(19) Schick, M. J. *J. Phys. Chem.* **1964,** *68,* 3585.
(20) Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley and Sons: New York, 1961.
(21) Strauss, U. P.; Gershfeld, N. L. *J. Phys. Chem.* **1954,** *65,* 747.
(22) McCormick, C. L.; Blackmon, K. P.; Elliot, D. L. *Angew. Makromol. Chem.* **1986,** *144,* 87.

Conformational and Motional Characteristics of *trans*-1,4-Diene Polymers Confined to Channels

A. E. Tonelli

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received November 10, 1989; Revised Manuscript Received January 17, 1990

ABSTRACT: Prompted by the studies of Sozzani and co-workers, who have polymerized diene monomers complexed with perhydrotriphenylene (PHTP) to form inclusion compounds, we have investigated the conformations and mobilities of the resulting isolated *trans*-1,4-diene polymer chains confined to the channels of their inclusion compounds with PHTP. This was achieved by a two-step procedure: (i) from all the possible conformations available to the free polymer chains, those conformations which fit into the channels of their inclusion compounds with PHTP were defined; (ii) a test was performed to determine whether or not it was possible to interconvert between these channel conformations while the *trans*-1,4-diene polymers remained inside their channels. This procedure was applied to *trans*-1,4-polybutadiene, *trans*-1,4-polyisoprene, and isotactic *trans*-1,4-poly(penta-1,3-diene) chains confined to the channels of their inclusion compounds with PHTP. We found the channel conformers of the butadiene and pentadiene polymers able to interconvert while inside their channels. By contrast, the isoprene polymer was not able to interconvert between its channel conformers without significant expansion of its confining PHTP channel (ca. 30% increase in channel diameter, compared to the 0–5% increase observed for interconverting butadiene and pentadiene chains). These results are consistent with the solid-state ^{13}C and ^{2}H NMR studies performed by Sozzani et al. to elucidate the conformations and mobilities of the same *trans*-1,4-diene polymers when restricted by the channels formed in their PHTP inclusion compounds.

Introduction

When the crystals of perhydrotriphenylene (PHTP) are exposed to small molecule liquids or gases, crystalline inclusion compounds are formed. Farina and co-workers[1] have studied many PHTP inclusion complexes, including those with polymers such as polyethylene. Generally the physical properties of both the PHTP matrix and the entrained molecules of the inclusion compound are markedly different from their separate pure phases. As an example, the melting temperature of the complex formed between the PHTP matrix and the included molecule is significantly elevated over the melting points of their pure phases.

Many polymers are easily prepared[1,2] in the channels of PHTP inclusion compounds. After diffusion of gaseous or liquid monomer into the PHTP crystals, the confined monomers of the inclusion compound are polymerized by irradiation of the complex. The polymerization propagates inside the PHTP crystal, linking together monomers to form high molecular weight polymers. No amorphous polymer is produced because polymerization cannot occur outside the crystal. The constraints imposed by the PHTP channels lead to a reduction in the side reactions that would introduce polymer defects;[3] thus the polymers produced in PHTP crystals have highly regular structures.

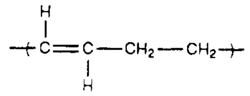
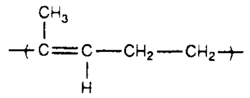
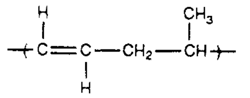
The polymerization of 1,3-butadiene in PHTP channels has been studied by X-ray crystallography[4] and ESR spectroscopy.[3b,5] During the polymerization, which proceeds through a living radical mechanism,[3b] the PHTP crystal structure is not destroyed. Instead the inclusion complex of PHTP with monomer is transformed to a crystalline complex with the polymer, resulting in significant changes in the crystalline lattice parameters. The X-ray diffraction pattern after polymerization does not reveal the presence of the *trans*-1,4-polybutadiene (TPBD) molecules in the PHTP channels. Similar results were observed for TPBD polymerized in urea channels.[6]

