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Strain-induced birefringence and molecular structure of glassy polymers

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The dynamic birefringence and viscoelasticity were measured for poly(ethylene naphthalene-2,6-dicarboxylate), and the contributions from the main chain orientation and the rotational orientation of repeating unit to the strain-induced birefringence were evaluated. The values, together with published ones for other glassy polymers, were compared with the anisotropy of polarizability tensor of the repeating units. The contribution from the main chain orientation for various polymers was in accord with that evaluated from the excess polarizability of the unit in the main chain direction assuming a quasi-affine orientation of the unit. The contribution from the rotation was well correlated with the anistropy in the plane perpendicular to the chain axis. The degree of the rotational orientation was similar among the polymers. The rotational orientation was high for vinyl polymers with large side-groups. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: glassy polymers; birefringence; stress-optical coefficient)

INTRODUCTION

When a polymeric material is deformed it becomes birefringent, i.e. the refractive index tensor becomes anisotropic. In the terminal flow or rubbery zones, the deviatoric component of refractive index tensor is proportional to that of the stress tensor, and this relation is called the stress-optical rule (SOR)[1]. The proportionality holds well for varying stresses due either to varying strains or to the stress relaxation. The rule can be interpreted in terms of the orientation of the flexible polymer chains. For polymer glasses, the birefringence is proportional to the stress for varying amount of strain, and the relation is called photoelasticity (PE). The proportionality coefficient, the photoelastic coefficient, is different from the stress-optical coefficient, in the SOR. Thus the birefringence is not proportional to the stress in the course of stress relaxation over the glassy, glass-to-rubber, and rubbery zones.

In a series of studies we have revealed that the birefringence is composed of two components (denoted by the subscripts R and G in the following) that relax with different rates for a large group of amorphous polymers; the stress is also composed of two components; the corresponding components (with the same subscript) of birefringence and the stress are associated with the same relaxation spectrum[2–4]. A modified SOR (MSOR) was proposed to represent these observations[2]. The MSOR can be written as follows for elongational oscillatory deformation:

$$E^*(\omega) = E_R^*(\omega) + E_G^*(\omega) \tag{1}$$

$$O^*(\omega) = O_R^*(\omega) + O_G^*(\omega) \tag{2}$$

$$O_R^*(\omega) = C_R E_R^*(\omega) \qquad O_G^*(\omega) = C_G E_G^*(\omega) \tag{3}$$

Here $E^*(\omega)$ is the complex Young's modulus whose real and imaginary parts are $E'(\omega)$ and $E''(\omega)$, respectively; $O^*(\omega) = O'(\omega) + iO''(\omega)$ is the complex strain-optical ratio defined as the complex ratio of the birefringence to the strain just as the complex Young's modulus is defined as the complex ratio of the stress to the strain. C_R and C_G are material constants. We assume that the G component does not include long relaxation times corresponding to the rubbery plateau zone. Then we recover the SOR in the rubbery plateau zone, and C_R can be determined from the following relation:

$$O^*(\omega) = O_R^*(\omega) = C_R E_R^*(\omega) = C_R E^*(\omega) \quad \text{rubbery zone} \tag{4}$$

Likewise the R component is assumed not to have short relaxation times corresponding to the glassy zone. Then the real parts of the R components, E'_R and O'_R, vanish in the glassy zone, and C_G can be determined:

$$O''(\omega) = O''_G(\omega) = C_G E''_G(\omega) = C_G E''(\omega) \quad \text{(glassy zone)} \tag{5}$$

These relations are in good agreement with experimental results for many glassy polymers. The properties of the component functions, $E_R^*(\omega)$ and $E_G^*(\omega)$, have been examined in detail[3]. In particular, the $E_R^*(\omega)$ could be described with a bead-spring model, and the segment of the model was well approximated by the Kuhn statistical segment. The coefficients, C_R and C_G, have been tabulated for many polymers. For vinyl polymers, the instantaneous values of the birefringence, represented by O'_R and O'_G at the limit of high frequency, were consistent with the concept that the R component was due to the main chain orientation and the G component to the rotational orientation of monomer unit around the chain axis[4].

