Optical Anisotropy of Structurally Modified Polycarbonates Having Cyclohexylidene and Methyl Substituents Using the Rotational Isomeric State Method

Muralidharan S. Sulatha, Swaminathan Sivaram, and Upendra Natarajan*

Division of Polymer Chemistry, National Chemical Laboratory, Pune-411 008, India

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ABSTRACT: An extension of the valence optical scheme−rotational isomeric state method (RIS) applicable to calculation of polarizability tensors and optical anisotropy (γ^2) of molecular fragments constituting substituted polycarbonate chains is presented. The theoretical approach utilizes experimentally derived anisotropic polarizability tensors of molecular groups in order to be able to account for induction effects and interdependence of backbone conformational states. The presence of a cyclohexylidene group at the bisphenyl C_α carbon significantly lowers γ^2 due to the low intrinsic polarizability of the cycloaliphatic substituent and due to the conformational states of backbone phenylene rings. Optical anisotropy value of the bisphenyl containing methyl substituents on the phenyl rings is lower than the value for the unsubstituted bisphenyl. Among the structures investigated here, the repeat unit containing cyclohexylidene group at C_α and methyl groups on phenylene rings, leads to the polycarbonate that shows the lowest optical anisotropy. Quantitatively, cyclohexylidene at C_α is more effective in lowering the optical anisotropy than methyl groups on backbone phenylene rings. Calculated $\langle\gamma^2\rangle/x$ of the repeat units follows a linear behavior with respect to experimentally observed stress−optical coefficient of these polycarbonates in the melt (C_m). Calculated $\langle\gamma^2\rangle/x$ of these structurally modified polycarbonate chains are all lower than that of BPAPC, and the relative trend in $\langle\gamma^2\rangle/x$ is similar to that observed for C_m and C_g (glassy state) from experiments in the literature.

1. Introduction

Polymers are indispensable in their use as materials for a variety of optical applications. Bisphenol A polycarbonate (BPAPC) and poly(methyl methacrylate) (PMMA) find wide applications as optical data substrate materials due to their optical clarity along with other useful properties. The disadvantages posed by these materials include high water absorption and low heat resistance in the case of PMMA and high birefringence in the case of BPAPC.[1,2] Birefringence in polymers occurs mainly due to the intrinsic (atomically bonded) chemical structure, which results in different polarizabilities (and hence refractive indices) in different directions. In amorphous samples in their glassy state, a part of the birefringence occurs due to the residual stresses prevailing as a result of molding conditions, which orient the chains in the direction of the stress.

Polarizable phenylene rings along the polymer backbone are known to provide positive birefringence, which is seen in the case of polycarbonate BPAPC. Researchers have attempted structural modification of the bisphenol unit by various strategies: (i) replacement of aromatic phenylene rings by less polarizable symmetric cyclic fused rings;[3] (ii) introduction of cycloaliphatic ring substitutions;[4] (iii) laterally attached polarizable groups to geometrically compensate for the optical anisotropy of the backbone phenylene rings.[5] Reduction in chain optical anisotropy is generally found to go in conjunction with a reduction in stress−birefringence and stress−optical coefficients. Polycarbonate based on spirobiindane bisphenol exhibits zero birefringence for the homopolymer due to its symmetric structure, but the material is extremely brittle.[3] The structurally modified polycarbonate based on trimethylcyclohexylidene bisphenol polycarbonate (TMCPC) shows a maximum birefringence ($\Delta n \times 10^3$) of 1.76 as compared to 2.06 for BPAPC, due to the presence of cycloaliphatic substituent group.[4] To design new polymeric materials that have useful optical properties, such as low optical anisotropy, $\langle\gamma^2\rangle$, and low birefringence, a thorough understanding of various structural and conformational features that control these properties is required.

Theoretically, polarizabilities of molecules can be formulated by tensorial addition of the polarizability components of various bonds or constituent groups by the valence optical scheme (VOS).[6] The tensor sum depends on the mutual orientations of these groups as dictated by the three-dimensional bonding structure and conformation. A straightforward bond additivity scheme does not satisfactorily take into account the mutual orientational and inductive effects between the groups. If larger groups are chosen instead of individual bonds, the polarizability tensors and optical anisotropies of molecules can be suitably derived. $\langle\gamma^2\rangle$ of polymer chains has been treated in the rotational isomeric state (RIS) approximation by proper averaging over various chain conformations with an accurate representation of the structural geometry as presented in the work of Jernigan and Flory.[7,8] In the pioneering work by Patterson and Flory, the experimentally observed dependence of $\langle\gamma^2\rangle$ on oligomer chain length of *n*-alkanes[9a] and poly(oxyethylene)[9b] was well reproduced by RIS calculations. The good agreement between calculated and experimentally measured values from depolarized Rayleigh scattering (DRS) provided strong support to the validity of the theoretical approach as a basis for comprehending

* To whom correspondence must be addressed. E-mail: upendra@poly.ncl.res.in. Telephone: (91)-020-5893234. Fax: (91)-020-5893234.

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the optical anisotropy of chains in solution.[7−9] The RIS method for the calculation of $\langle\gamma^2\rangle$ of organic molecules and oligomers in solution has shown promise and has been applied to several systems in the past such as atactic polystyrene as a function of stereochemical composition,[10] aliphatic esters,[11] aromatic esters, and poly(*p*-oxybenzoate),[12] and several other systems. For all of these polymers the use of mutually consistent polarizability parameters for their small fragments and the allowance for inductive effects of substitution and neighboring groups have been exemplified and shown to be important in order that calculations are able to successfully reproduce experimental data.

BPAPC is the only polycarbonate for which experimental measurement of $\langle\gamma^2\rangle$ using DRS and theoretical calculation via the RIS method has been performed.[14,15] To estimate $\langle\gamma^2\rangle$, DRS measurements were carried out for structural analogues dimethyl carbonate (DMC), diphenyl carbonate (DPC), and diphenyl propane (DPP) in CCl_4 and for the BPAPC oligomer ($M_n = 2700$ g/mol, $x = 10.7$) in dioxane.[15] Polarizability tensors corresponding to phenyl groups in DPC and DPP and for the carbonate group have been accurately estimated combining information on optical anisotropy from DRS experiments in CCl_4 and the geometry of the molecule as obtained from crystal structure data (DPC) and conformational energy calculations (DPP). The calculated optical anisotropies of DPC and DPP agree well with their corresponding experimental values.[14] Using information derived from polarizabilities of constituent groups of the repeat unit (i.e., polarizability tensors of phenylene groups subjected to the effects of oxy and isopropylidene group substitution and the tensor for the carbonate group), $\langle\gamma^2\rangle$ of BPAPC has been determined by the RIS method.[15] The calculated value 111 Å^6 for $\langle\gamma^2\rangle/x$, the mean-squared optical anisotropy of the repeat unit in BPAPC chain, is found to be in good agreement with the experimental value of 120 ± 5 Å^6.[15] Low-frequency DRS measurements by Floudas et al.[16] give results similar to those obtained from the earlier report,[15] but the actual values of $\langle\gamma^2\rangle$ slightly differ. At 25 °C, $\langle\gamma^2\rangle/x$ {$8 < x < 163$) obtained from the measurements tends to be 117.3 Å^6 in solution and 115 Å^6 for the bulk amorphous state, indicating only slight differences in this optical property between the single chain and the amorphous states. As pointed out by Floudas et al.,[16] earlier DRS measurements of amorphous BPA-PC,[17] obtained without the use of a Fabry−Perot interferometer which resulted in $\langle\gamma^2\rangle/x = 136$ Å^6, is an overestimation due to inclusion of collision-induced anisotropy. The work by Navard and Flory, in which $\langle\gamma^2\rangle$ of cyanocyclohexane, bicyclohexyl, and *trans*-4-cyano-*trans*-4-*n*-alkyl bicyclohexyls were determined from DRS experiments, is of particular relevance to our present study.[18] Their data were treated on the basis of additive contributions of group anisotropies.[18] The formulation of the polarizability tensors of substituted cyclohexanes based on group tensor additivity,[18] leads to calculation results for cyclohexanes and related compounds in agreement with the experimental and calculated values based on correct bond polarizability additivity as given Le Fevre et al. for these small cycloaliphatic organic molecules.[19]

The motivation for the present work here is the lack of theoretical studies on $\langle\gamma^2\rangle$, of structurally modified polycarbonates and a lack of experimental studies with systematic structural variation, even though few experimental reports exist at this time.[3] Our work addresses a new understanding of the relationship of atomic level structure, monomer conformations, chain conformational structure, and intrinsic group polarizabilities, to the single chain optical anisotropy of BPAPC and four structurally modified polycarbonates. The focus of the present work is the new formulation of the polarizability tensors for bisphenyls and repeat units constituting structurally modified polycarbonates and the extension of the existing formalism of BPAPC to the application of RIS/VOS for the calculation of single chain optical anisotropy. We specifically investigate the effects of (i) the cyclohexylidene group at the C_α carbon (BPCPC), (ii) additional methyl substituents on the cyclohexylidene group (TMCPC), (iii) methyl substituents on the phenyl rings (DMPC), and (iv) the cyclohexylidene group at the C_α carbon as well as methyl groups on the phenyl rings (DMBPC). The input to the calculations is the geometry derived from force-field-based conformational energy calculations and the polarizability tensors of constituent groups which are derived from DRS experiments reported in the literature. Formulation of the polarizability tensors of repeat units of polycarbonates having cyclohexylidene group at the C_α carbon and methyl substituents on the phenylene rings is presented and incorporated fruitfully into a RIS scheme for $\langle\gamma^2\rangle$ estimation. The conformational characteristics, RIS models, and single chain properties of the structurally different polycarbonates chosen in the present work have been studied in detail in an earlier work,[20] where the statistical weights for the probable rotational states of various bond pairs are given. Results of the calculations of optical anisotropy of bisphenyl fragments, carbonate moieties and repeat units of structurally modified polycarbonates are presented and compared with results for BPAPC. The structures of bisphenyls, carbonates, and repeat units corresponding to these polycarbonates are shown in Figure 1. These polycarbonates correspond to a set where we make a systematic change of the chemical structure to see the effect on optical anisotropy at the level of the monomer and the chain.

