as those detailed above, we find

$$g_1 = \lambda^3 + 3\lambda^2(1-\lambda) + 9/4\lambda(1-\lambda)^2 + 5/8(1-\lambda)^3 \quad \text{(B8)}$$

$$g_2 = [\lambda^6 + 6\lambda^5(1-\lambda) + 15\lambda^4(1-\lambda)^2 + 65/4\lambda^3(1-\lambda)^3 + 495/64\lambda^2(1-\lambda)^4 + 21/16\lambda(1-\lambda)^5 + 46/256(1-\lambda)^6]/{g_1}^2 \quad \text{(B9)}$$

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$$\langle \mathbf{r}_i \mathbf{r}_j \rangle = a^2 \delta_{ij}$$

$$\langle \mathbf{r}_i \mathbf{r}_j \mathbf{r}_k \mathbf{r}_l \rangle = a^4[\delta_{ij}\delta_{jk}\delta_{kl} + \delta_{ij}\delta_{kl}(1-\delta_{ik}) + {}^1\!/_3(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})(1-\delta_{ij})]$$

where δ_{ij} is the Kronecker delta function.
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Random Coil Configurations of Aromatic Polyesters: Temperature Coefficient of the Unperturbed Dimensions of Poly(diethylene glycol terephthalate) Chains

Evaristo Riande* and Julio Guzmán

Instituto de Plásticos y Caucho (CSIC), Madrid-6, Spain

Miguel A. Llorente

Departamento de Química General y Macromolécular, Facultad de Ciencias, Universidad a Distancia (UNED), Madrid-3, Spain.

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ABSTRACT: Hydroxyl-terminated poly(diethylene glycol terephthalate) chains having number-average molecular weights of 7200 were end-linked into noncrystallizable trifunctional networks using an aromatic triisocyanate. The networks thus obtained were studied with regard to their stress–strain isotherms at 62, 70, and 88 °C. For elongation ratios up to 400% none of the isotherms displayed an increase or upturn in the reduced forces $[f^*]$, indicating that the polymer does not crystallize under stress, probably due to very unfavorable kinetic conditions. Force–temperature measurements at constant length and pressure are also reported for these networks. The ratio of the energy contribution to the total tension, f_e/f, calculated from these measurements and the thermal expansion coefficient were used to calculate the temperature coefficient of the mean-square end-to-end distance. It was found that $\mathrm{d} \ln \langle r^2 \rangle_0 / \mathrm{d}T = (1.01 \pm 0.14) \times 10^{-3}\ \mathrm{K}^{-1}$. A similar value was obtained for this coefficient from thermoelastic measurements carried out on swollen networks. The analysis of the temperature coefficient of poly(diethylene glycol terephthalate) in terms of the rotational isomeric state model confirms the results obtained from ^{1}H NMR studies, according to which the gauche states about CH_2–CH_2 bonds in the polymer chain have an energy significantly lower than these states about similar bonds in poly(oxyethylene).

Introduction

Studies on the random configurations of aromatic polyesters are meager due to the difficulties involved in the experimental determination of their configuration-dependent properties.[1-6] Most of these materials are highly crystalline and melt well above room temperature, so they are insoluble in ordinary solvents.[7] Measurements of configurational properties in solution are therefore precluded. Even in the cases in which the determination of a particular property can be carried out in bulk, as, for example, in the measurements of the temperature coefficient of the unperturbed dimensions by thermoelastic experiments, it is necessary to make the pertinent experiments above the melting temperature at which most of the molecular networks prepared from these polymers would undergo chemical and physical aging.