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In the present paper we examine the features of the instantaneous values of birefringence for a wider group of polymers. Specifically we compare the polymers which have bulky groups such as a benzene ring or a naphthalene ring as a part of the main chain or as a side-group. The dynamic viscoelasticity and birefringence have been newly measured for poly(ethylene naphthalene-2,6-dicarboxylate).

METHOD

Material

A specimen of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), supplied by Teijin Co. Ltd. as a sheet of 0.5 mm thickness, was amorphous and optically isotropic. It remained amorphous and isotropic during the course of dynamic measurements. The glass transition temperature was evaluated by d.s.c. as 117°C.

Measurement

Oscillatory elongation was applied to the sample. The tensile stress and the excess refractive index in the stretch direction were measured. Details of the apparatus and procedure of measurements are found elsewhere[2]. The frequency ranged from 1 to 130 Hz. The measurements were performed at several temperatures in the range from 155 to 118°C. The material constants, C_R and C_G, were evaluated with equations (4) and (5), respectively.

EXPERIMENTAL RESULT

Master curves of the complex Young's modulus and the complex strain-optical ratio are shown in *Figure 1*. The reference temperature was 135°C. $E'(\omega)$, $E''(\omega)$, $O'(\omega)$, and $O''(\omega)$ of other temperatures were plotted against a reduced angular frequency ωa_T so that the data superimposed on those of the reference temperature.

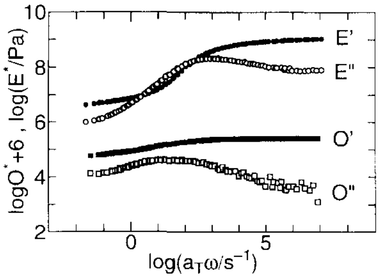

Figure 1 Master curves of the complex Young's modulus, $E^* = E' + iE''$, and the complex strain-optical ratio, $O^* = O' + iO''$, for PEN. The reference temperature was 135°C

The frequency dependence of the complex Young's modulus exhibits characteristics of ordinary glassy polymers. The lowest frequency range of the master curve corresponds to the high-frequency end of the rubbery plateau zone. The fast increase of $E'(\omega)$ and the maximum of $E''(\omega)$ in the intermediate frequency range are characteristic of the glass-to-rubber transition zone. The high-frequency range corresponds to the glassy zone.

The real part of the strain-optical coefficient, $O'(\omega)$, increases with increasing frequency, and the imaginary part, $O''(\omega)$, exhibits a maximum. $O'(\omega)$ and $O''(\omega)$ are always positive. These features are qualitatively the same as those for any polymers with positive C_R and C_G such as polycarbonate. The material constants for the PEN were $C_R = 1.24 \times 10^{-8}\,\mathrm{Pa}^{-1}$ and $C_G = 6.3 \times 10^{-11}\,\mathrm{Pa}^{-1}$, and the photoelastic coefficient was $2.7 \times 10^{-10}\,\mathrm{Pa}^{-1}$. The values of C_R and C_G are listed in *Table 1* together with those for other polymers to be compared in the following section.

The functions $E_R^*(\omega) = E'_R(\omega) + iE''_R(\omega)$ and $E_G^*(\omega) = E'_G(\omega) + iE''_G(\omega)$ were evaluated from the data of $E^*(\omega)$ and $O^*(\omega)$ with the modified stress-optical rule of equations (1)–(3). The obtained functions of PEN were very similar to those for polycarbonate reported earlier[5].

DISCUSSION

R *component*

The relation between the R components of Young's modulus and the birefringence is equivalent to the traditional SOR. It is believed that the birefringence is due to the orientation of the monomer unit along the stretch direction. One may define a reduced birefringence, O^r_R, which is related to the anisotropy of the polarizability, $\Delta\alpha_R$, and the degree of orientation or the orientation function, $P_R(\epsilon)$, of the monomer unit in a simple manner:

$$O^r_R = \frac{9nM_0O'_R(\infty)}{2\pi\rho N_A(n^2+2)^2} = \Delta\alpha_R\, P_R(\epsilon) \qquad (6)$$

Here n is the refractive index and ρ is the density of the polymer, M_0 is the molecular weight of the repeating unit and N_A is the Avogadro number.

