correspond to Φ values larger than 0.3, with a systematic shift to higher Φ values as the number of rays is increased. The arrows in Figure 2 show the corresponding values of the radii of gyration at Φ = 0.275 as estimated by Mazur and McCrackin,[23b] which agree with the present estimations.

Since in our study the Θ point (or region) is not distinct (Figure 2) as observed for computer-simulated linear chains,[23a] the Θ point (or region), i.e., the Φ_Θ value, was estimated by considering the following two factors: (i) the condition of $\langle S^2 \rangle_\Theta \sim N$ and (ii) the increase of $\langle S^2 \rangle_\Theta / N$ in a self-avoiding walk (SAW) of a linear chain to that of the random-flight chain.

Plots of log $\langle S^2 \rangle$ vs. log N show no clear linear relation over the Φ region 0.275–0.4 (see Figure 3) while at higher temperatures a good linearity was observed.[23b] A similar tendency (data scattering) has also been observed in the simulation of comb-shaped chains.[22] The line drawn in Figure 3 for the random-flight case as was calculated according to Zimm and Stockmayer,[18] however, suggests that the Θ region lies somewhere in the Φ range 0.275–0.35.

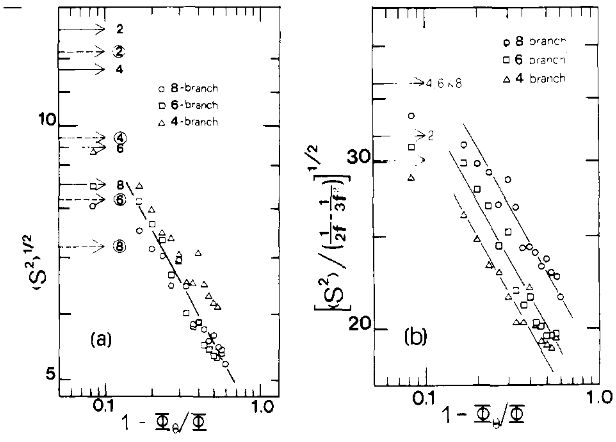

Figure 4. Radii of gyration of branched-chain molecules ((a) unnormalized and (b) normalized by the structure factor) plotted vs. $1 - \Phi_\Theta / \Phi$ on a double-logarithmic scale. The numbered horizontal arrows represent respective radii of gyration at the Θ point for 8-branch (8), 6-branch (6), 4-branch (4), and linear (2) chain molecules, where the solid-line arrows denote those observed (the value for the linear chain is due to McCrackin et al.) and the broken-line arrows denote the predicted radii of gyration for the random-flight model according to eq 1. The numbers of chain units are 601 (4 branch), 602 (6 branch), and 603 (8 branch), respectively. The solid straight line shows the slope $-^1/_3$.

The simulated chain by SAW on a lattice is expanded at the Θ point with respect to the random-flight chain. According to the results of McCrackin et al.,[23a] one has for linear chains on a 5-choice simple cubic lattice $\langle S^2 \rangle_\Theta / N = 0.282$, which is about 13% larger than the value for the corresponding random-flight chain, where $\langle S^2 \rangle / N = 0.250$. This discrepancy is due to the SAW model, where no lattice site is visited more than once, and is expected to increase by branching. Thus the chain contraction is limited to the distance of a lattice bond, though the favored contacts between nonadjacent units in poor solvent are taken into account by the nearest-neighbor attraction. (Alternative models are proposed to deal with the chain configuration when the attraction between nonadjacent units is favored. Here a lattice site is allowed to be visited more than once with or without the restriction that no lattice bond is used more than once. The model is termed the crossing[27b] or the interacting random walk,[29] respectively.) If we assume also for the star-shaped molecules an increase of 13% for $\langle S^2 \rangle / N$ for the SAW compared to the random walk value of eq 1, a value of $\Phi_\Theta = 0.30$ is obtained. Thus the Θ point is expected to be between $\Phi_\Theta = 0.275$ (a value of the linear chain) and 0.30 (for example, see Figure 4b).

Since no other criterion (see section 3.3) is available, the Θ point for the present system is assumed to coincide with that for the corresponding linear system (i.e., $\Phi_\Theta = 0.275$). Here the second moment of chain configuration seems approximately proportional to N (see Figure 3) though the chain is more expanded due to higher segment density than its linear homologue (see Figure 4). A similar tendency has been observed by Mazur and McCrackin,[23b] who also estimated the same value $\Phi_\Theta = 0.275$ for star-shaped chain molecules by computer simulation.