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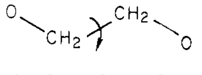
There is, however, a polyester which may be useful for these studies. We are referring to poly(diethylene glycol terephthalate) (PDET), an alternating copolymer of ethylene terephthalate and ethylene oxide. The presence of an ether group in the repeat unit of the chains provides this polymer with peculiar behavior. Thus, it is soluble in common organic solvents at room temperature. Moreover, it does not crystallize from the melt, but it does from dilute solutions.[5,8,9] Repeating units of this polyester are present in poly(ethylene terephthalate) (PET). Actually, during the melt polycondensation of PET from dimethyl terephthalate and ethylene glycol, the glycol may self-condense to produce diethylene glycol, which is then preferentially incorporated into the polymer chain due to the fact that it has the same reactivity as ethylene glycol and lower volatility. The presence of these units in PET influences its physical properties.[10-12] For this reason it would be interesting to investigate the conformational features of PDET chains.

A recent conformational analysis carried out on PDET by ^{1}H NMR spectroscopy[13] suggests that the gauche population about



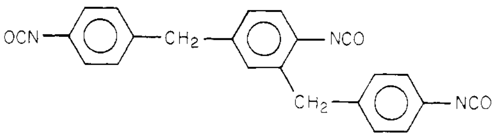
bonds is significantly higher than that of similar bonds in poly(ethylene oxide) (POE). This would indicate that gauche states about CH_2–CH_2 bonds which give rise to first-order O···O interactions have an energy which is significantly lower in the former polymer than in the latter. Although in an earlier study[5] the dipole moments of PDET were measured and the results were interpreted in terms of the rotational isomeric state (RIS) model, the results were not conclusive with regard to the value of this particular energy. A goal of this investigation is, therefore, to measure the temperature coefficient of the unperturbed dimensions of PDET chains and to analyze the experimental data by the RIS model in order to gain additional insight into the conformational properties of these chains.

Another aim of this work is to study the potentiality of PDET to prepare model networks which might be useful for studies on rubber-like elasticity. At present, few studies have been done in which relationships between the equilibrium elastic properties of a polymer network and the details of its molecular structure have been established.[14] The reason is that most of the networks were prepared from polymeric chains by introducing cross-links between chain segments in a highly random manner. However, there are now available techniques which permit the preparation of model networks by controlling the selectivity of the cross-linking reaction. Some of these techniques involve linking the chains exclusively through functional groups placed at the ends.[15-20] Whenever the cross-linking reaction is complete, the molecular weight M_c between cross-links is then the known molecular weight of the chain prior to its incorporation in the network. PDET chains are adequate for this purpose because they can be prepared with two end hydroxyl groups which can be cross-linked with appropriate chemical compounds. Moreover, an important feature of PDET is that its glass transition lies below room temperature[8,9] and therefore the elastomeric properties of the networks prepared with this polymer can be examined at temperatures lying in the range 50–100 °C, without noticeable degradation effects occuring in the networks. In this work, preliminary results are also reported concerning the modulus of PDET networks in the limits of large and small deformations. These experimental results are then compared with theoretical predictions in order to contribute to elucidating the molecular aspects of rubber-like elasticity.

Experimental Part

Synthesis of the Polymer. Poly(diethylene glycol terephthalate) was prepared by the standard melt-phase procedure[8] from dimethyl terephthalate and diethylene glycol in the presence of tetraisopropyltitanate as catalyst. An initial 1:2.2 molar ratio of dimethyl terephthalate to glycol was used, and the reaction was allowed to proceed under a nitrogen atmosphere. The first step of ester interchange was complete in 2–3 h at 160–180 °C, with elimination of the theoretical amount of methanol; the second step, polycondensation, was carried out at 230–250 °C under vacuum (0.1 mmHg) for 1 h. In order to remove the low molecular weight chains, the polyester was dissolved in chloroform and precipitated with methanol. Finally, it was dried under vacuum. The number-average molecular weight of the fractions used in the thermoelastic measurements was determined by vapor pressure osmometry and turned out to be 7200.