The anisotropy of polarizability is given as

$$\Delta\alpha_R = \left(\alpha_1 - \frac{\alpha_2 + \alpha_3}{2}\right) \qquad (7)$$

Here α_j are components of the polarizability tensor of

Table 1 Summary of characteristic parameters

Polymer[a]	M_0	C_R ($10^{-12}\,\mathrm{Pa}^{-1}$)	C_G ($10^{-12}\,\mathrm{Pa}^{-1}$)	O_R	O_G	O^r_R ($10^{-30}\,\mathrm{m}^{-3}$)	O^r_G ($10^{-30}\,\mathrm{m}^{-3}$)	$\Delta\alpha_R$ ($10^{-30}\,\mathrm{m}^{-3}$)	$\Delta\alpha_G$ ($10^{-30}\,\mathrm{m}^{-3}$)
PEN	242	12400	63	0.1984	0.060	6.76	2.06	11.13	1.59
PC	254[b]	4700	35	0.122	0.053	4.91	2.11	9.09	1.07
PS	104	−4700	32	−0.0564	0.080	−1.03	1.46	−0.685	0.958
PVBPh	180	−6900	130	−0.0545	0.15	−1.71	4.57	−3.02	2.02
PVN	154	−8300	160	−0.0830	0.27	−1.88	6.17	−2.57	1.90

[a] PC, bisphenol A polycarbonate; PS, polystyrene; PVBPh, poly(vinylbiphenyl); PVN; poly(2-vinyl naphthalene)

[b] For PC the repeating unit is taken as $M_0/2$, implying one ring for each unit

the monomer unit (assumed diagonal for simplicity) with respect to the coordinate fixed to the unit; axis 1 is taken parallel to the direction of the main chain bonding axis; axis 2 is taken in the direction of maximum polarizability in the plane perpendicular to axis 1.

The orientation function for elongation is given by

$$P_R(\epsilon) = \frac{3}{5}\epsilon \tag{8}$$

if a quasi-affine orientation is assumed. Here ϵ is the elongational strain, i.e. the elongation ratio minus 1.

The reduced strain-optical ratio, O_R^r, is plotted against the anisotropy of polarizability, $\Delta\alpha_R$, for a few polymers that contain benzene rings or naphthalene rings in *Figure 2*. In estimating $\Delta\alpha_R$, as listed in *Table 1*, we assumed the concept of the bond additivity of the polarizability tensor. The bond polarizabilities of Denbigh[6], and the polarizabilities of benzene (12.27×10^{-30}, 12.27×10^{-30} and $6.65 \times 10^{-30}\,m^3$) and naphthalene ($24.3 \times 10^{-30}$, 18.5×10^{-30} and $12.6 \times 10^{-30}\,m^3$)[7] were used except for the case of bisphenol A polycarbonate (PC). For this polymer, the group polarizability was available, determined from the dense phase by the electric birefringence measurement[8–10]. When calculating for the vinyl polymers, it was assumed that the benzene and naphthalene rings in the side-group stick out perpendicularly from the main chain and rotate rapidly around the connecting bond. In the calculation for PEN the *all-trans* form was assumed, and the chain (axis 1) was fixed as shown in *Figure 3*. The angle between the naphthalene and the chain direction was estimated as 18°. The naphthalene group was assumed to rotate rapidly around the direction of the C2–C6 carbons.

As shown in *Figure 2*, obviously the measured values of the strain-optical coefficient is quite close to the theoretical value apart from some deviations for polystyrene (PS) and poly(2-vinyl naphthalene) (PVN). The deviation probably comes from the simplification of free rotation assumption of the benzene and naphthalene groups. Actually, adjustments of the statistical weight for the rotational angle of the phenyl ring around the connecting bond gives a better agreement[11]. The above result implies that the customary method of evaluating the orientation birefringence is a good approximation.