2. Theoretical Framework and RIS Formalism

2.1. Optical Anisotropy of Bisphenyl DMBP, Carbonate DMDPC, and Polycarbonate DMPC. The formalism employed by Erman et al.[14,15] for BPAPC is used here with some modifications for the case of DMPC by suitable group polarizabilities and geometrical parameters. The Cartesian coordinate reference frames employed to express individual group polarizability tensors for substituted structures is the same as that which was earlier used for DPP and DPC.[14] The reference frames for DMBP and DMDPC are given in Figure 2. According to the original method,[14] the polarizability tensor of DPP is formulated by adding up contributions of two phenyl rings which are subject to the effect of the isopropylidene group. Following a similar approach, DMBP can be considered to be formed from neopentane and two molecules of toluene according to the hypothetical process

$$CH_3{-}C_6H_4{-}H + C(CH_3)_4 + H{-}C_6H_4{-}CH_3 \rightarrow (CH_3{-}C_6H_4)_2C(CH_3)_2 + 2CH_4 \quad (1)$$

involving no net changes in the numbers of C−C and

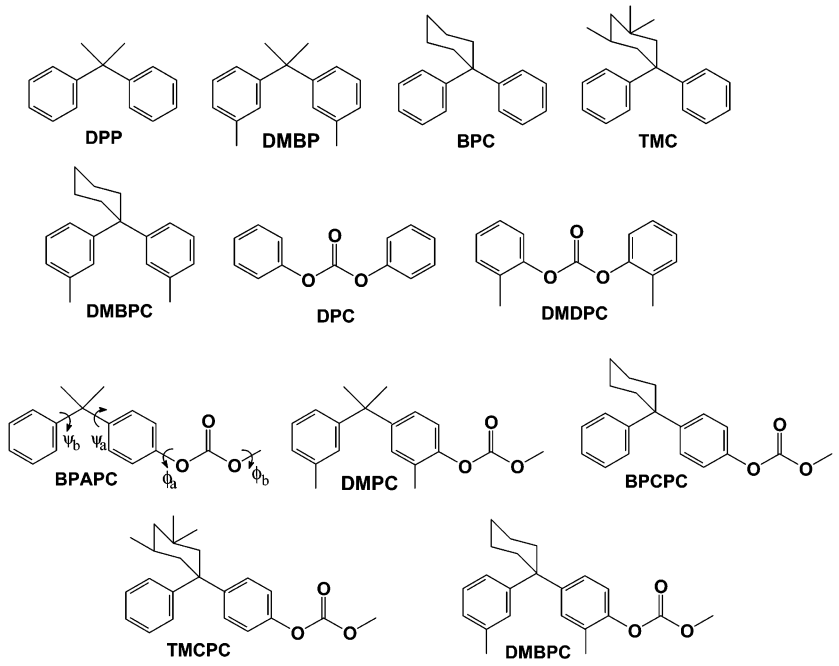

Figure 1. Structures of the bisphenyls, carbonate fragments, and repeat units of the structurally modified polycarbonates.

C−H bonds. Neopentane and methane being symmetric, the polarizability tensor for DMBP is constructed from two phenyl ring tensors subjected simultaneously to the presence of isopropylidene group between the rings as well as methyl groups on the rings, such as

$$\hat{\alpha}_{\mathrm{DMBP}} = \hat{\alpha}_{\mathrm{ph,a}} + \hat{\alpha}_{\mathrm{ph,b}} \tag{2}$$

The polarizability tensor for the phenyl group in DPP in the *xyz* frame can be derived as diag[3.46, −0.23, −3.23] and that for an unsubstituted phenyl group in the same reference frame is diag[1.21, 1.21, −2.42].[14] From these values the polarizability tensor corresponding to the effect of isopropylidene substitution is derived as diag[2.25, −1.44, −0.81]. The tensor for a phenyl group with methyl substitution can be equated to that of toluene and is given by diag[2.32, 0.34, −2.66] in a reference frame (x'',y'',z'') where the $x''y''$ plane is the plane of the molecule with x'' axis in the direction of the C−C bond.[10] This tensor is then transformed to the reference frames $x_by_bz_b$ and $x_ay_az_a$ on the phenyl rings by the equations

$$\begin{aligned}(\hat{\alpha}_{\mathrm{ph,b}})x_by_bz_b &= R_z(-\theta)\,(\hat{\alpha}_{\mathrm{ph,b}})_{x''y''z''}\,R_z^{-1}(-\theta)\\ (\hat{\alpha}_{\mathrm{ph,a}})x_ay_az_a &= R_z(\theta)\,(\hat{\alpha}_{\mathrm{ph,a}})_{x''y''z''}\,R_z^{-1}(\theta)\end{aligned} \tag{3}$$

where $\theta = 120°$. Subsequently, the components of the tensor are summed up along with the contribution from the isopropylidene group. The tensors in the *xyz* reference frames for the phenyl groups in DMBP are

$$\begin{aligned}(\hat{\alpha}_{\mathrm{ph,b,DMBP}})_{xyz} &= \begin{bmatrix}3.085 & 0.857 & 0\\ & 0.385 & 0\\ & & -3.47\end{bmatrix}\\ (\hat{\alpha}_{\mathrm{ph,a,DMBP}})_{xyz} &= \begin{bmatrix}3.085 & -0.857 & 0\\ & 0.385 & 0\\ & & -3.47\end{bmatrix}\end{aligned} \tag{4}$$

The tensor for DMBP is formulated by adding the contributions from the two phenyl groups expressed in the same reference frame. The ring tensors which are now in their own corresponding *xyz* frames are then transformed to the $X'Y'Z'$ frame by using the same equations of transformation as given earlier:[14]

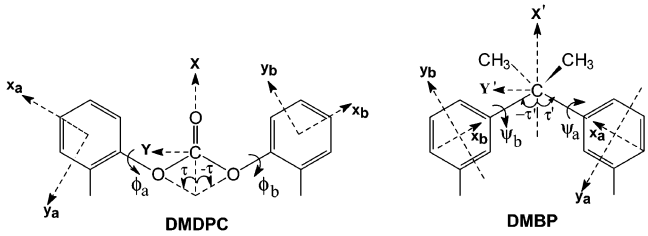

Figure 2. Coordinate reference frames of the various groups in DMDPC and DMBP.

$$(\hat{\alpha}_{\mathrm{ph,b}})_{X'Y'Z'} = R_z(-\tau')\,R_x(\psi_b)\,(\hat{\alpha}_{\mathrm{ph,b}})_{xyz}\,R_x^{-1}(\psi_b)\,R_z^{-1}(-\tau') \tag{5}$$

$$(\hat{\alpha}_{\mathrm{ph,a}})_{X'Y'Z'} = R_z(\tau')\,R_x(\psi_a)\,(\hat{\alpha}_{\mathrm{ph,a}})_{xyz}\,R_x^{-1}(\psi_a)\,R_z^{-1}(\tau')$$

The tensor of DPC is constructed from those of two phenyl groups with the influence of oxy substitution and the carbonate moiety.[14] The tensor of the phenyl groups in DPC (with effects of oxy substitution) in the *xyz* frame is diag[2.67, 0.17, −2.84], and from this, the tensor corresponding to *oxy* substitution is obtained as diag[1.46, −1.04, −0.42]. The tensor for the carbonate group in the *XYZ* frame is diag[0.17, 1.04, −1.21] which is identified with the same as that for dimethyl carbonate.[14] The tensor for DMDPC can be formulated from the sum of contributions from two phenyl groups (with effects of oxy as well as methyl substitution) and from the carbonate group when all of these tensors are in the same reference frame. To get the former tensor, the tensors of toluene and that corresponding to oxy substitution are added up after transformation to the common frame, *XYZ*, which is located at the carbonate group as shown in Figure 2. The tensors corresponding

to the phenyl groups "a" and "b" in DMDPC are obtained as

$$(\hat{\alpha}_{\mathrm{ph,b,DMDPC}})_{xyz} = \begin{bmatrix} 2.295 & 0.857 & 0 \\ & 0.785 & 0 \\ & & -3.08 \end{bmatrix}$$

$$(\hat{\alpha}_{\mathrm{ph,a,DMDPC}})_{xyz} = \begin{bmatrix} 2.295 & -0.857 & 0 \\ & 0.785 & 0 \\ & & -3.08 \end{bmatrix} \quad (6)$$