It was suggested that either the TPBD repeat distance, when confined by the channel, was identical with the PHTP matrix repeat (4.78 Å) or the polymer was disordered and only produced diffuse scattering. Freely rotating TPBD chains in the PHTP channels would explain this observation, but the X-ray data could not distinguish between time-averaged or space-averaged conformational disorder. Sozzani and co-workers[7,8] have subsequently employed solid-state ^{13}C and ^{2}H NMR spectroscopy in an attempt to resolve the question of disorder among the TPBD chains in their PHTP channels. They have found the TPBD chains to be mobile, probably as a consequence of intrachannel conformational transitions. The motions and conformations of TPBD chains included in the complex with PHTP were found[7,8] to be very similar to those experienced[9,10] by pure TPBD above 60 °C in their form II crystals. Unlike pure TPBD, which transforms[11] to rigid form I crystals below 60 °C, TPBD chains in the PHTP complex remain mobile down to very low temperature (−160 °C).

Sozzani and co-workers[12,13] have also synthesized and investigated the PHTP channel polymerization of isoprene and 1,3-pentadiene to yield *trans*-1,4-polyisoprene (TPIP) and isotactic *trans*-1,4-poly(penta-1,3-di-

0024-9297/90/2223-3129$02.50/0

Table I
Structures of *trans*-1,4-Diene Polymers

polymer	abbreviation	structure
trans-1,4-polybutadiene	TPBD	 $-\!\!\left(\overset{\displaystyle H}{\overset{\vert}{C}}=\underset{\displaystyle H}{\underset{\vert}{C}}-CH_2-CH_2\right)\!\!-$
trans-1,4-polyisoprene	TPIP	 $-\!\!\left(\overset{\displaystyle CH_3}{\overset{\vert}{C}}=\underset{\displaystyle H}{\underset{\vert}{C}}-CH_2-CH_2\right)\!\!-$
trans-1,4-poly(penta-1,3-diene)	TPPD	 $-\!\!\left(\overset{\displaystyle H}{\overset{\vert}{C}}=\underset{\displaystyle H}{\underset{\vert}{C}}-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}\right)\!\!-$

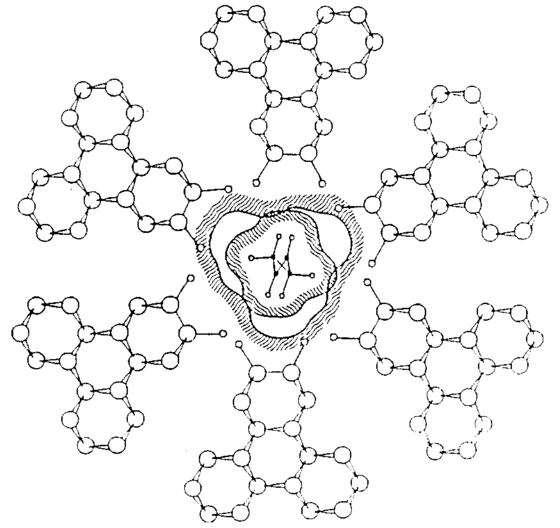


Figure 1. Schematic drawing[7,8] of a TPBD chain in the channel of its inclusion compound with PHTP.

ene) (TPPD). The backbones of TPBD, TPIP, and TPPD are identical, while the isomeric TPIP and TPPD can be considered as methyl-substitituted derivatives of TPBD (see Table I for structures). Their NMR studies have revealed that, unlike TPBD, TPIP in the channels of its PHTP complex is rigid and confined to adopt a conformation similar to its pure β-form crystalline polymorph.[14] TPPD, on the other hand, appears to exhibit a wide range of mobilities when complexed with PHTP, with a fraction that is mobile down to -120 °C.

In the present study, we attempt to model the conformations and mobilities of all three diene polymers when complexed to PHTP by means of confining them to cylinders with radii comparable to the PHTP channels in which they reside.