3.2. Θ Point Depression. In experiments, an apparent depression of the Θ point by branching has been observed for star- and comb-shaped molecules.[10] Here the Θ point was estimated from the condition that the second virial coefficient is zero by processing the light scattering data customarily with linear extrapolation. A computer analysis of the light scattering data of the cross-linked polystyrene samples in cyclohexane suggests, however, that this Θ point

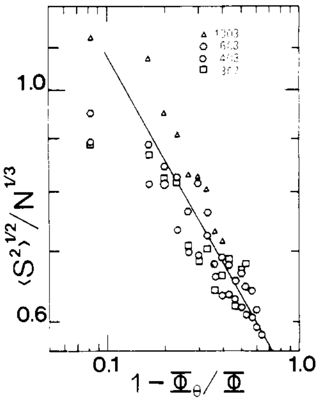

Figure 5. Radii of gyration of 8-branch star-shaped chain molecules of various numbers of units (as indicated in the figure) plotted vs. $1 - \Phi_\Theta/\Phi$ on a double-logarithmic scale. Here the radii of gyration are normalized by $N^{1/3}$. The solid straight line shows the slope $-^1/_3$.

depression may be an artifact due to the influence of the third virial coefficient, which was not properly taken into account. No depression of the Θ point of star-shaped molecules was also concluded by Mazur and McCrackin.[23b]

3.3. Chain Collapse. As discussed in the preceding section, the polymer chain never follows its ideal statistics even at the Θ point. This nonideal situation seems more pronounced for branched chains, probably due to higher segment density. Further below the Θ point, the chain collapses to a globular form where the segment density is supposed independent of chain structure. Then from the viewpoint of tricritical conjecture, the radius of gyration follows eq 3 regardless of chain structure, provided that the Θ point is given. The temperature dependence of eq 3 has been tested experimentally with positive results.[30,31] Our results seem to confirm this tricritical conjecture also for the star-shaped molecules, where $\Phi_\Theta = 0.275$ was taken as estimated for the linear homologue and as discussed in the preceding section. Figure 4 shows that the radius of gyration becomes independent of the chain structure in the collapse region. In Figure 4a the radius of gyration *itself* is plotted against the temperature parameter $1 - \Phi_\Theta/\Phi$ $(=1 - T/\Theta)$ on a double-logarithmic scale whereas in Figure 4b the radius of gyration normalized by the structure factor $(=(1/2f - 1/3f^2)^{1/2})$ is used. When normalized by the structure factor, the radius of gyration at the Θ point (shown by the horizontal line in Figure 4b) no more depends on the number of branches. On the other hand, the radius of gyration falls approximately on a common line of slope $-^1/_3$ in Figure 4a while the radius of gyration at the Θ point (shown by the horizontal lines, respectively) depends now strongly on the number of branches. Figure 5 confirms the $N^{-1/3}$ dependence of the radius of gyration where the radius of gyration divided by $N^{1/3}$ falls approximately on a common line of slope $-^1/_3$ regardless of the number of chain units when plotted against $1 - \Phi_\Theta/\Phi$ $(=1 - T/\Theta)$ on a double-logarithmic scale. Since the slope of these straight lines in Figures 4 and 5 depends on the position of the Θ point, this slope $-^1/_3$ indirectly confirms $\Phi_\Theta \simeq 0.275$ for branched chains.

The predicted transition at $\Phi \simeq 0.55$ was not observed in the present simulation.

3.4. Some Remarks on the Experimental Verification of the Coil–Globule Transition. Several attempts have been made to observe the coil–globule transition. Eventually Tanaka et al.[31] succeeded in observing the coil–globule transition through quasi-elastic light scattering from cyclohexane solutions of extremely low concentration of polystyrene whose molecular weight was as high as 27×10^6. In addition, they also determined the phase separation curve to illustrate the competition between the intra- and intermolecular interaction. This competition may be evaluated simply as follows: A coil–globule transition can be observed only if the probability P of finding an isolated coil is very near to unity. Following an estimate by Koningsveld et al.,[32] this probability is given as

$$P = \exp(-\lambda_0 N^{1/2} \phi_2) \tag{4}$$

where N is the degree of polymerization and λ_0 a parameter that is related to the unperturbed coil dimension $(\langle S^2 \rangle_\Theta / M)^{3/2} \sim \lambda_0$. For polystyrene in cyclohexane $\lambda_0 \simeq {}^1/_2$ was found. Assuming $P = 0.99$, i.e., allowing a 1% overlapping of coils, the maximum concentration ϕ_2 to observe the coil–globule transition must be smaller than 4×10^{-5} and is in good agreement with the finding by Tanaka et al.