The transformation equations which are similar to that used by Erman et al. are employed to transform the tensors of the phenyl groups in DMDPC to the *XYZ* frame.[14] These are

$$(\hat{\alpha}_{\mathrm{ph,a}})_{XYZ} = R_z(\tau)\, R_x(\phi)\, (\hat{\alpha}_{\mathrm{ph,a}})_{xyz}\, R_x^{-1}(\phi)\, R_Z^{-1}(\tau)$$

$$(\hat{\alpha}_{\mathrm{ph,b}})_{XYZ} = R_z(-\tau)\, R_x(\phi)\, (\hat{\alpha}_{\mathrm{ph,b}})_{xyz}\, R_x^{-1}(\phi)\, R_Z^{-1}(-\tau) \quad (7)$$

In order to calculate the polymer chain optical anisotropy of DMPC, its repeat unit is treated in a manner similar to that of BPAPC.[15] The polarizability tensor is constructed by adding contributions from two phenylene groups which are subjected to effects of isopropylidene group, oxy and methyl group substitution (groups 1 and 3) and the carbonate group (group 2). Thus, for the constituting groups in DMPC

$$(\hat{\alpha}_1)_{xyz} = \begin{bmatrix} 4.545 & 0.857 & 0 \\ & -0.655 & 0 \\ & & -3.89 \end{bmatrix}$$

$$(\hat{\alpha}_2)_{XYZ} = \mathrm{diag}[0.17 \;\; 1.04 \;\; -1.21] \quad (8)$$

$$(\hat{\alpha}_3)_{xyz} = \begin{bmatrix} 4.545 & -0.857 & 0 \\ & -0.655 & 0 \\ & & -3.89 \end{bmatrix}$$

$\hat{\alpha}_1 = \hat{\alpha}_{\mathrm{ph,b}}$; $\hat{\alpha}_2 = \hat{\alpha}_{\mathrm{C}}$; $\hat{\alpha}_3 = \hat{\alpha}_{\mathrm{ph,a}}$ with indices $i = 1, 2, 3$ corresponding to those in eq 8. The equations of transformation, T_1, T_2, and T_3 are identical to those used for BPAPC from a previous report.[15]

2.2. Optical Anisotropy of Cyclohexylidene Bisphenyl Fragments. The formulation of polarizability tensors for bisphenyls BPC, TMC, and DMBPC having cyclohexyl substitution at the C_α atom is as follows. Consider the fragment BPC, which is hypothesized to be formed from two molecules of benzene and one molecule of 1,1-dimethylcyclohexane (DMCYX) as shown structurally in Figure 3 and through the equation

$$C_6H_5{-}H + C_6H_{10}(CH_3)_2 + H{-}C_6H_5 \rightarrow (C_6H_5)_2C_6H_{10} + 2CH_4 \quad (9)$$

which involves no net changes in the number of C−C and C−H bonds. Since the polarizability tensor for methane is considered to be zero and the polarizability tensor for BPC can be formulated from sums of contributions from two phenyl groups and DMCYX (where all tensors are expressed in a common reference frame), this gives

$$\hat{\alpha}_{\mathrm{BPC}} = \hat{\alpha}_{\mathrm{ph,a}} + \hat{\alpha}_{\mathrm{DMCYX}} + \hat{\alpha}_{\mathrm{ph,b}} \quad (10)$$

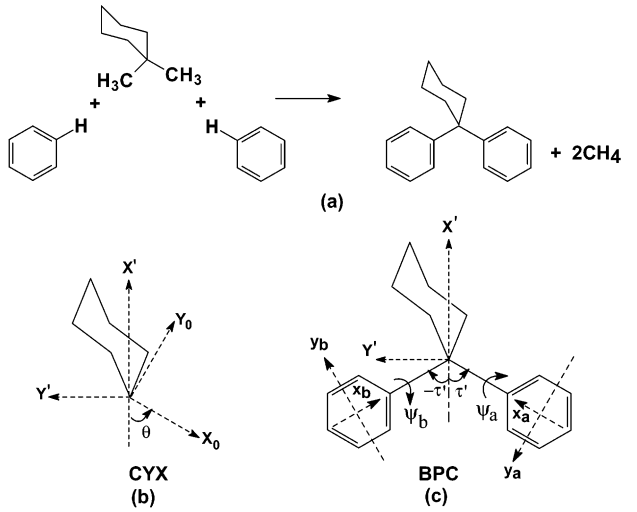

Figure 3. (a) Hypothetical process for the formation of BPC from phenyl groups and dimethylcyclohexane. Coordinate reference frames of (b) cyclohexane and (c) phenyl groups in BPC.

The tensor of DMCYX can be obtained from that of cyclohexane by taking into account the replacement of two hydrogen atoms by two methyl groups, one axial and the other equatorial. The method described by Navard and Flory is conveniently adopted here for the formulation of tensors of substituted cyclohexanes.[18] For methylcyclohexane, the tensor construction is obtained by replacing a hydrogen atom of cyclohexane by a methyl group, either in the equatorial or axial orientation, which corresponds to the formation of a C−C bond with the contribution equal to Γ_{cc}. Here Γ_{cc} is taken to be 0.53 Å^3.[8] For the equatorial orientation of the methyl group

$$(\hat{\alpha}_{\mathrm{CYX-Me,e}})_{X_0Y_0Z_0} = (\hat{\alpha}_{\mathrm{CYX}})_{X_0Y_0Z_0} + \hat{\alpha}_{\mathrm{e}}$$

$$\hat{\alpha}_{\mathrm{e}} = \Gamma_{cc}\, \mathrm{diag}\left[\frac{2}{3} - \frac{1}{3} - \frac{1}{3}\right] \quad (11)$$

while when the methyl group is oriented axially ($\xi = \cos^{-1}(-1/3)$)

$$(\hat{\alpha}_{\mathrm{CYX-Me,a}})_{X_0Y_0Z_0} = (\hat{\alpha}_{\mathrm{CYX}})_{X_0Y_0Z_0} + R_Z(\xi)\, \hat{\alpha}_{\mathrm{e}} R_Z^{-1}(\xi) \quad (12)$$

The tensor for DMCYX in the $X_0Y_0Z_0$ frame is therefore

$$(\hat{\alpha}_{\mathrm{DMCYX}})_{X_0Y_0Z_0} = (\hat{\alpha}_{\mathrm{CYX}})_{X_0Y_0Z_0} + \hat{\alpha}_{\mathrm{e}} + R_Z(\xi)\hat{\alpha}_{\mathrm{e}} R_Z^{-1}(\xi) \quad (13)$$

The transformation from the $X_0Y_0Z_0$ frame to the $X'Y'Z'$ frame is performed by the following equation, where $\theta = 54.75°$ and is half of the tetrahedral bond angle.

$$(\hat{\alpha}_{\mathrm{DMCYX}})_{X'Y'Z'} = R_z(\theta)\, (\hat{\alpha}_{\mathrm{DMCYX}})_{X_0Y_0Z_0} R_Z^{-1}(\theta) \quad (14)$$

The tensors of the phenyl groups in the *xyz* frame, which is diag[1.21, 1.21, −2.42], are then transformed to the *X′Y′Z′* frame by using eq 5. The contributions of the phenyl rings are then added to the tensor components for DMCYX in the same reference frame. For the formulation of DMBPC, instead of the tensor for the

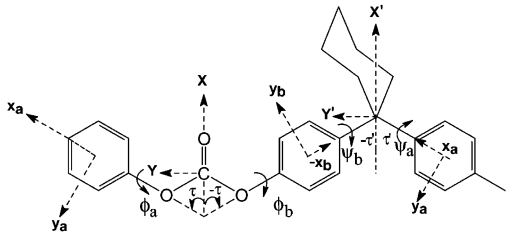

Figure 4. Coordinate reference frames of the various groups in the BPCPC segment.

phenyl group (eq 10), the tensor corresponding to that for toluene in the appropriate reference frame (*xyz*) is employed.

Bisphenyl molecule TMC is considered to result from two molecules of benzene and one molecule of 1,1,3,3,5-pentamethylcyclohexane (PMCYX). The tensor for TMC is formulated as the sum of contributions from two phenyl groups and PMCYX, all expressed in a common reference frame.

$$\hat{\alpha}_{\mathrm{TMC}} = \hat{\alpha}_{\mathrm{ph,a}} + \hat{\alpha}_{\mathrm{PMCYX}} + \hat{\alpha}_{\mathrm{ph,b}} \tag{15}$$

The methyl group at the 5-position of PMCYX can be oriented either as equatorial or axial. Depending on the orientation of this methyl group two tensors can be derived which are given as

$$(\hat{\alpha}_{\mathrm{PMCYX},e})_{X_0Y_0Z_0} = \left(\frac{\Gamma_{cc}}{9}\right)\begin{bmatrix} 18 & 0 & 0 \\ & -9 & 0 \\ & & -9 \end{bmatrix}$$
$$(\hat{\alpha}_{\mathrm{PMCYX,a}})_{X_0Y_0Z_0} = \left(\frac{\Gamma_{cc}}{9}\right)\begin{bmatrix} 10 & -2\sqrt{2} & 0 \\ & -1 & 0 \\ & & -9 \end{bmatrix} \tag{16}$$

These are then transformed to the $X'Y'Z'$ frame using eq 14 where the components corresponding to PMCYX are used instead of those corresponding to DMCYX. This tensor corresponding to PMCYX, when added to those of the phenyl groups in the $X'Y'Z'$ frame, provides the final polarizability tensor for bisphenyl TMC.