Modeling Diene Polymers in Channels. Channel Conformers. In Figure 1, we reproduce[7,8] a schematic drawing of TPBD chains in the PHTP inclusion compound, as determined by X-ray diffraction.[4] The polymer is constrained to lie in channels perpendicular to the plane of the drawing. To model a TPBD chain confined to the channels illustrated in Figure 1, we have simply restricted our considerations to any and all TPBD conformations which fit into a cylinder with a diameter comparable to the channels (ca. 5.5 Å) shown in this figure. The portion of TPBD considered in our modeling is drawn in Figure 2 and contains four monomer repeat units.

We adopt the rotational isomeric state (RIS) description of the conformations of a TPBD chain derived by Mark,[15] where each $=C-CH_2$ bond is permitted to adopt the skew (s±, ±60°) and cis (c, 180°) rotational states, while each CH_2–CH_2 bond is restricted to the trans (t, 0°) and gauche (g±, ±120°) conformations. Each $CH{=}CH$ bond is of course fixed in the trans configuration, and the following bond lengths and valence angles are adopted[16] and assumed fixed in all conformations: $l_{CH=CH} = 1.34$ Å, $l_{CH-CH_2} = 1.51$ Å, $l_{CH_2-CH_2} = 1.53$ Å, $l_{C-H} = 1.10$ Å, $\angle CH_2-CH{=}CH = 125°$, and $\angle CH-CH_2-CH_2 = \angle H-C-H = 110°$.

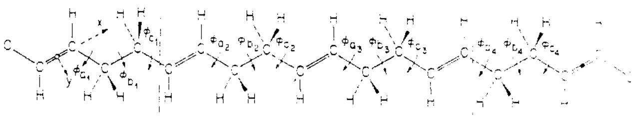


Figure 2. Four repeat unit fragment of TPBD used to derive the conformations of its channel-bound chains.

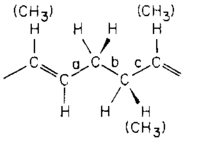
A Cartesian coordinate system affixed to the middle of the first $CH{=}CH$ bond (see Figure 2) is used as a reference frame for expressing the x,y,z coordinates of each of the atoms in the TPBD fragment shown in Figure 2. Of course the atomic coordinates depend on the four sets of rotation angles $CH\overset{\phi_a}{\curvearrowright}CH_2$, $CH_2\overset{\phi_b}{\curvearrowright}CH_2$, $CH_2\overset{\phi_c}{\curvearrowright}CH$ $(\phi_a,\phi_b,\phi_c)_{1,2,3,4}$ resulting in $[(3)(3)(3)]^4 = 531\,441$ total conformations for this four repeat unit fragment of a free TPBD chain. For each of these conformations, the x,y,z coordinates of all the atoms are calculated and transformed to a Cartesian coordinate system x',y',z' whose z'-axis connects the midpoints (○,●) of the terminal $CH{=}CH$ bonds (see Figure 2). The radius of the corresponding cylindrical coordinate system with coincident z'-axis is $r = (x'^2 + y'^2)^{1/2}$.

In the selection of channel conformations, we simply check each conformation generated to determine if $r = (x'^2 + y'^2)^{1/2} < r_c$, where r_c is the radius of the cylindrical channel. If each atom in the TPBD fragment passes this test, then the conformation is considered a channel conformer.

Average Properties of Channel Conformers. Matrix multiplication techniques[17] are used to calculate various properties of the TPBD chain fragment, averaged over all conformations and averaged over just the set of channel conformers found. The averaging is made possible by Mark's RIS model[15] for TPBD. The average probability or population of channel conformers and the bond conformations averaged over all conformations and just the set of channel conformers are obtained in this manner for channels (cylinders) of various radii.