Elastic Measurements. The hydroxyl-terminated polyester chains were end-linked with 2,4-bis(*p*-isocyanatobenzyl)phenyl isocyanate, whose molecular structure is



Stoichiometric equivalent amounts of polyester and isocyanate, both completely dried, were dissolved in a small amount of dried methylene chloride. The solvent was removed by evaporation in a dry atmosphere, and the mixture of cross-linked agent and polymer was placed in a Teflon mold at 80 °C for 72 h. No soluble fraction of polymer was detected after the resulting network was extracted with chloroform for 3 days. Stress–strain experiments were carried out on strips cut from the network sheets, using standard techniques described elsewhere.[15,18,22] Forces exhibited by the strips, at constant length, were determined over the range 50–100 °C. These forces were recorded when they became sensibly constant, up to 48 h being required in some cases. In all the experiments reversibility was tested. All the thermoelastic experiments were made at elongation ratios larger than 2, so that the effects of the correction necessary to transform data at constant pressure into data at constant volume are minimized. In addition to this, the cubical thermal coefficient of the network over the temperature range studied was measured by dilatometry and it was found to have a value of 0.80×10^{-3} K^{-1}. Stress–strain isotherms were made at 62, 70, and 88 °C, using a sequence of increasing values of elongation, with some inclusions of values out of sequence to test for reversibility.

Results and Discussion

Stress–Strain Isotherms. The fact that PDET is able to crystallize under certain conditions, for example, from dilute solutions, raises the question of the possibility that the polymer crystallizes under stress. In order to investigate this point a few stress–strain isotherms were made at three different temperatures. They are shown in Figure 1. The data are represented by the usual Mooney–Rivlin formulation[23,24]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (1)$$

in which $2C_1$ and $2C_2$ are constants independent of the elongation ratio α and $[f^*]$ is the "reduced force" or modulus, defined by[22,25]

$$[f^*] = f/(\alpha - \alpha^{-2})A^* \qquad (2)$$

where f is the elastic force at equilibrium and A^* is the cross section of the undistorted strip. As can be seen in Figure 1 no deviations from linearity occur even though elongation ratios larger than 400% were reached. These data indicate, therefore, that the polymer does not crystallize under stress, probably due to very unfavorable

Table I
Elastomeric Properties of Unswollen PDET Networks

T/°C	$2C_1$/(N mm^{-2})	$2C_2$/(N mm^{-2})	$2C_2/2C_1$		A_3	A_3'
62	0.2108	0.2602	1.234		0.45	1.01
70	0.1902	0.2650	1.393		0.40	0.96
88	0.2216	0.2225	1.004		0.45	0.90
				av	0.43 ± 0.02	0.96 ± 0.04

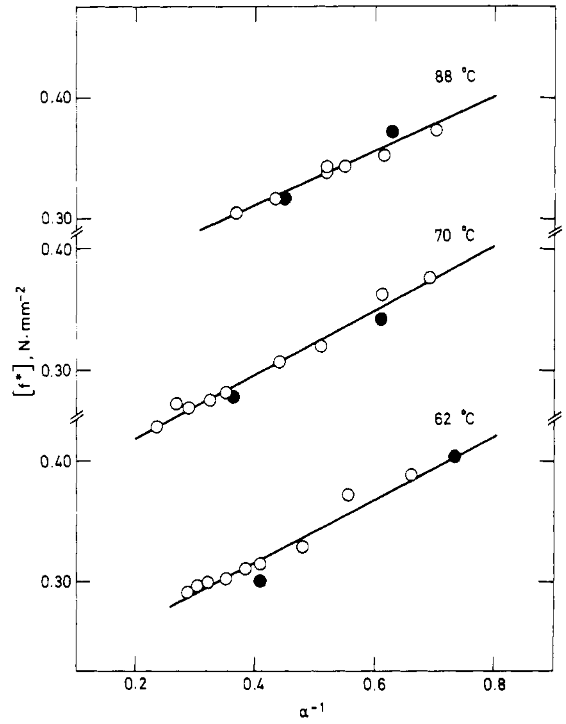


Figure 1. Stress–strain isotherms for PDET unswollen networks.