2.3. Optical Anisotropy of Cyclohexylidene-Substituted Polycarbonate Chains. A segment of the polycarbonate BPCPC depicting the reference frames of various groups is shown in Figure 4. The polarizability tensor of the repeat unit of BPCPC comprises of contributions from four groups: two phenylenes (group 1 and group 3) subject to the effects of oxy substitution, DMCYX (group 4) and carbonate group (group 2). The tensors for these groups in their respective reference frames are

$$(\hat{\alpha}_1)_{xyz} = (\hat{\alpha}_3)_{xyz} = \mathrm{diag}[2.67 \;\; 0.17 \;\; -2.84]$$
$$(\hat{\alpha}_2)_{XYZ} = \mathrm{diag}[0.17 \;\; 1.04 \;\; -1.21]$$
$$(\hat{\alpha}_4)_{X'Y'Z'} = \begin{bmatrix} -0.3142 & 0.3884 & 0 \\ & 0.3142 & 0 \\ & & 0 \end{bmatrix} \tag{17}$$

For TMCPC the corresponding groups comprising the repeat unit are (a) two phenylenes (group 1 and group 3) subject to the effects of oxy substitution, (b) PMCYX (group 4) and (c) carbonate group (group 2). The tensor for PMCYX in the $X'Y'Z'$ frame is

$$(\hat{\alpha}_{4,e})_{X'Y'Z'} = \begin{bmatrix} 0 & 0.7493 & 0 \\ & 0.5303 & 0 \\ & & -0.5303 \end{bmatrix}$$
$$(\hat{\alpha}_{4,a})_{X'Y'Z'} = \begin{bmatrix} 0.3137 & 0.3608 & 0 \\ & 0.2163 & 0 \\ & & -0.53 \end{bmatrix} \tag{18}$$

Similarly, the repeat unit tensor of DMBPC is formulated from the sum of contributions from (a) two phenylene groups subject to the effects of oxy as well as methyl substitution, (b) DMCYX, and (c) the carbonate group. The tensor for the phenylene groups in DMBPC is similar to those in DMDPC, as given in eq 6. The transformation matrices for the calculation of the optical anisotropy of cyclohexylidene-substituted polycarbonates are

$$T_1 = R_x(-\psi_b)R_Z(\tau')$$
$$T_2 = R_Z(-\tau)R_x(\phi_b)$$
$$T_3 = R_x(-\phi_a)R_z(-\tau)$$
$$T_4 = R_Z(\tau')R_x(\psi_a) \tag{19}$$

2.4. Optical Anisotropy of Isolated Repeat Units. Separate calculations were performed for $\langle\gamma^2\rangle$ of each type of polycarbonate single repeat unit, with a consideration of all most probable rotational states. In the case of BPAPC, the tensor for the repeat unit is expressed in the frame of the phenyl group "b" ($x_by_bz_b$) and the tensors for the phenyl group ("a") and carbonate group are transformed to the $x_by_bz_b$ frame

$$(\hat{\alpha}_{\mathrm{RU}})^C = \hat{\alpha}_1{}^C + (T_1 \otimes T_1)\hat{\alpha}_3{}^C + (T_1 \otimes T_1)(T_3 \otimes T_3)\hat{\alpha}_2{}^C \tag{20}$$

where transformation matrices T_1 and T_3 are the same as given in the earlier work for BPAPC.[15] For cyclohexylidene-substituted polycarbonates, repeat unit optical anisotropies are calculated following a similar procedure using the expression

$$(\hat{\alpha}_{\mathrm{RU}})^C = \hat{\alpha}_1{}^C + (T_1 \otimes T_1)\hat{\alpha}_4{}^C + (T_1 \otimes T_1)(T_4 \otimes T_4)\hat{\alpha}_3{}^C + (T_1 \otimes T_1)(T_4 \otimes T_4)(T_3 \otimes T_3)\hat{\alpha}_2{}^C \tag{21}$$

where matrices T_1, T_3, and T_4 are those which are given by eq 19. The $\langle\gamma^2\rangle$ values provided in Table 2 are obtained by averaging over all conformations of the repeat unit for each polycarbonate structure.

2.5. Conformationally Averaged Chain Optical Anisotropy of Substituted Polycarbonates. The mean-squared optical anisotropy $\langle\gamma^2\rangle$ which is averaged over the probable conformations of the chain having *x* repeat units is obtained by incorporating the statisti-

Table 1. Geometrical Parameters of the Repeat Units of Polycarbonates

PC	ϕ_a	ϕ_b	ψ_b	ψ_a	$2\tau'$	τ
BPAPC	−130, −50, 50, 130	−130, −50, 50, 130	−130, −50, 50, 130	−130, −50, 50, 130	110.7	67
DMPC	−95, 95	−95, 95	−130, −50, 50, 130	−130, −50, 50, 130	110.7	65
BPCPC	−130, −50, 50, 130	−130, −50, 50, 130	−110, −70, 70, 110	−125, −55, 55, 125	107.7	67
TMCPC	−130, −50, 50, 130	−130, −50, 50, 130	−70, 110	−60, 120	106.7	67
DMBPC	−95, 95	−95, 95	−110, −70, 70, 110	−125, −55, 55, 125	107.7	65

Table 2. Mean-Squared Optical Anisotropies of Bisphenyls, Carbonates, and Single Repeat Units

	$\langle\gamma^2\rangle$ (Å^6)		
		repeat unit	
PC fragments	monomer fragments	equal weights	PCFF weights
DPP	39.08	89.38	89.63
DMBP	40.71	74.38	75.20
BPC	14.74	26.05	26.30
TMC	13.58 (*e*)	29.14 (*e*)	29.44
	10.55 (*a*)	18.17 (*a*)	
DMBPC	28.00	23.38	24.51
DPC	73.18		
DMDPC	52.92		

cal weight matrices into the respective P matrices as[7,13]

$$\langle\mathscr{P}_i\rangle = (U_i \otimes I_p)||P_i||;$$

$$\text{where } P_i = \begin{bmatrix} 1 & 2\hat{\alpha}_i^R(T_i \otimes T_i) & \hat{\alpha}_i^2 \\ 0 & T_i \otimes T_i & \hat{\alpha}_i^C \\ 0 & 0 & 1 \end{bmatrix} \quad (22)$$

$$\langle\gamma^2\rangle = \frac{3}{2} \times Z^{-1} J^* \langle\mathscr{P}_1\rangle\langle\mathscr{P}\rangle^{x-1}\langle\mathscr{P}_3\rangle J$$

for BPAPC and DMPC

where $\langle\mathscr{P}\rangle = \langle\mathscr{P}_3\rangle\langle\mathscr{P}_2\rangle\langle\mathscr{P}_1\rangle$

$$\langle\gamma^2\rangle = \frac{3}{2} \times Z^{-1} J^* \langle\mathscr{P}_1\rangle\langle\mathscr{P}\rangle^{x-1}\langle\mathscr{P}_4\rangle\langle\mathscr{P}_3\rangle J$$

for BPCPC, TMCPC, and DMBPC (23)

where $\langle\mathscr{P}\rangle = \langle\mathscr{P}_4\rangle\langle\mathscr{P}_3\rangle\langle\mathscr{P}_2\rangle\langle\mathscr{P}_1\rangle$ and Z is the partition function. The contributions of the end groups are taken into account by $J^*\langle\mathscr{P}_1\rangle$ and $\langle\mathscr{P}_3\rangle J$ (for BPAPC and DMPC) and $J^*\langle\mathscr{P}_1\rangle$ and $\langle\mathscr{P}_4\rangle\langle\mathscr{P}_3\rangle J$ for cyclohexylidene-substituted polycarbonates.