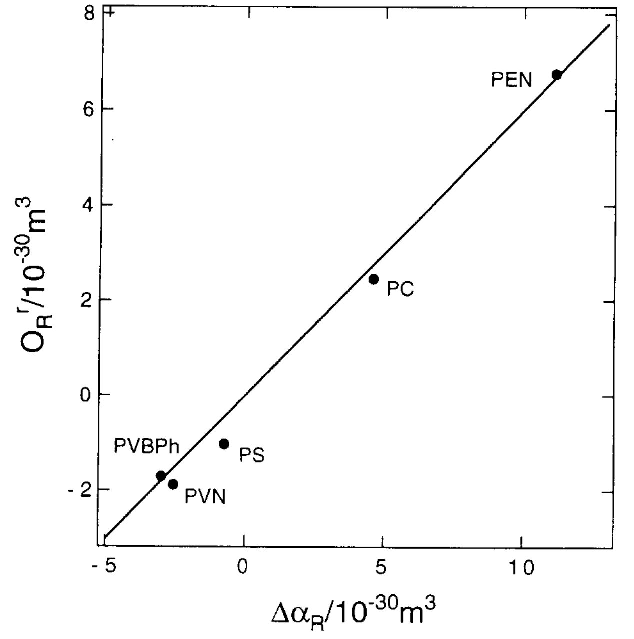

Figure 2 *R* component of reduced strain-optical ratio, O_R^r, plotted against anisotropy of polarizability along the chain axis. The line represents the theoretical result using a quasi-affine orientation (equation (8))

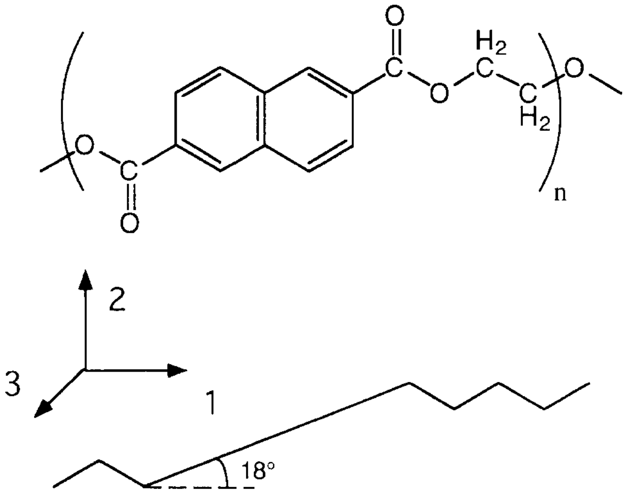

Figure 3 Structure and local frame of PEN

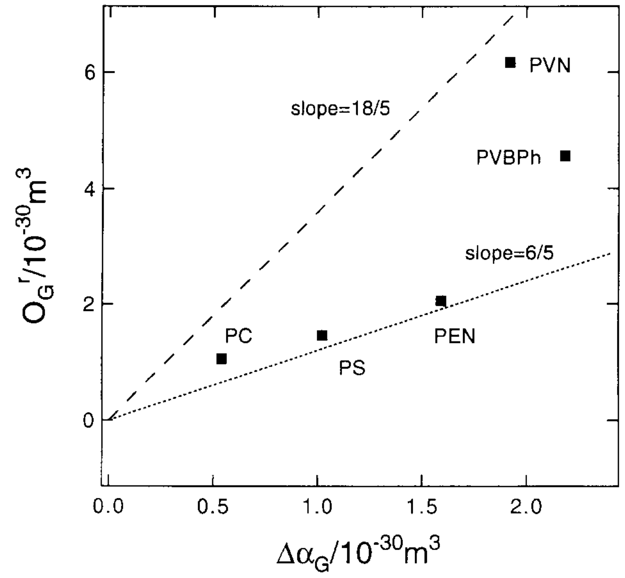

Figure 4 Reduced strain-optical coefficient for the *G* component, O_G^r, plotted against the lateral anisotropy of polarizability, $\Delta\alpha_G$