The RIS models[15,17,18] for TPBD and the two methyl-substituted polydienes, TPIP and TPPD, are presented in Figure 3, where one olefinic and one paraffinic carbon in TPBD are methyl-substituted in TPIP and TPPD, respectively. Statistical weight matrices $\mathbf{U}_a$, $\mathbf{U}_b$, and $\mathbf{U}_c$ for the three single C–C backbone bonds in each repeat unit are also presented in this figure. The columns of $\mathbf{U}_{a,b,c}$ are indexed by the rotational states of bonds a, b, or c, while the rows correspond to the rotational states of the preceding bonds $CH{=}CH$, a, or b. Summation of the elements of the matrix product $\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c$ yields the partition function Z_p of a repeat unit. For the four repeat unit fragment considered here, the configurational partition function is simply $Z_4 = (Z_p)^4$.

Let us suppose that the TPBD fragment in Figure 2 adopts the $(s^+ts^-)(cg^-c)(s^-ts^+)(cg^+c)$ conformation. Its probability of occurrence is obtained from $[\mathbf{U}_a(1)\cdot\mathbf{U}_b(1,1)\mathbf{U}_c(1,3)\mathbf{U}_a(2)\mathbf{U}_b(2,3)\mathbf{U}_c(3,2)\mathbf{U}_a(3)\mathbf{U}_b(3,1)\mathbf{U}_c(1,1)\cdot\mathbf{U}_a(2)\mathbf{U}_b(2,2)\mathbf{U}_c(2,2)]/Z_4$, where for example $\mathbf{U}_c(1,3)$ is the 1,3 element of the $\mathbf{U}_c$ matrix (see Figure 3). To determine the probability of finding the second CH_2–CH_2



$$U_a = \begin{array}{c}\begin{array}{ccc} s^+ & c & s^- \end{array}\\ \begin{bmatrix} 1 & \alpha & 1 \end{bmatrix}_{\text{TPBD}}\end{array};\ \begin{bmatrix} 1 & 0 & 1 \end{bmatrix}_{\text{TPIP}};\ \begin{bmatrix} 1 & \alpha' & 1 \end{bmatrix}_{\text{TPPD}}$$

$$U_b = \begin{array}{c|ccc} a\backslash b & t & g^+ & g^- \\ \hline s^+ & 1 & \sigma & \sigma \\ c & 1 & \sigma\beta & \sigma\beta \\ s^- & 1 & \sigma & \sigma \end{array}_{\text{TPBD}};\ \begin{bmatrix} 1 & \sigma' & \sigma' \\ 0 & 0 & 0 \\ 1 & \sigma' & \sigma' \end{bmatrix}_{\text{TPIP}};\ \begin{bmatrix} \sigma' & \sigma'' & \sigma \\ \sigma' & \sigma''\beta & \sigma\beta \\ \sigma & \sigma'' & \sigma \end{bmatrix}_{\text{TPPD}}$$

$$U_c = \begin{array}{c|ccc} b\backslash c & s^+ & c & s^- \\ \hline t & 1 & \alpha & 1 \\ g^+ & 1 & \alpha\beta & 1 \\ g^- & 1 & \alpha\beta & 1 \end{array}_{\text{TPBD}};\ \begin{bmatrix} 1 & \alpha & 1 \\ 1 & \alpha\beta & 1 \\ 1 & \alpha\beta & 1 \end{bmatrix}_{\text{TPIP}};\ \begin{bmatrix} 1 & \alpha & \alpha \\ 1 & \alpha\beta & \alpha \\ 1 & \alpha\beta & \alpha \end{bmatrix}_{\text{TPPD}}$$

Figure 3. Summary of the statistical weight matrices $\mathbf{U}_a$, $\mathbf{U}_b$, and $\mathbf{U}_c$ of the RIS models for TPBD, TPIP, and TPPD, which were used to calculate the conformational properties of their channel conformers.

bond in the TPBD fragment of Figure 2 in the g^+ rotational state, or conformation, we simply divide the matrix product $(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c)(\mathbf{U}_a\mathbf{U}_b(g^+)\mathbf{U}_c)(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c)(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c)$ by Z_4, where $\mathbf{U}_b(g^+)$ is the statistical weight matrix for bond b with first and third column elements, which correspond to the t and g^- conformers, replaced by zeros.