The conditions for star-shaped molecules appear more favorable for observing the coil–globule transition, since the mean-square radius of gyration shrinks by a factor $g = \langle S^2 \rangle_b / \langle S^2 \rangle_l$ at the Θ point, and the concentration may thus be increased by a factor of $g^{-3/2}$. For example, the concentration can be increased approximately 5-fold for 8-branch star-shaped polystyrene to observe the coil–globule transition according to eq 4 in comparison with linear polystyrene of the same molecular weight. However, branch segregation of star-shaped molecules may cause intermolecular interaction at lower polymer concentration to spoil the coil–globule transition. The situation will certainly improve for regular treelike branched molecules, where the spatial extension of the chain due to segregation remains restricted.

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Optical Anisotropies of Model Analogues of Polycarbonates

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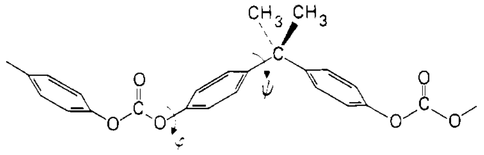
ABSTRACT: Depolarized light scattering and electric birefringence have been used to evaluate the optical anisotropy tensors for dimethyl carbonate, methyl phenyl carbonate, diphenyl carbonate, and 2,2-diphenylpropane. Rotational potentials about the phenyl axes in diphenyl carbonate and in diphenylpropane are estimated from force field calculations of interactions between nonbonded atoms. Rotations of the same sign ≈ |46°| of the phenyl groups in diphenylpropane and uncorrelated rotations ≈ |46°| about carbonate bonds are indicated. By combination of the information on structure, anisotropy, and conformation of these model compounds, the optical anisotropy tensors for carbonate and phenyl groups are estimated for these analogues of units occurring in the polycarbonate chain.

Introduction

The structure of the polycarbonate



derived from 2,2-bis(4-hydroxyphenyl)propane presents a number of interesting features. The phenylene groups exhibit large anisotropies both in their electric (optical) polarizability[1,2] and in their magnetizability.[3] The carbonate group, like phenylene, is essentially rigid and coplanar; its configuration appears to be trans,trans to the virtual exclusion of other forms.[4] The optical anisotropy of the carbonate group is smaller than that of phenylene, but it possesses an appreciable dipole moment. Torsional rotations may occur about both of the bonds pendant to the phenylene group. Potentials affecting rotations ϕ about C^{ph}–O bonds are twofold symmetric. Examination of models assures that rotation about the pair of these bonds adjoining a given carbonate group should be independent. Rotations ψ about the pair of C^{ph}–C bonds at the isopropylidene group are dominated by severe steric interactions between ortho hydrogen atoms of the respective phenylene groups. The rotations for the bond pair at a given isopropylidene group, consequently, are strongly interdependent, rotations of the same sign being overwhelmingly preferred.

The investigations reported in this paper and in its sequel[5] were undertaken for the express purpose of examining the tenability of treating the anisotropy of the optical polarizability as a constitutive property. The question specifically addressed is the following: Can molecular polarizability tensors be formulated realistically as sums of contributions from constituent groups? Since addition of tensor contributions is required, the structural geometry must be accurately represented, and proper averaging over various conformations is essential. Being the tensor sum of constitutive contributions, the optical anisotropy may be an especially sensitive index of molecular conformation.[2,6]

In the work reported in this paper, we have examined the optical anisotropies of model compounds that embody the structural components comprising the polycarbonate chain. The four compounds chosen for this purpose are dimethyl carbonate (DMC), methyl phenyl carbonate (MPC), diphenyl carbonate (DPC), and 2,2-diphenylpropane (DPP). The intensities of depolarized Rayleigh scattering (DRS) by solutions of each compound in carbon tetrachloride have been measured over ranges of concentration. By extrapolation to infinite dilution, the results yield the (squared) molecular anisotropy defined by

$$\gamma^2 = (3/2)\ \mathrm{tr}\ \langle \hat{\alpha}\hat{\alpha} \rangle \qquad (1)$$

where tr denotes the trace and $\hat{\alpha}$ is the traceless, or anisotropic, part of the molecular polarizability tensor α; i.e.

$$\hat{\alpha} = \alpha - (1/3)(\mathrm{tr}\ \alpha)\mathbf{E} \qquad (2)$$

E being the identity matrix. The angle brackets in eq 1 and elsewhere below denote the configurational average.

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