G *component*

Previous results for vinyl polymers strongly imply that the *G* component of the birefringence is originated by the rotational orientation around the chain axis of the repeating unit[4]. An equation similar to equation (6) may be expected to hold valid:

$$O_G^r = \frac{9nM_0O'_G(\infty)}{2\pi\rho N_A(n^2+2)^2} = \Delta\alpha_G P_G(\epsilon) \tag{9}$$

The lateral anisotropy of the polarizability, $\Delta\alpha_G$, is given by

$$\Delta\alpha_G = \frac{\alpha_2 - \alpha_3}{4} \qquad (10)$$

So far, we have no idea of the rotation orientation function, $P_G(\epsilon)$.

The reduced strain-optical coefficient for the G component, O_G^r, is plotted against the anisotropy of the polarizability, $\Delta\alpha_G$, in *Figure 4*. Although there is a scattering of data points, O_G^r is well correlated to $\Delta\alpha_G$. The present result clearly indicates that the birefringence originated by the G component is related to the anisotropy of polarizability in the plane perpendicular to the main chain axis.

O_G^r values for PVN and poly(vinylbiphenyl) (PVBPh), vinyl polymers with large side-groups, are large. In view of equation (9) they have larger P_G/ϵ values than the other polymers. On the other hand, for the case of PEN, which does not have a large side-group, P_G/ϵ is relatively small. Thus, the degree of rotational orientation, P_G/ϵ, seems to depend on the size of the side-groups: P_G/ϵ could increase with increasing geometrical anisotropy of the repeating units.

The broken line with slope $\frac{18}{5}$ corresponds to a deformation model in which axis 2 of the local frame fixed on the structure units is assumed to be quasi-affinely oriented to the direction of the deformation without regard to the orientation of axis 1:

$$P_G(\epsilon)/\epsilon = \frac{18}{5} \qquad (11)$$

The details of this model are given in the Appendix. This model is not realistic because axes 1 and 2 are not orthogonal after deformation if both of the axes undergo quasi-affine deformation. *Figure 4* shows that the model may give the upper bound of P_G.

A more realistic model is obtained by assuming that axis 2 rotates around axis 1, which orients according to the quasi-affine deformation. As shown in the Appendix, this model gives

$$P_G(\epsilon)/\epsilon = \frac{6}{5} \qquad (12)$$

The dotted line of *Figure 4* indicates that this model agrees well with PC, PS and PEN, and may give a lower bound of P_G.

Comparison with other works

I.r. dichroism has been measured on amorphous polymers under oscillatory deformations in order to study the dynamics of the chain orientations. In i.r. dichroism experiments, the measured quantity is the orientation function of electron dipole transition moments. Because of the specificity of i.r. absorption, combination with oscillatory deformation can provide information on the deformation and relaxation behaviour of polymeric materials at the molecular level. Interestingly, it is known that i.r. bands arising from molecular vibrations of different functional groups often exhibit substantially different time-dependent variations[12,13]. These variations have been attributed to characteristics of the type and local environment of submolecular structures. The fact that dipole transition moments reorient at different rates can be effectively visualized by a correlation analysis to the time-dependent variation of i.r. dichroism signals. This method developed by Noda *et al.* is called two-dimensional i.r. spectroscopy[14,15]. They reported many interesting results such that the main chain and side-chain of PS have different mobilities based on the different rates of the reorientation of dipole transition moments.