Similar searches for channel conformations were conducted for TPIP and TPPD, but in these cases either one olefinic proton in each repeat unit was replaced by a methyl group (TPIP) or one paraffinic proton was replaced by a methyl group (TPPD). Of course the statistical weight matrices appropriate to TPIP and TPPD were substituted for those of TPBD. At room temperature, the following rotational-state statistical weights appear appropriate[15,17,18] (see Figure 3): $\alpha = \alpha' = 0.96$, $\beta = 0.24$, $\sigma = 1.0$, $\sigma' = 0.54$, and $\sigma'' = 0.15$. Bond rotational-state probabilities were calculated only for the two central repeat units in the four repeat unit fragment of each polydiene.

For each channel conformer generated, the angles between the z'-axis of the channel conformers and the C—H bonds belonging to the olefinic carbons of the central CH=CH bond of the TPBD fragment in Figure 2 and the adjacent methylene carbon C—H bonds were calculated. In addition, these angles were averaged over all the channel conformers generated for each channel or cylinder size r_c. It was hoped that this information might eventually be used to interpret the ^{2}H NMR studies[8,12,13] of these polydienes when complexed to PHTP.

Mobility of Channel Conformers. In an attempt to characterize the mobility of these polydiene chains when confined by the channels of their complexes with PHTP, we sought to determine the possibility of interconverting between channel conformers without any part of the chain leaving the channel during any step in the interconversion process. Only that portion of the TPBD chain fragment in Figure 2 between the vertical dashed lines was considered, because its conformation depends solely on the C—C bond rotations in two consecutive repeat units, i.e., six rotation angles compared to the 12 bond rotations necessary to define the conformation of the entire fragment. Because the CH_2—CH_2 and CH_2—$CH(CH_3)$ bonds in the channel conformers of all three polydienes were found to be almost exclusively trans for cylinders with r_c near the channel size of their PHTP inclusion compounds (vide infra), $\phi_{b_2} = \phi_{b_3} = 0° \pm 30°$ (see Figure 2) was assumed during all conformer interconversions. Each of the other four rotation angles (ϕ_{a_2}, ϕ_{c_2}, ϕ_{a_3}, ϕ_{c_3}) was stepped sequentially in 20° increments throughout their complete range.

One of the channel conformers was selected as the starting conformation. As each rotation angle was incremented, the x', y', z' coordinates of each atom in the fragment between vertical dashed lines were calculated and checked to see that all atoms remained inside the cylinder of the starting channel conformer. This procedure was repeated until one or more atoms passed through the cylinder wall or another channel conformer was reached. If the former occurred, then another channel conformer was selected as the starting conformer, and the channel conformer interconversion procedure was repeated. When another channel conformer was reached, all rotation angles were reinitialized to the values of the new starting channel conformer, and the interconversion process was restarted. The test for interconversion between channel conformers was complete after each cylinder conformer had been used as the starting conformation.

Results and Discussion

Channel Conformations. The channel conformers found for all three polydienes are partially characterized and described in Table II, where their numbers and bond rotational state probabilities are presented for cylinders of various radii. Because in the search for channel conformers each atom was considered a volumeless point, a channel conformer found to fit in a cylinder of diameter $D' = 2r_c$ would actually fill a cylinder with a diameter $D = D' + 1$ Å if van der Waals spheres of radius 0.5 Å were assigned to each proton. All cylinder diameters given in Table II reflect the steric requirement of 0.5-Å van der Waals spheres placed on each proton.