The statistical weights for energetically favorable conformers and their corresponding torsional states and bond angles, which were derived earlier using conformational analysis with bonded and interatomic nonbonded potentials described by the PCFF force-field,[20] are used here for the calculation of $\langle\gamma^2\rangle$. The minimum energy torsions and bond angles for these polycarbonates are given in Table 1. Calculations of optical anisotropy are also performed here for these polycarbonates by assigning equivalent weights for all the energetically favorable conformational rotational isomeric states which were obtained from previous conformational energy calculations.[20] In the case of BPAPC, the calculation was performed using torsions and bond angles as provided by Erman et al.,[14] and also independently by using the values derived from our PCFF-based simulations. It should be noted that in the calculation method of $\langle\gamma^2\rangle$ of polycarbonate chains outlined here, only the trans−trans conformations of the carbonate groups are considered. NMR studies on bulk amorphous BPAPC suggest that the conformation of the carbonate groups is predominantly trans−trans with less than 10% in the cis−trans conformation.[21] Calculations of the mean-squared optical anisotropy $\langle\gamma^2\rangle$ of the polycarbonate chains were performed using a FORTRAN code by incorporating the matrix multiplication scheme in the RIS formalism as provided by Flory.[7] The polycarbonate chains consisted of 11 repeat units in accordance with the earlier reports on BPAPC in that $\langle\gamma^2\rangle/x$ reaches an asymptotic value for $x \approx 10$.[15,16] $\langle\gamma^2\rangle/x$ is calculated as a function of x as well, and our results for all five polycarbonates show the same asymptotic behavior. The detailed analysis is provided in this paper specifically by comparing tabulated values of $\langle\gamma^2\rangle/x$ calculated for $x = 11$. The chemical constitution of the polycarbonate chain, for example for BPCPC, for the purpose of chain optical anisotropy calculation via RIS is given as R−(O−CO−O−C_6H_4−C_6H_{10}−C_6H_4)$_{x-2}$−O−CO−O−R, where R = HO−C_6H_4−C_6H_{10}−C_6H_4, and these are the same end groups on either side of the chain.

3. Results and Discussion

3.1. Mean Squared Optical Anisotropy of Bisphenyls, Carbonates, and Repeat Units. $\langle\gamma^2\rangle$ of bisphenyls, carbonate segments, and the repeat units for the five polycarbonates are given in Table 2. The use of PCFF-based torsions and bond angles for DPP[20] leads to a $\langle\gamma^2\rangle$ value of 39.1 Å^6 resulting from our calculation, while using the geometry reported by Erman et al.[14] leads to a value of 43.61 Å^6. The experimental value reported for DPP from depolarized Rayleigh scattering is 40 ± 2 Å^6.[14] The values provided in Table 2 were averaged over the energetically accessible most probable rotational isomeric conformations of these bisphenyl fragments. In cases where methyl substitution is absent on the phenyl rings (DPP, BPC, and TMC) the energetically accessible conformers in each of these fragments are symmetric and have a unique value of γ^2. In the case of fragments with methyl substitution on the phenyl rings (DMBP, DMBPC), the rotational isomeric conformers are not structurally and optically symmetric and these have different values of γ^2 and energy statistical weights. To see the influence of statistical weights on optical anisotropy, for DMBP and DMBPC, $\langle\gamma^2\rangle$ was also calculated based on equal probability of the conformers. Compared to DPP, it is observed that the cyclohexyl group at the C_α atom leads to significant reduction in $\langle\gamma^2\rangle$, whereas presence of methyl substituents on the phenyl rings *slightly enhances* $\langle\gamma^2\rangle$ such as in the case of DMBP and *significantly enhances* $\langle\gamma^2\rangle$ when one compares DMBPC with BPC. The effect of structural modification on the optical anisotropy of bisphenyls can be explained based on two factors: (1) substituent structural effects and (2) conformational effects. It is important to understand the separate influences of these effects.

Cyclohexylidene group at C_α lowers $\langle\gamma^2\rangle$ by approximately a factor of 2 (comparing DPP and BPC). The aliphatic cyclohexyl group and its low intrinsic anisotropy make these fragments more optically isotropic. The conformational effects are manifested through torsions (ψ) and the bond angle ($2\tau'$). The phenyl rings are

inequivalent due to the presence of cyclohexylidene group and in order to minimize the steric repulsions that arise from 1,3-diaxial interactions, the axial phenyl ring (ψ_b) prefers an orientation which is twisted by about 70° out-of-the-plane while the torsion about the equatorial phenyl ring (ψ_a) is 55°.[20] The axial phenyl ring prefers more of a perpendicular orientation and this leads consequently to a reduction in $\langle\gamma^2\rangle$. The same explanation holds true for TMC as well, where the bisphenyl conformers having either axial or equatorial orientation of the methyl group at the 5 position on cyclohexane ring give lower value of $\langle\gamma^2\rangle$ than for BPC. Calculation of $\langle\gamma^2\rangle$ of DPP was also performed using the same geometrical parameters as BPC, to get a quantitative understanding of the effect of only the torsions on the $\langle\gamma^2\rangle$ of DPP. For DPP, $\langle\gamma^2\rangle$ for a geometry derived from BPC (70°, 55° for ψ and $2\tau'$ of 107.7°) is 23.86 Å^6, which is about 15 Å^6 lower than $\langle\gamma^2\rangle$ for the minimum energy DPP (50°, 50°) conformation. This reduction of 15 Å^6 resulting from torsional differences between BPC and DPP is the dominating effect than the effect of intrinsic group polarizability differences, in facilitating a lower optical anisotropy for BPC as compared to DPP. The higher value of $\langle\gamma^2\rangle$ for TMC-e (having equatorially oriented methyl substituent at the 5-position of cyclohexyl ring) than for TMC-a (having axially oriented methyl substitution at the 5-position on cyclohexyl ring) is due to a higher polarizability arising from the equatorially oriented methyl group. Equatorial substituents tend to enhance the anisotropy in substituted cyclohexanes.[19] The preferred torsions about the C_α carbon are (−70°, −60°) and (−80°, −65°) for TMC-e and TMC-a respectively, where the phenyl rings are closer to a perpendicular orientation in the latter, and this feature also contributes to the lower anisotropy. For TMC, the axial conformer has energy of about 6 kcal/mol greater than the equatorial conformer, hence the population of the former can be considered to be negligible at 300 K. Thus, the conformationally averaged anisotropy of TMC will be dictated by the equatorial conformers.

DMBP has eight energetically favorable conformers, which we categorize into three sets with different γ^2 values, with conformers in each set having the same γ^2 value. Among these, conformers at (50°, 50°) and (−50°, −50°) states, have the lowest anisotropy (18.17 Å^6), where the methyl groups are pointing in the same direction with respect to the backbone and away from the isopropylidene group. For conformers with (ψ_b, ψ_a) values of (50°, −130°), (−50°, 130°), (130°, −50°) and (−130°, 50°), we obtain γ^2 as 38.44 Å^6, where the methyl groups on the two phenyl rings are pointing in opposite directions. When both methyl groups are oriented in the same direction and toward the isopropylidene group, this leads to a relative increase in the optical anisotropy of the bisphenyl as seen by the value of γ^2 which is 67.8 Å^6 for conformers (130°, 130°) and (−130°, −130°). By weighting all eight conformers equally, $\langle\gamma^2\rangle$ is obtained as 40.71 Å^6. In comparison, energetic averaging done using statistical weights derived using PCFF leads to a slightly lower value of 38.66 Å^6. From the statistical weight matrices it is found that the weights corresponding to the conformers that have higher optical anisotropy are lower than that of the conformers having lower optical anisotropy (1, 0.843, and 0.716 for the three sets respectively). Importantly, it should be noted that the geometry (in terms of ψ and $2\tau'$) is identical for DPP and DMBP. Hence the slight differences in $\langle\gamma^2\rangle$ for DPP and DMBP are due to the asymmetric conformers for the latter resulting from methyl substituents on the phenyl rings.

BPC and DMBPC are also conformationally identical, each having the same torsional and bond angle values about the C_α carbon.[20] DMBPC by virtue of the methyl substituents on the phenyl rings has conformers which do not have a unique γ^2 value, and these can be divided into four sets of two optically identical conformers which are as follows: (i) (70°, 55°), (−70°, −55°); (ii) (70°, −125°), (−70°, 125°); (iii) (110°, −55°), (−110°, 55°); and (iv) (110°, 125), (−110°, −125°). For these sets, γ^2 values are 9.42, 23.66, 28.87, and 50.05 Å^6, respectively. Since the phenyl rings are inequivalent, conformers ii and iii do not possess the same optical anisotropy. Comparing fragments DPP vs DMBP and BPC vs DMBPC, it turns out that the effect of methyl substituents on the optical anisotropy is not uniform for these fragments. In fact, one would expect that methyl substitution on the phenyl rings should increase the polarizability in the *xy* plane and thus enhance the optical anisotropy, in a manner similar to a $\langle\gamma^2\rangle$ comparison between benzene and toluene. But we find that this behavior does not apply uniformly for bisphenyls, which no longer remain symmetric due to methyl substituents on the phenyl rings. For BPC and DMBPC, presence of methyl substituents have a pronounced effect by which $\langle\gamma^2\rangle$ is higher for the latter by almost a factor of 2. The results show that the reason for this behavior is that six out of eight conformers of DMBPC have higher γ^2 than that which the conformers for BPC have (8 conformers of BPC which have a unique value of γ^2). Therefore, the conformationally averaged $\langle\gamma^2\rangle$ of the bisphenyl fragments decreases in the order DPP > DMBP > DMBPC > BPC > TMC.