Table II
Thermoelastic Data at 70 °C of Unswollen PDET Networks

α		f_e/f	10^3(d ln $\langle r^2\rangle_0$/dT), K^{-1}
2.781		0.43	1.24
2.811		0.35	1.01
2.811		0.40	1.16
2.908		0.33	0.96
3.122		0.28	0.83
3.305		0.29	0.84
3.572		0.34	1.00
	av	0.35 ± 0.05	1.01 ± 0.14

kinetic conditions. The constants $2C_1$ and $2C_2$ are given in columns 2 and 3 of Table I.

The elastic data given in Table I, although preliminary, are very interesting from the point of view of testing the recent molecular theories of rubber-like elasticity. The moduli at high ($\alpha^{-1} \rightarrow 0$) and low ($\alpha^{-1} \rightarrow 1$) deformations are given by $2C_1$ and $2C_1 + 2C_2$, respectively. They are given in terms of molecular parameters of the network by[18,20,26,27]

$$2C_1 = \rho A_\phi RT/M_c \qquad (3)$$

$$2C_1 + 2C_2 = \rho A_\phi' RT/M_c \qquad (4)$$

where ρ is the density of the network and M_c is the molecular weight between cross-links. M_c is taken as equal to M_n, the molecular weight of the chains prior to cross-linking, due to the apparent completeness of the reaction as indicated by the fact that no soluble material was extracted. The structure factor A_ϕ is related to the modulus at high deformation, $2C_1$. In this situation the deformation should be nonaffine, approaching the phantom limit, in which the junctions are free to fluctuate around their mean positions independently of strain.[26,28] The value of A_ϕ is given by $1 - 2/\phi$ and, therefore, should be 0.33 for a trifunctional network.[20,26-30] The experimental value of 0.43 ± 0.02 is in good agreement with theory and within experimental error for this sort of measurement.

In the limit at small deformation ($\alpha^{-1} \rightarrow 1$) we are approaching the affine limit, in which the junctions are firmly embedded in the network structure and they deform affinely with the macroscopic strain. In this limit, theory predicts for the structural factor A_ϕ' a value equal to unity,[26-28] independent of the functionality ϕ. The experimental value of 0.96 ± 0.04 is in very good agreement with theory.

According to these theories the constant $2C_2$ is now interpreted as a measure of how the deformation changes from affine to the phantom limit with increasing strain. Usually the data are better represented by the ratio $2C_2/2C_1$. This ratio may depend on the degree of cross-linking of the network, with an upper value of 2 for a trifunctional network. The experimental values of $2C_2/2C_1$ are given in the fourth column of Table I.

All the above results seem to be in agreement with conclusions reached by other authors,[14,18,20] according to which topological entanglements do not make significant contributions to the equilibrium elastic properties of amorphous polymer networks. At present, there is a great deal of interest in this problem. Some authors[19,31,32] find a big contribution to the modulus from the entanglements, in some cases even much more important than the chemical cross-links. On the other hand, other workers[14,18,20] find no need to invoke any contribution from entanglements to account for the modulus observed; the only role of them would be to prevent the fluctuations of junctions and so to determine the degree of affineness of the deformation, but without increasing the effective cross-link density. As was stated above, our results seem to support the latter group. At present, only a few polymers have been used in the preparation of model networks and, therefore, more systems should be used to reach a definitive conclusion. PDET is a very promising polymer in this regard and more work will follow.

Temperature Coefficient of the Unperturbed Dimensions. Whenever the network obeys the generalized Gaussian theory of rubber elasticity, the temperature coefficient of the unperturbed dimensions, d ln $\langle r^2\rangle_0$/dT, may be obtained from force–temperature measurements by means of the equation[33,34]

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -\left[\frac{\partial \ln (f/T)}{\partial T}\right]_{P,L} - \frac{\beta}{\alpha^3 - 1} = f_e/fT \qquad (5)$$

where β is the expansion coefficient. The quantity $f_e = (\partial E/\partial L)_{V,T}$ is the internal energy component and, in this context, f_e/f serves as a measure of nonideality of the elastomeric network. Values of ln (f^*/T), where f^* is expressed in N/mm^2 of undistorted cross section, are plotted as a function of temperature in Figure 2; each line in the figure was located by least-squares analysis and it is labeled