Not surprising is the observation that TPBD chains fit into channels smaller than the methyl-substituted TPIP and TPPD chains. Also, more different TPBD conformers fit into a cylinder of a given D than was found for TPIP or TPPD (see Figure 4). For $D < 4.5$ Å, even TPBD does not fit into the cylinder. In a cylinder with $D = 4.5$ Å, only two different TPBD conformers are allowed, $=s^{\pm}ts^{\mp}=$ and $=ctc=$. The first conformer is the low-temperature form I crystalline conformation[19] found to be stable[11] below ca. 60 °C. The alternating cis, trans conformer ($=ctc=$), also able to fit in a $D = 4.5$ Å cylinder, has a higher energy and lower probability (0.25 vs 0.75) than the form I crystalline conformation. Expansion of the cylinder diameter to $D = 5.0$ Å results in the incorporation of additional TPBD conformers of the type ($=cts^{\pm}=$) suggested by De Rosa et al.[16] for form II crystalline TPBD stable[11] above 60 °C.

The channel conformers found for all three polydienes have trans ($\phi_b = 0°$) CH_2—CH(H or CH_3) bonds until the cylinder diameter exceeds 7–8 Å and gauche ($\phi_b = \pm 120°$) conformers are accommodated by the expanded channels (see Figure 5). At the same time, channel conformers have a higher content of cis bonds than the free polydiene chains (see Figure 6). (Note that ϕ_a = c is not allowed in the TPIP chain $(CH_3)C{=}CH\overset{\phi_a}{+}CH_2$—$C^*H_2$—$C(CH_3){=}CH$ because of the steric overlap between CH_3 and C^*H_2 in this conformation.) Thus, as the channel diameter increases more gauche and fewer cis conformers are allowed.

TPIP may be obtained in two crystalline polymorphs:[14,20] the α and β forms with $=s^{\pm}tc=$ and $=s^{\pm}ts^{\mp}=$ conformations, respectively. For cylinders with $D < 6.0$ Å, no channel conformers with cis CH_2—$C(CH_3)=$ bonds are found. Only β conformations fit into cylinders with diameters corresponding to the channels in the TPIP inclusion compound with PHTP.

Table II
Polydiene Channel Conformers

	no.of channel conformers			$P(\phi_a$=c)			$P(\phi_b$=t)			$P(\phi_c$=c)		
D, Å	TPBD	TPIP	TPPD	TPBD	TPIP	TPPD	TPBD	TPIP	TPPD	TPBD	TPIP	TPPD
4.5	3	0	0	0.318			1.0			0.318		
5.0	11	4	3	0.26–0.36	0.0	0.263	1.0	1.0	1.0	0.26–0.36	0.0	0.263
5.5	109	14	39	0.32–0.33	0.0	0.376	1.0	0.99	1.0	0.31–0.34	0.0	0.327
6.0	511	54	315	0.28–0.31	0.0	0.427	1.0	0.99	1.0	0.28–0.31	0.0–0.077	0.345
6.5		126			0.0			0.97			0.068–0.110	
7.0	3 211	336	2416	0.292	0.0	0.400	0.96	0.96	0.99	0.292	0.138–0.157	0.352
8.0	10 021	1540	7914	0.305	0.0	0.330	0.92	0.92	0.92	0.305	0.255–0.295	0.315
9.0	52 691	7496	39146	0.293	0.0	0.295	0.88	0.89	0.85	0.293	0.264–0.281	0.286
10.0	100 849	15710	90822	0.273	0.0	0.285	0.77	0.85	0.78	0.273	0.251–0.283	0.279
11.0	163 727	27760	149113	0.253	0.0	0.263	0.67	0.80	0.71	0.253	0.242–0.271	0.258
13.0	333 857	60959	314380	0.221	0.0	0.226	0.54	0.68	0.56	0.221	0.229–0.255	0.225
free chain	531 441	104976	531441	0.210	0.0	0.204	0.47	0.55	0.45	0.210	0.226	0.206