In the case of carbonate fragments, for DPC, the calculated $\langle\gamma^2\rangle$ as reported previously by Erman et al. is 77.2 Å^6 ($\phi_a = \phi_b = 46°$, $\tau = 67°$) and the experimentally determined value is 72 ± 4 Å^6.[14] From our calculations the $\langle\gamma^2\rangle$ value for DPC for its twisted conformation as obtained using PCFF-based geometry ($\phi_a = \phi_b = 50°$, $\tau = 67°$) by considering only the trans−trans conformation, is 73.18 Å^6, which is in good agreement with the experimental value.[14] For DMDPC, conformational analysis has shown that the torsion about the Ph−O bond is 95° and that here also the trans−trans conformation is the most stable one.[20] Calculated $\langle\gamma^2\rangle$ for DMDPC (trans−trans) is 52.92 Å^6, which is significantly lower (by 20 Å^6) than that for DPC. The predominant effect leading to the reduction of $\langle\gamma^2\rangle$ of DMDPC relative to $\langle\gamma^2\rangle$ of DPC arises from the preferred conformation for DMDPC where phenyl rings are oriented perpendicular to the plane of the carbonate group. A reduction by 17 Å^6 is observed when the relative orientation of the phenyl rings in DPC changes from twisted conformation to being perpendicular ($\langle\gamma^2\rangle = 56.22$ Å^6 when $\phi_a = \phi_b = 90°$). Reduction in conformationally averaged anisotropy due to polarizability contribution from methyl groups is only ~3 Å^6, while the major effect comes from the torsional differences between DPC and DMDPC.

For the isolated polycarbonate repeat units, the calculations performed considering a single repeat unit (for, e.g., those having the formula $\{(C_6H_5)_2C(CH_3)_2\text{-}COO\}$ such as for BPAPC) which can take different permitted variations of torsions ψ and ϕ, over which the averages were taken. The number of permissible con-

formers is 128 each for BPAPC and BPCPC, 64 for TMCPC, and 32 each for DMBPC and DMPC. The number of unique conformers having different values of γ^2 were 4 each for BPAPC, BPCPC, TMCPC, and DMPC and 8 for DMBPC. $\langle\gamma^2\rangle$ of these repeat units are provided in Table 2. Methyl groups on the phenylene rings lead to a lowering of $\langle\gamma^2\rangle$ of the repeat units (see DMPC vs BPAPC), while this is in contrast to the trend in the case of the bisphenyl fragments. Similar to the behavior observed in the case of bisphenyls, $\langle\gamma^2\rangle$ of the three different cyclohexylidene-substituted polycarbonate repeat units are considerably lower than the value seen for BPAPC. Since the geometry of the carbonate group is similar in BPAPC, BPCPC, and TMCPC, their relatively lower $\langle\gamma^2\rangle$ values are due to structural as well as conformational effects that are brought about by the presence of the cyclohexyl group. For TMCPC, the orientation of the methyl group determines whether $\langle\gamma^2\rangle$ should be higher or lower relative to BPCPC. This trend is in contrast to the observation for the bisphenyl fragments, where irrespective of the orientation of the methyl group (at 5 position), $\langle\gamma^2\rangle$ of TMCPC is lower than that of BPCPC. All the four unique conformers of TMCPC-e (equatorial) have higher optical anisotropy than their corresponding counterparts of BPCPC. Polycarbonate repeat units possessing methyl groups on the phenyl rings have lower mean-squared optical anisotropy than their unsubstituted counterparts which comes from the conformational rigidity of the Ph−O torsion. The resulting conformation is one in which the phenyl rings orient perpendicular to the carbonate group and this is the major factor quantitatively contributing to the optical anisotropy. Methyl groups lower the optical anisotropy to different extents in DMPC and DMBPC in comparison to their respective unsubstituted counterpart polycarbonates. For DMPC the reduction amounts to 15 Å^6, while for DMBPC it is only 2.67 Å^6, which is due to a significant lowering of optical anisotropy already affected by the presence of a cyclohexylidene ring in the case of DMBPC. An examination of the calculated $\langle\gamma^2\rangle$ for the various types of repeat units reveals that cyclohexylidene group is far more effective in lowering the anisotropy as compared to methyl groups which are on the phenyl rings. In a case where both types of substitution are present, such as for DMBPC, the reduction in optical anisotropy is 66 Å^6 which signifies the nonadditivity of polarizability changes due to different contributing groups.

3.2. Conformationally Averaged Single Chain Optical Anisotropy of Polycarbonates. The calculations were performed for polycarbonates as a function of chain length. However, as seen from previous reports on BPAPC,[15,16] 11 repeat units are sufficient to obtain constancy of $\langle\gamma^2\rangle/x$. The variation of $\langle\gamma^2\rangle/x$ with x for all polycarbonates provided in Figure 5 is also in agreement with the above observation. Results are provided in Table 3. The relative trend in $\langle\gamma^2\rangle/x$ among these polycarbonates is the same as that for their isolated single repeat units, but the absolute values differ due to the influence of the neighboring repeat units in the case of the chains. Calculation of $\langle\gamma^2\rangle/x$ for BPAPC using the bond angle geometry and conformations used by Erman et al.[15] (with equal probability for all the energetically favorable conformers) using our matrix multiplication code gives a value of 111.3 Å^6, which is in perfect agreement with their reported value of 111 Å^6. Torsional values of ϕ and ψ in our work were

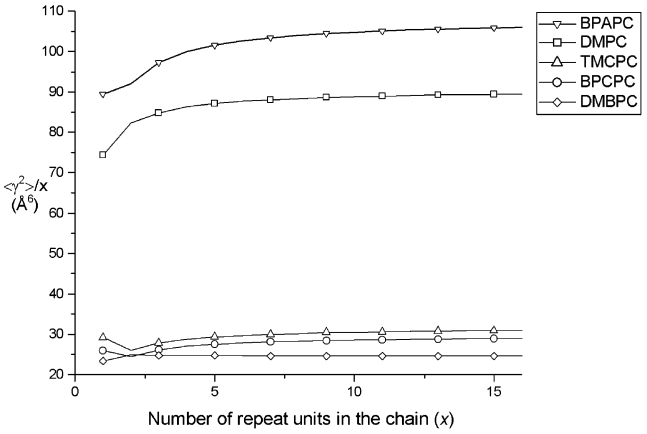

Figure 5. Conformational averaged optical anisotropy per repeat unit in polycarbonate chain, $\langle\gamma^2\rangle/x$, as a function of the number of repeat units, x.

Table 3. Mean-Squared Optical Anisotropy per Repeat Unit in Polycarbonate Chains (x = 11) from RIS Calculations

	$\langle\gamma^2\rangle/x$ (Å^6)	
PC	equal weights	PCFF weights
BPAPC[a]	105.20	105.10
	109.00	
	111.00	
DMPC	89.00	80.40
BPCPC	28.67	29.16
TMCPC	30.61 (*e*)	33.10 (*e*)
	20.03 (*a*)	20.45 (*a*)
DMBPC	24.63	26.37

[a] The three different $\langle\gamma^2\rangle/x$ values given here for BPAPC correspond to the three different values used for the torsional pair (ψ_b, ψ_a) which are (50°, 50°), (48°, 48°), and (47°, 47°), respectively. The values of (ψ_b, ψ_a) used for other polycarbonates correspond to the minimum energy states from a 5° conformational search from results of ref 20.

obtained from conformational analysis of the bond pairs using PCFF and a grid size of 5°.[20] Using these torsions and bond angles obtained from PCFF conformational analysis and by assigning equal probability for all the conformers, we obtain an anisotropy value of 105.2 Å^6 for BPAPC. Incorporation of PCFF derived conformational energy statistical weights does not alter the anisotropy value for BPAPC ($\langle\gamma^2\rangle/x$ = 105.1 Å^6), but for the methyl-substituted polycarbonates there are considerable differences between the optical anisotropy values. For BPAPC, a superior level agreement between calculations and experiment is met if (ψ_b, ψ_a) = (47°, 47°) is used, which are the minimum energy conformational states obtained from a 1° incremental search, as shown in Table 3. Nonetheless, the relative trends and accuracy of results are not substantially different. The optical anisotropy calculations presented here for substituted polycarbonates and those reported earlier for BPAPC[15] deal with a single chain having an all-trans carbonate linkage. For the carbonate group, cis−trans conformers are not included in the formalism employed. NMR experiments in the glassy state of BPAPC at 135 K have shown that the carbonate group is predominantly in the planar trans form (tt) and less than 10% of all carbonate groups are in the cis conformation (ct).[21] Additionally, we performed a parametric sensitivity analysis for BPAPC, using different values of torsions ϕ and ψ, where only one of the torsions was changed (reflecting a change in the torsional state at the rotational energy minima) and the optical anisotropy was

accordingly calculated. Performing the conformer searches for ϕ and ψ with a step size of 1° from 45 to 55° shows that for the pair (ψ_b, ψ_a) the torsional states (49°, 49°), (48°, 48°) and (47°, 47°) have similar energies as the state (50°, 50°). For (ϕ_a, ϕ_b), the lowest energy conformations are found to correspond to the (50°, 50°) state from the conformational analysis performed with 5° increments. $\langle\gamma^2\rangle/x$ calculated for a geometry of the BPAPC chain is 109 Å^6 when the set of parameters $\{\psi = 48°, \phi = 50°, \tau = 67°, 2\tau' = 110.7°\}$ is used, while the value comes out to be 111 Å^6 when $\psi = 47°$ is used (keeping other parameters the same). $\langle\gamma^2\rangle/x$ is critically dependent on the value of ψ rather than ϕ, where a 5° change in ψ torsion results in 5.3% change in $\langle\gamma^2\rangle/x$, whereas a similar variation of the ϕ torsion results in only 0.8% change. For substituted polycarbonates, as seen for BPCPC, the lowering of $\langle\gamma^2\rangle/x$ is appreciable and this is true for TMCPC and DMBPC as well. Axially oriented TMCPC-a gives the lowest optical anisotropy. The reduction in $\langle\gamma^2\rangle/x$ in going from BPCPC to DMBPC, due to the methyl groups, is 4 Å^6, which is not insignificant. Significant differences in the optical anisotropy come about due to the presence of the methyl group (comparing DMPC with BPAPC).