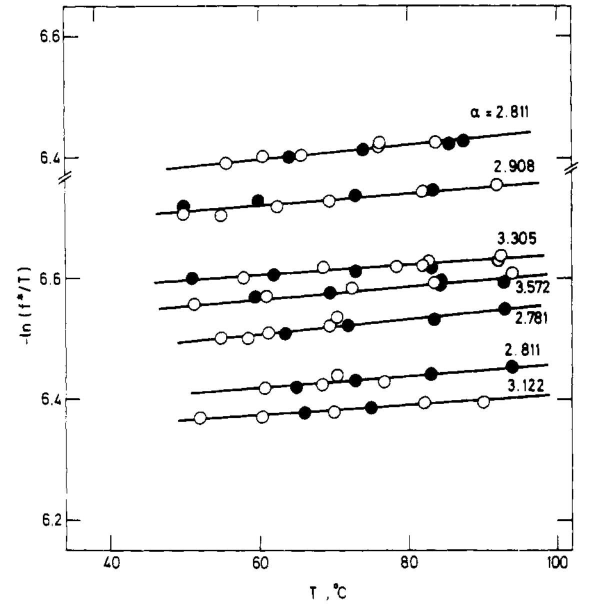


Figure 2. Thermoelastic results for unswollen PDET networks at different elongations. Filled circles represent values obtained at increasing temperatures.

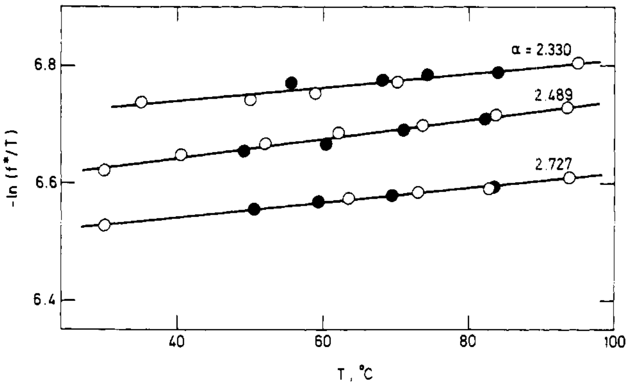


Figure 3. Thermoelastic results at different elongations for PDET networks swollen with dimethyl phthalate (volume fraction of the polymer v_2 = 0.90).

Table III
Thermoelastic Data at 60 °C for PDET Networks Swollen with Dimethyl Phthalate in Which the Volume Fraction of Polymer Is 0.90

α	f_e/f	10^3(d ln $\langle r^2\rangle_0$/dT), K^{-1}
2.330	0.31	0.92
2.489	0.50	1.49
2.727	0.38	1.13
av	0.40 ± 0.08	1.18 ± 0.24

with the corresponding elongation ratio α. Values of f_e/f and d ln $\langle r^2\rangle_0$/dT at the mean temperature of 70 °C are given in the third and fourth columns, respectively, of Table II for different values of α. It can be observed that the temperature coefficient of PDET chains is positive, its average value being (1.01 ± 0.14) × 10^{-3} K^{-1} in the vicinity of 70 °C. In order to confirm this value, thermoelastic experiments were also made on PDET networks swollen with dimethyl phthalate. The force–temperature data are plotted in Figure 3. The values of f_e/f and d ln $\langle r^2\rangle_0$/dT for swollen networks are given in Table III. It can be observed that the average value of the temperature coefficient obtained in these measurements, (1.18 ± 0.24) × 10^{-3} K^{-1}, is in good agreement with that obtained from thermoelastic measurements on PDET unswollen networks.