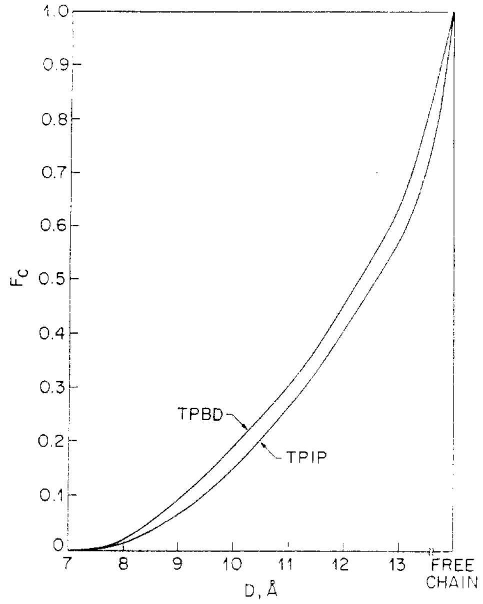


Figure 4. Fraction F_c of all polydiene conformers which fit into a cylinder of diameter *D*. The upper (lower) curve corresponds to TPBD (TPIP) channel conformers, while the channel fractions for TPPD lie within the shaded region.

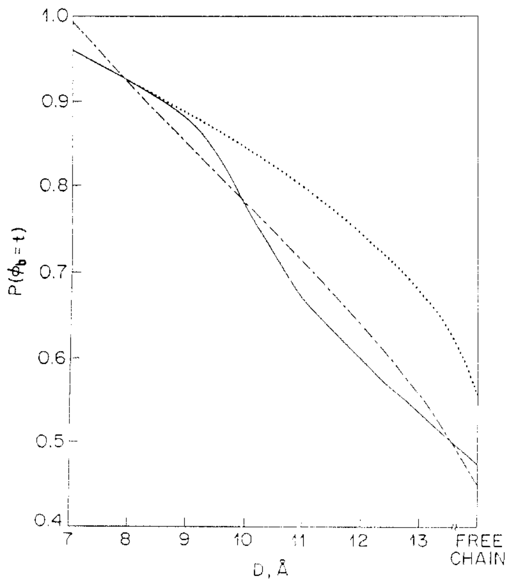


Figure 5. Probability $P(\phi_b$=t) of finding the —C—C— bonds in the trans conformation for the channel conformers of TPBD (—), TPIP (···), and TPPD (- · -).

The fractions of all TPPD conformers which fit into cylinders, F_c, fall between those of TPBD and TPIP (see Figure 4). Like TPBD, but not TPIP, some TPPD cylinder conformers with diameters in the range of the channels in its PHTP inclusion compound do possess cis =C—C bonds.

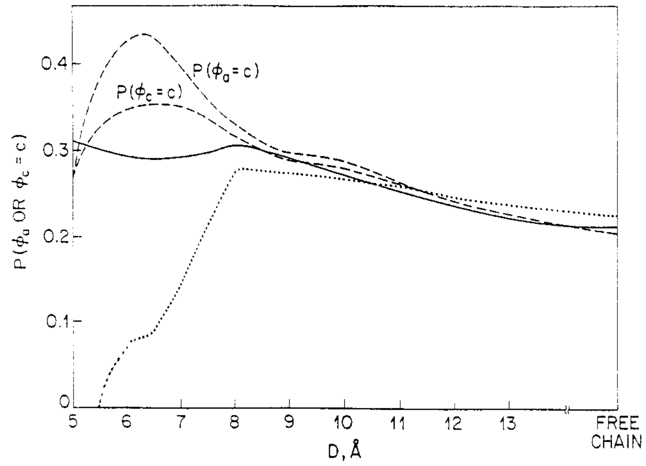
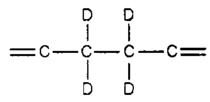
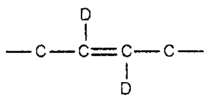


Figure 6. Probability $P(\phi_{a\text{ or }c}$=c) of finding the =C—G and —C—C= bonds in the cis conformation for the channel conformers of TPBD (—), TPIP (····), and TPPD (- - -).