To obtain a thorough understanding of the influence of the various conformers, calculations were performed which were conformationally biased (details given in Table 1S in the supplementary information section). For BPAPC, when ϕ and ψ have similar absolute torsion values for, e.g., (ϕ, ψ) of (50°, 50°), (130°, 130°), and so forth (and all positive and negative combinations of the dihedrals), the value of $\langle\gamma^2\rangle/x$ is 168.2 Å^6. When torsions ϕ and ψ are (50°, 130°) or (130°, 50°) (and all positive and negative combinations), $\langle\gamma^2\rangle/x$ is 68.1 Å^6. There are two sets of conformers which act in opposite directions in determining the final averaged optical anisotropy. Similar results were obtained for BPCPC and TMCPC-e as well. For DMPC and DMBPC, the higher anisotropy conformers are those for which the methyl groups are oriented on the same side of the backbone and toward the backbone-to-side-group directional vector at the C_α, whereby these are extended conformations of the repeat unit. For the conformers having lower optical anisotropy, the methyl groups are oriented away from the backbone-to-side-group directional vector at C_α, and the overall conformation is less extended. In general extended conformations lead to higher optical anisotropy. Therefore, the difference in the optical anisotropy of various conformers (sets with different torsional values) is greater with respect to the cumulative conformationally averaged values in the case of DMPC and DMBPC. These polycarbonates contain bisphenyls which have optically nonsymmetric minimum energy rotational isomers, leading to relatively large differences in their optical anisotropy values. Calculations were also performed, by averaging over each set of repeat unit conformations which are optically symmetric. The detailed information is given in Table 2S in the Supporting Information section of this paper. Some representative conformers of the polycarbonate chain segments, which have different γ^2 values, are given in Figure 6 in order to highlight how conformational structure dictates optical anisotropy. Calculations show that the repeat unit γ^2 in each polycarbonate varies over a significant range of values depending on the energetically accessible conformation. In a conformation where the angle between the planes defined by the carbonate group and the phenyl ring is large, γ^2 is lower as compared to when they are closer to a parallel orientation.

For BPCPC, TMCPC, and DMBPC, the values of $\langle\gamma^2\rangle/x$ increase, but not significantly, by the use of PCFF statistical weights. For DMPC there is considerable reduction (by 8.6 Å^6) when more realistic PCFF weights are used. For DMPC, the results reveal that conformers with higher optical anisotropies {(ϕ, ψ) of (±95°, ±130°)} have lower statistical weight ($\sigma = 0.717$) than those with lower anisotropies (ϕ, ψ) = (±95°, ±50°) ($\sigma = 1.0$). About the (ψ_b, ψ_a) bond pair it is found that states (130°, 130°) and (−130°, −130°) give higher $\langle\gamma^2\rangle/x$ than that shown by states (50°, 50°) and (−50°, −50°). In contrast, for DMBPC, the statistical weights corresponding to higher anisotropy conformers {(ϕ, ψ) = (±95°, ±125°), $\sigma = 1.0$} are higher than those for the lower anisotropy {(ϕ, ψ) = (±95°, ±55°), $\sigma = 0.79$}. DMBPC bisphenyl fragment, for states at the (ψ_b, ψ_a) pair, the (110°, 125°) and (−110°, −125°) conformers have higher γ^2 than (70°, 55°) and (−70°, −55°) conformers. Statistical weight of the former set of conformational states is higher than that of the latter (1 vs 0.83) and this effect also contributes to higher $\langle\gamma^2\rangle/x$ values by using the PCFF statistical weights.

3.3. Relationship between Chain Optical Anisotropy and Bulk Optical Properties. The mean-squared optical anisotropy of polycarbonates estimated in this study were compared to the optical properties of the bulk polymer as manifested through the birefringence and stress optical coefficients in the glassy and melt states. Two measures of the suitability of a material as optical data storage disk are its stress optical coefficient in the melt (C_m) and its stress optical coefficient in the glassy state (C_g). C_m is directly proportional to the polarizability anisotropy of the polymer chains.[5] These coefficients represent the degree of orientation of the segments and the optical anisotropy inherent in the polymer chains. BPAPC has positive values of C_m and C_g, which are 5600 and 82 brewsters respectively (for samples with $M_w = 20\,000$).[22] C_m and C_g values of the polycarbonate of spirobisindane (6,6′-dihydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobis(indan), SBIPC) are −650 and 20 brewsters, respectively.[23] It is found that the copolymer of SBIPC (86.3 mol %) and BPAPC (13.7 mol %) has C_m close to zero and is an intrinsically isotropic polymer ($M_w = 59\,000$, C_m measured at $T_g + 15$ °C).[23] C_g for DMPC[24] and DMBPC ($M_w = 35\,200$ g mol^{-1})[25] are found to be 51 and 47 brewsters, and the values for C_m are 4500 and 2350 brewsters respectively, and are lower than those corresponding to BPAPC. C_g and C_m for BPAPC:DMBPC copolymers are available for a range of compositions (molar composition → C_g, C_m in the following order: {20:80 → 54.3, 2910}; {40:60 → 59.7, 3480}; {60:40 → 68.4, 3940}). These data indicate that both C_g and C_m increase linearly with BPA content (mol %) in the copolymer.[25] Similar behavior is also reported for TMCPC:BPMPC copolymer (copolymer of TMCPC and polycarbonate of 4,4′-(*m*-phenylenediisopropylidene) diphenol) where C_g increases linearly with the BPM content.[26] From a regression analysis of the copolymer data, we extrapolated the C_g for TMCPC homopolymer to a value of 33.4 brewsters. C_m for TMCPC is reported to be around 2500 brewsters (high M_w, measurement temperature is T_g+10K).[27] C_m for BPCPC homopolymer is 2300 brewsters while that for a copolymer with BPAPC (50:50) is 3400 brewsters (viscosity average