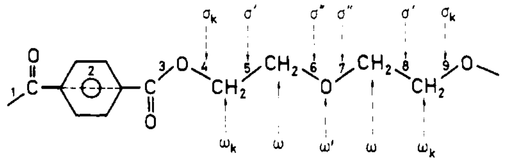


Figure 4. Poly(diethylene glycol terephthalate) chain. First-order Boltzmann factors are given above the formula; second-order factors are given below.

Table IV
Structural Parameters

bond length/Å	bond supplement angles/deg
l_{C-C} = 1.53	$\theta_1 = \theta_2$ = 66
l_{O-C} = 1.43	$\theta_3 = \theta_9$ = 67
l_{O-CO} = 1.34	$\theta_4 = \theta_5 = \theta_7 = \theta_8$ = 70
$l_{CO\cdots CO}$ = 5.74	θ_6 = 69

The unusually high value of d ln $\langle r^2\rangle_0$/dT found for PDET chains is very surprising in view of the fact that the presence of two planar trans ester groups in the repeat unit of the chains confers freedom of rotation on adjoining bonds. It should be stressed in this regard that the temperature coefficient of the unperturbed dimensions of most polymeric chains seldom exceeds about 1 × 10^{-3} K^{-1}.[35,36]

The experimental value of d ln $\langle r^2\rangle_0$/dT was interpreted in terms of the rotational isomeric state model. Information on the conformational energy associated with the different states of the different bonds of the repeat unit are given elsewhere.[13] Studies carried out by ^{1}H NMR spectroscopy on the rotational states about CH_2–CH_2 bonds in diethylene glycol dibenzoate show that the gauche population might be about[13] 90%. This suggests that the energy associated with gauche states about CH_2–CH_2 bonds in PDET should be lower than that corresponding to these states about similar bonds in POE. It should be pointed out that careful studies carried out by Abe and Mark[37] on the configurational properties of POE show that gauche states about CH_2–CH_2 bonds have an energy 0.5 kcal mol^{-1} lower than the alternative trans states. Given the uncertainty of the value of the energy involved in the transition trans to gauche about CH_2–CH_2 bonds in PDET, the calculations were carried out as a function of the rotational energy $E_{\sigma'} = [E(g^{\pm}) - E(t)]_{O\cdots O}$.

The temperature coefficient of the unperturbed molecular dimensions was evaluated by means of the expression

$$\frac{\mathrm{d}\ln\langle r^2\rangle_0}{\mathrm{d}T} = -(1/T)\sum \ln \xi_k \frac{\partial \ln \langle r^2\rangle_0}{\partial \ln \xi_k} \tag{6}$$

where ξ_k refers to the statistical weight parameters or Boltzmann factors. The calculations were made using the structural parameters given in Table IV. It was assumed that the rotational states for bonds 4–9 in Figure 4 are located at 0° (trans), +120° (gauche positive), and −120° (gauche negative). The theoretical calculations were carried out at 70 °C using the set of statistical weights σ_k = 0.55, σ'' = 0.27, ω = 0.60, ω_k = 0.14, and ω' = 0.00. Values of σ' lying in the range 1.5–6 were used in the present analysis. The results obtained, plotted in Figure 5, show that the value of d ln $\langle r^2\rangle_0$/dT is strongly dependent on the value of $E_{\sigma'}$ in such a way that it increases as $E_{\sigma'}$ decreases, a reasonable agreement between theory and experiment being reached for values of $E_{\sigma'}$ below −0.8 kcal mol^{-1}. Thus, for $E_{\sigma'}$ = −0.8 kcal mol^{-1}, 10^3(d ln $\langle r^2\rangle_0$/dT) = 0.9_5 while for $E_{\sigma'}$ = −1.0 kcal mol^{-1}, 10^3(d ln $\langle r^2\rangle_0$/dT) = 1.2. The high dependence of the temperature coefficient on $E_{\sigma'}$ arises from the fact that the unperturbed dimensions of PDET chains are very sensitive to the gauche population