The i.r. results for the reorientation of the various dipole transition moments may be compared with our model for the interpretation of MSOR. The i.r. method gives the orientation function of dipole transition moments, F^j, which in the laboratory frame can be defined as follows:

$$F^j = (3 < \cos^2\theta_j > -1)/2 \qquad (13)$$

Here θ_j is the polar angle of the dipole moment, j, in the laboratory frame. The orientation function F^j can be described by using the orientation functions of the structure unit in the local frame which is fixed on the units, P_R and P_G:

$$F^j = \frac{3\cos^2\Theta - 1}{2} P_R + \frac{1}{4}\sin^2\Theta\cos 2\Phi P_G \qquad (14)$$

Here Θ and Φ are the polar and azimuthal angles of the dipole moment in the local frame. Equation (14) gives an explanation for the peak separation mechanism for the two-dimensional i.r. method. According to equation (14), the reorientation of F^j can show a unique time dependence on Θ and Φ if P_G is not zero in accord with the present study. Therefore, if two dipole moments have similar absorption frequencies, the time correlation analysis can separate the two absorptions according to the direction of the moments in the local frame. Thus, the two-dimensional i.r. method is a powerful method to identify absorption peaks.

However, in the discussion on the molecular motion of polymers we believe that the relaxation of the orientation functions P_R and P_G are more fundamental because the apparently independent reorientations of several dipole moments may be described by using the two reorientation processes denoted by P_R and P_G. The contribution of the P_G term should be considered in the interpretation of the i.r. dichroism data collected by using mechanical stimulation such as two-dimensional i.r. measurement.

CONCLUSION

The instantaneous values of the strain-optical ratio are investigated in detail for polymers incorporating a benzene ring or a naphthalene ring either in the main chain or as a side-group. The contribution from the main chain orientation for various polymers was in accord with that evaluated from the excess polarizability of the unit in the main chain direction assuming a quasi-affine orientation of the unit. The contribution from the rotation is correlated with the anisotropy in the plane perpendicular to the chain axis. For vinyl polymers the rotational contribution to the birefringence might increase with a higher rate with increasing bulkiness of the side-group than for polymers with benzene and naphthalene rings in the main chain. The significance of the rotational orientation should be taken into account for the interpretation of the i.r. dichroism data collected under deformation, particularly for the glassy state.

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APPENDIX. CALCULATION OF THE ORIENTATION FUNCTION FOR THE ROTATIONAL ORIENTATION

We consider a simplified model. Suppose the polymer is composed of identical units that do not change the shape over the time-scale to be investigated; the shape of the polymer chain is due exclusively to the rotation of the units. Since the structure unit of real polymers could be regarded as flat in any orientation, we assume that the unit of the model is flat. The orientation of this structure unit may be described by the orientation of two characteristic vectors: one is denoted as $\boldsymbol{v}_1$, which is taken along the chain direction, and the other one is $\boldsymbol{v}_2$, which is perpendicular to $\boldsymbol{v}_1$ and taken so that it is included in the characteristic plane. If axis 1 of the local frame is taken along $\boldsymbol{v}_1$ and axis 2 is $\boldsymbol{v}_2$, these vectors can be described by using the laboratory frame as follows:

$$\boldsymbol{v}_1 = \begin{pmatrix} \cos\theta \\ \sin\theta\cos\phi \\ \sin\theta\sin\phi \end{pmatrix}$$

$$\boldsymbol{v}_2 = \begin{pmatrix} -\cos\eta\sin\theta \\ \cos\eta\cos\theta\cos\phi - \sin\eta\sin\phi \\ \cos\eta\cos\theta\sin\phi + \sin\eta\cos\phi \end{pmatrix} \tag{A1}$$

where ϕ, θ and η are Euler's angles. If the affine deformation is assumed, these vectors after elongation in direction 1 in the laboratory frame can be written as follows:

$$\boldsymbol{v}_1' = \begin{pmatrix} \lambda\cos\theta \\ \lambda^{-1/2}\sin\theta\cos\phi \\ \lambda^{-1/2}\sin\theta\sin\phi \end{pmatrix}$$

$$\boldsymbol{v}_2' = \begin{pmatrix} -\lambda\cos\eta\sin\theta \\ \lambda^{-1/2}\cos\eta\cos\theta\cos\phi - \lambda^{-1/2}\sin\eta\sin\phi \\ \lambda^{-1/2}\cos\eta\cos\theta\sin\phi + \lambda^{-1/2}\sin\eta\cos\phi \end{pmatrix} \tag{A2}$$