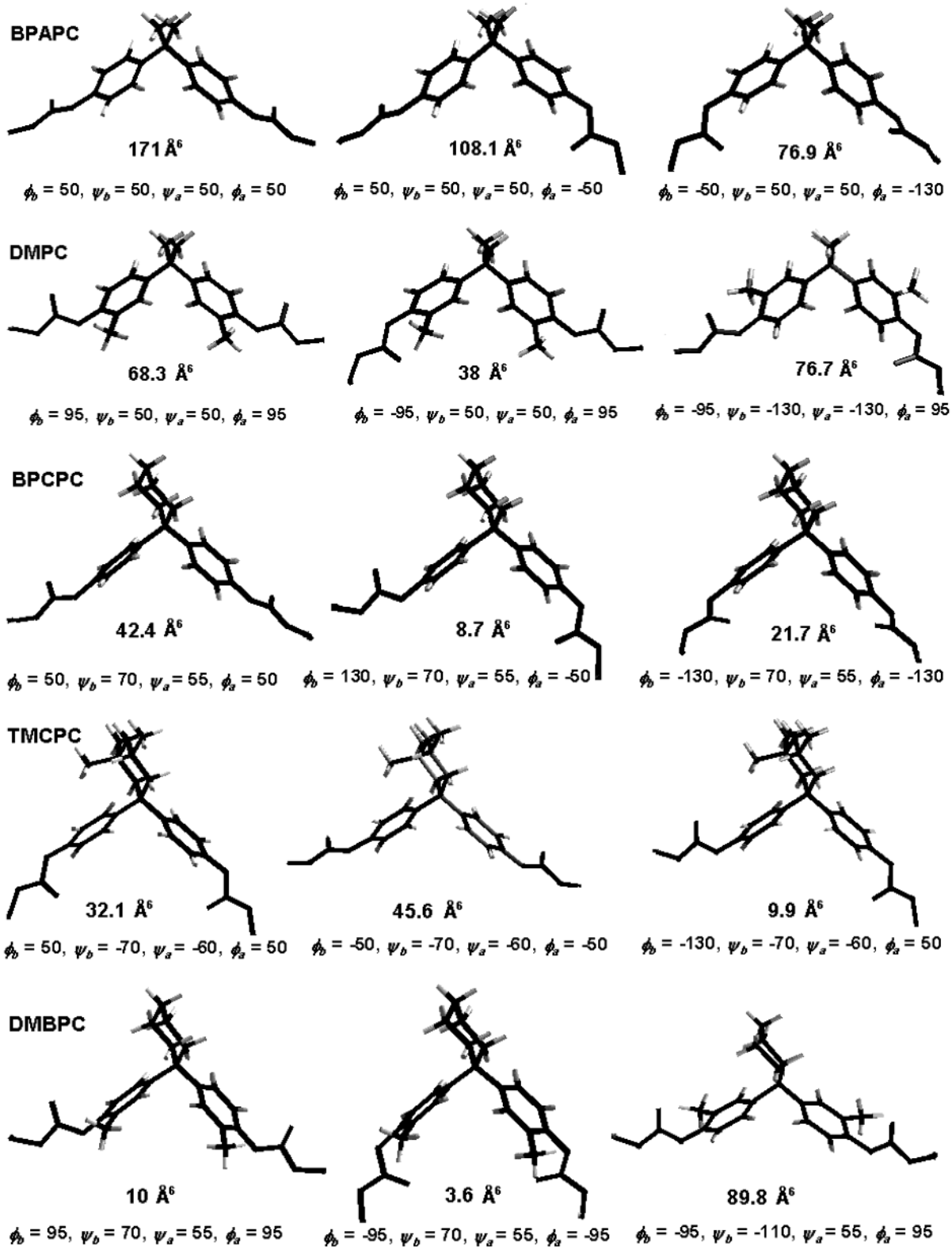

Figure 6. Conformations of repeat units of polycarbonates having different values of optical anisotropy. The conformers are depicted as segments of the chain and the torsional specifications follow the order ϕ_b, ψ_b, ψ_a, ϕ_a as given in Figure 1 for the BPAPC repeat unit.

molecular weight of 16 200 and 15 700 g mol^{-1} respectively).[28] The experimental values of C_m reported for the homopolycarbonates were plotted against the mean-squared optical anisotropy obtained from RIS calculations in this work for isolated repeat units as well as for repeat units in a chain. The results are given in Figure 7. C_m for these polycarbonates increases linearly with $\langle\gamma^2\rangle/x$ of the repeat unit in the chain and with $\langle\gamma^2\rangle$ of isolated single repeat unit. The same linear trend is also observed between C_m and $\alpha_{||} - \alpha_{\perp}$ (which is $\{\langle\gamma^2\rangle/x\}^{1/2}$) of the repeat unit in a chain. The same linear behavior of C_m with the polarizability anisotropy of a Kuhn statistical segment, when comparing different polymer structures having little variation in their refractive index, is experimentally known and also specifically brought forth for polycarbonate melts.[5] Use

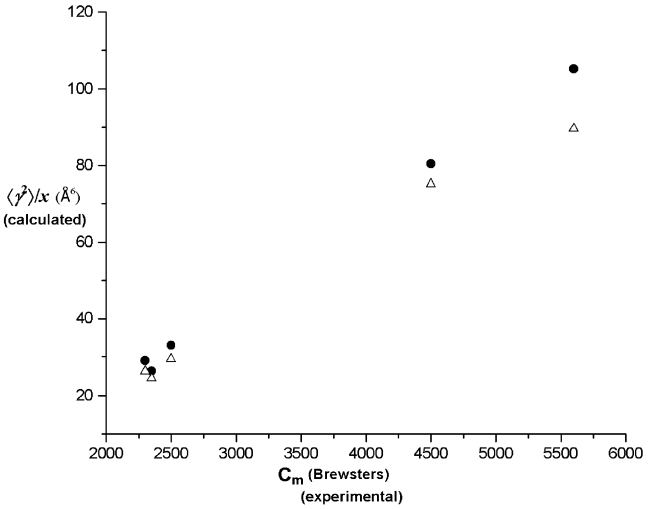

Figure 7. Plot of the calculated optical anisotropy per repeat unit, $\langle\gamma^2\rangle/x$, vs experimental values of C_m: (●) repeat unit in a chain; (Δ) isolated repeat unit.

of $\langle\gamma^2\rangle/x$ as the molecular scale optical property (parameter) based on the smallest exactly definable structure as shown here, instead of the polarizability anisotropy of a Kuhn statistical segment[5] which is typically used in describing the effect of structure on melt stress−optical coefficient, would provide a more accurate way of scaling of the macroscopic optical property of polymers as a function of chemical structure. Molecular dynamic simulations of stress relaxation and stress−optical coefficient of freely rotating united-atom polyethylene chain melts[29] have shown that the use of a monomer polarizability anisotropy for CH_2 beads, derived from anisotropic components of the C−C and C−H bond polarizabilities, into the relationship between the stress−optical coefficient and monomer level polarizability anisotropy shows a comparison to within an order of magnitude with the experimental data. However, for polymer chains that are more complicated than polyethylene in their chemical structure, an exact definition of the monomer level optical anisotropy parameter, which can be used to either confirm theoretical calculations or to make predictions for new systems, has not been specifically presented in the literature. Experimental C_g data were available only for three polycarbonates (BPAPC, DMPC and DMBPC) and the plot of C_g vs $\langle\gamma^2\rangle/x$ (for repeat unit in the chain) did not show a linear trend even though C_g increases with $\langle\gamma^2\rangle/x$. C_g for TMCPC (extrapolated from the copolymer data) is lower than that for DMBPC, even though optical anisotropy follows the opposite trend. This behavior may be attributed to the predominant conformational effects as manifested through bond angle distortion occurring in the glassy state under stress and/or packing effects in the condensed phase which can occur during sample stretching. Orientation of the bulky trimethylcyclohexylidene group in TMCPC also would lead to stringent interchain correlation, packing effects, and residual stresses.

Birefringence caused by the reorientation of polymer chains mainly results from the intrinsic polarizability of the constituent units and hence is directly proportional to the polarizability and optical anisotropy of the repeat units. The intrinsic birefringence (Δn_o) of amorphous BPAPC obtained from experimental measurements is 0.192 ± 0.006.[30] Δn_o calculated via the Lorenz−Lorentz equation is 0.164 (14% deviation) by using the polarizability anisotropy of BPAPC obtained from our RIS calculation and a density value of 1.2 g/cm^3. Using theoretical polarizability anisotropy of the BPAPC repeat unit reported earlier[15] results in a value of 0.173 (9.8% deviation). One possible reason for the deviation between experimental and calculated values could be the fact that for complete orientation of the polarizable units in the chains along the stretch axis of a sample in the condensed phase the density would be higher than 1.2 g/cm^3. Use of the correct density would therefore lead to a very good agreement of our calculated intrinsic birefringence with the reported experimental value. Finally, using 115 Å^6 (for $\langle\gamma^2\rangle/x$ in amorphous phase),[16] with other parameters remaining the same, gives an agreement between calculated and experimental Δn_o values to within 6%.

4. Conclusions

A general extension of the Flory method for formulation of the polarizability tensors of bisphenol A polycarbonate molecular fragments, applicable to substituted bisphenyl fragments, diphenyl carbonates and repeat units of various structurally modified polycarbonates is presented in this study. The methodology utilizes polarizability tensors of constituent groups that have been derived from DRS measurements in solvents like CCl_4 and the geometry (bond angles and torsions) from conformational energy calculations.

For the bisphenyl fragments, a significant reduction in optical anisotropy is observed due to the presence of a cyclohexylidene group substitution at the C_α, carbon in comparison to fragments of BPAPC. Methyl substitutions on the phenyl rings tend to increase the optical anisotropy of the bisphenyls. Because of the preferred mutually perpendicular orientation of the phenyl rings arising from interactions of *o*-methyl groups, the optical anisotropy of carbonate fragment DMDPC is lower than that of DPC. The presence of cyclohexylidene group at C_α results in a change in the conformations of the bisphenyl fragment and this is the predominant effect responsible for lowering of the optical anisotropy in cyclohexylidene-substituted polycarbonates. The contribution of the various conformers toward the optical anisotropy is analyzed in detail in this paper. Calculated optical anisotropy of the repeat units were compared with the experimental bulk optical properties reported in the literature. The substituted polycarbonates have lower values of stress optical coefficients C_g and C_m in comparison to those for BPAPC, in accordance with the calculated optical anisotropy values of these repeat units. It is also found that experimentally observed C_m of the polycarbonates studied here increase linearly with the calculated value of the repeat unit optical anisotropy from the RIS approach, which provide validity to the calculations since C_m is known to be a linear function of monomer level polarizability anisotropy.[5] The polycarbonates studied here are some of the most complicated polymer chain structures for which RIS method with group polarizability has been applied in order to calculate optical anisotropy. The scheme presented here for calculation of optical properties of cyclohexylidene-substituted polycarbonates can be applied to bisphenols and their polycarbonates with any kind of substitution on the cyclohexylidene ring provided accurate group polarizability tensors corresponding to the substituents are known a priori.

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Supporting Information Available: Text and Table 1S giving details and compilation of the results of calculation of the optical anisotropies of polycarbonate chains by considering lesser number of rotational state per bond, and text and Table 2S giving details and compilation of results of calculation of the optical anisotropies averaged over torsionally symmetric conformers (which have the same optical anisotropy for the repeat unit), showing the effect of specific repeat unit level conformer polarizability and optical anisotropy on the chain property when all repeat units in the chain have only these prescribed specific conformations. This material is available free of charge via the Internet at http://pubs.acs.org.

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