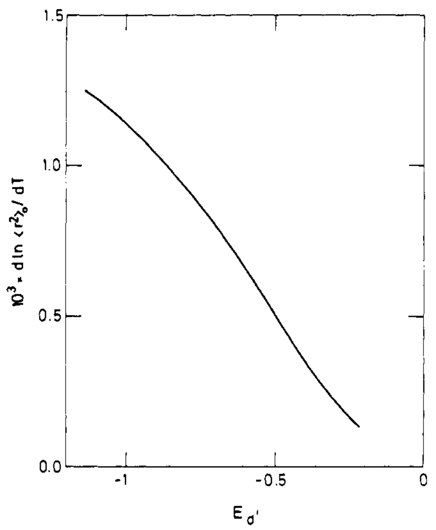


Figure 5. Dependence of the temperature coefficient on the energy associated with gauche states about CH_2–CH_2 bonds in PDET chains.

Table V
Coefficients Calculated Using the Set of Parameters Indicated in the Text (T = 70 °C, σ' = 4)

coefficient	value
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma'$	−0.25
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma''$	0.06
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \sigma_k$	0.00
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \omega$	−0.01
$\partial \ln \langle r^2 \rangle_0 / \partial \ln \omega_k$	−0.02

about CH_2–CH_2 bonds as can be seen in Table V, where the values of the coefficients $\partial \ln \langle r^2 \rangle_0 / \partial \ln \xi_k$ are indicated. As the temperature increases, the fraction of trans states about CH_2–CH_2 bonds becomes larger and therefore the value of $d \ln \langle r^2 \rangle_0 / dT$ also increases. The contribution of the conformations of the other bonds to the changes on molecular dimensions with temperature is in comparison rather small as can be seen in Table V.

An important point which arises from the above analysis is that the theoretical values of the temperature coefficient come near the experimental result for values of $E_{\sigma'}$ lying in the range −0.8 to −1 kcal mol^{-1}. This is surprising in view of the fact that these values are almost 2 times lower than the value corresponding to the conformational energy associated with gauche states about CH_2–CH_2 bonds in POE.[37] It should be pointed out, however, that a value of $E_{\sigma'}$ equal or less than −0.8 kcal mol^{-1} is consistent with the results obtained from ^1H NMR analysis of diethylene glycol dibenzoate,[13] according to which the fraction of gauche states about CH_2–CH_2 bonds in this compound is about 0.90. Moreover, in a recent study on the ^1H NMR spectra of copolyesters of diethylene glycol and neopentyl glycol with terephthalic acid, Henrichs and Hewitt[38] found that the spectra of the polymers show more resolved peaks in the aromatic region than would initially be expected. The fine structure reflects that a high fraction of the diol units present in the polymer chains causes it to fold back on itself. This implies, therefore, that a high fraction of CH_2–CH_2 bonds in the diol are in the gauche conformation.

Let us now analyze how the values of $E_{\sigma'}$ affect the dipole moments of the polymer. In an earlier work[5] the dipole moment ratio $\langle \mu^2 \rangle / nm^2$ of PDET chains of number-average molecular weight 2500 was reported to be 0.66 at 35 °C. Since the dipole moments of these chains converge very rapidly, it would be reasonable to assume that the value of the dipole moment ratio of high molecular weight chains will be in the vicinity of 0.65. This configurational property was calculated by the RIS model for a chain with more than 432 bonds using the information on bond dipole moments gathered elsewhere.[5] The only difference was that in the present calculations a value of 1.07 D[37] was used for the dipole moment associated with the C–O bond instead of the value of 0.99 D utilized earlier. It was found that for $E_{\sigma'}$ = −0.67 kcal mol^{-1}, $\langle \mu^2 \rangle / nm^2$ = 0.62, and this quantity reduces to 0.59 for $E_{\sigma'}$ = −1 kcal mol^{-1}. Since the error involved in the determination of $\langle \mu^2 \rangle / nm^2$ may be of the order of 10%, the low values of $E_{\sigma'}$ found in the study of the temperature coefficient of the unperturbed molecular dimensions still reproduce the dipole moments of the chains.

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