where λ is elongation ratio. In the quasi-affine model these vectors are assumed not to change their length. The P_2 orientation function of the two vectors under the quasi-affine assumption in infinitesimal strain is obtained as follows:

$$F^{v_1} = \frac{3\langle \boldsymbol{v}_1' \cdot \boldsymbol{u}_1 / |\boldsymbol{v}_1'|\rangle - 1}{2} \tag{A3}$$

$$F^{v_2} = \frac{3\langle \boldsymbol{v}_2' \cdot \boldsymbol{u}_1 / |\boldsymbol{v}_1'|\rangle - 1}{2} \tag{A4}$$

Here $\boldsymbol{u}_1$ is the unit vector of axis 1 of the laboratory frame, and the bracket indicates the statistical average over the orientation before deformation,

$$\langle\cdots\rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \cdots N(\theta,\phi,\eta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\eta \tag{A5}$$

where $N(\theta,\phi,\eta) = 1/8\pi^2$ is the orientation distribution function before deformation. With a simple calculation we obtain

$$F^{v_1} = \frac{3}{5}\epsilon \tag{A6}$$

$$F^{v_2} = \frac{3}{5}\epsilon \tag{A7}$$

The orientation function of axes 1 and 2 of the orthogonal local frame, $F^1(\epsilon)$ and $F^2(\epsilon)$, can be related to $P_\mathrm{R}(\epsilon)$ and $P_\mathrm{G}(\epsilon)$ through equation (14):

$$F^1 = P_\mathrm{R} \tag{A8}$$

$$F^2 = -\frac{1}{2}P_\mathrm{R} + \frac{1}{4}P_\mathrm{G} \tag{A9}$$

If we assume

$$F^1(\epsilon) = F^{v_1}(\epsilon) \tag{A10}$$

$$F^2(\epsilon) = F^{v_2}(\epsilon) \tag{A11}$$

we obtain

$$P_\mathrm{G} = \frac{18}{5}\epsilon \tag{A12}$$

The assumption of equations (A10) and (A11) is not valid; equations (A8) and (A9) require that $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$ in the deformed state presume orthogonality. The breakdown of the orthogonality between $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$ corresponds to the deformation of the structure units, and is in conflict with the model assumption.

To avoid such a difficulty, we consider a new model in which $\boldsymbol{v}_1$ is transformed quasi-affinely and $\boldsymbol{v}_2'$ rotates about axis 1 by an angle in accord with the quasi-affine deformation so as to keep orthogonality between $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2'$. Such a transformation of $\boldsymbol{v}_2$ may be obtained by considering the projection of $\boldsymbol{v}_2'$ in the plane perpendicular to $\boldsymbol{v}_1'$. The projected vector, $\boldsymbol{v}_2''$, can be written as follows:

$$\boldsymbol{v}_2'' = \left(\boldsymbol{I} - \frac{\boldsymbol{v}_1'\boldsymbol{v}_1'}{|\boldsymbol{v}_1'|^2}\right)\cdot\boldsymbol{v}_2' \tag{A13}$$

The vectors $\boldsymbol{v}_1'$ and $\boldsymbol{v}_2''$ are orthogonal, and the rotation angle of $\boldsymbol{v}_2''$ around the direction of $\boldsymbol{v}_1'$ coincides with that of $\boldsymbol{v}_2'$. In the new model $\boldsymbol{v}_1'$ is assumed to be transformed to $\boldsymbol{v}_1'/|\boldsymbol{v}_1'|$, and $\boldsymbol{v}_2$ to $\boldsymbol{v}_2''/|\boldsymbol{v}_2''|$.

By a simple calculation it can be shown that the P_2 orientation function of $\boldsymbol{\nu}_2''$ becomes independent of the strain amplitude under infinitesimal strain:

$$F^{\nu_2''}(\epsilon) = 0 \qquad \text{(A14)}$$

Setting $F^2(\epsilon) = F^{\nu_2''}(\epsilon)$, we obtain

$$P_G = \frac{6}{5}\epsilon \qquad \text{(A15)}$$