Table III
Average Angle between C–D Vector and *z*′-Axis of Polydiene Channel Conformers[a]

	$\langle$C–D$\rangle_{z'}$[b]	
polydiene	 $=\!C-CD_2-CD_2-C\!=$	 $-C-C(D)\!=\!C(D)-C-$
TPBD	53–57°	53–59°
TPIP	63°	81–82°
TPPD	46–55°	58–64°

[a] *D* = 5.5 Å. [b] Averaged over the 109-, 14-, and 39-channel conformers of TPBD, TPIP, and TPPD, respectively, which fit into a cylinder with *D* = 5.5 Å.

In Table III, the angles made by the C–D bond vectors of the olefinic and paraffinic carbons with the *z*′-axis of the cylindrical coordinate system are presented. These C–D vector angles have been averaged over all the polydiene conformations which are able to fit in a cylinder with *D* = 5.5 Å. We hope to eventually attempt a simulation of their observed ^{2}H NMR spectra by means of modeling the motions of their channel conformations in terms of the allowed interconversions between cylindrical conformers generated here for each polydiene (see below).

Mobility of Polydiene Channel Conformers. The 11 TPBD conformers that were found to fit in a *D* = 5.0

Å cylinder could not be interconverted by the procedure outlined above. However, a 5% expansion of the cylinder diameter to 5.25 Å did permit their interconversion. TPIP conformers derived for 5.0-Å cylinders could not be interconverted until the cylinder was expanded 30% to D = 6.5 Å. The D = 5.0 Å conformers found for TPPD could not be interconverted even after expansion of the cylinder diameter to 7.0 Å. On the other hand, those additional TPPD conformers found to fit in a cylinder with D = 5.5 Å could be interconverted without any channel expansion.

On the basis of these observations, we would expect that, in the channels of their inclusion compounds with PHTP, TPBD chains would exhibit the greatest mobility, TPIP chains would be the most rigid, and TPPD chains would have mobilities somewhere in between the mobilities of TPBD and TPIP chains. Sozzani et al.[7] have observed by high-resolution ^{13}C NMR that the chemical shifts and the spin–lattice relaxation times T_1 of TPBD in its inclusion compound with PHTP are very similar to those exhibited by pure TPBD in its form II crystals above 60 °C. Neither form II nor the PHTP inclusion compound of TPBD exhibits spinning side bands in their CPMAS/DD ^{13}C NMR spectra. The ^{2}H NMR studies of TPBD complexed with PHTP performed by Sozzani et al.[8] also indicate that the mobilities of TPBD chains in pure, bulk form II crystals and isolated in the PHTP channels are very similar.

Drawing from the conformational energy calculations of De Rosa et al.,[16] Sozzani et al.[7,8] have interpreted their solid-state ^{13}C and ^{2}H NMR observations of TPBD–PHTP complexes as providing strong evidence that the conformations and motions of the TPBD chains in both environments are very similar, where a rapid interconversion of $s^{\pm}ts^{\mp}$ and $cts^{\pm}$ conformations is believed to occur along the TPBD chains. This description is consistent with the TPBD conformers generated here for cylinders with diameter similar (5.5 Å) to the channels of the PHTP inclusion compound (see Table II). These conformers all have trans CH_2—CH_2 bonds and an ca. 30% probability for cis =CH—CH_2 bonds. Furthermore, it was found that these channel conformers were able to interconvert without any significant expansion of the cylinder from which they were derived.

Sozzani et al.[12] have also studied the PHTP inclusion compound of TPIP by solid-state ^{13}C and ^{2}H NMR spectroscopy. They found the δ ^{13}C values and their associated T_1 values to be similar to the values observed[12,21] for bulk TPIP when crystallized into its β form. Unlike TPBD, the TPIP chains in their inclusion compound with PHTP were observed to be rigid. These observations are consistent with the TPIP conformers generated in cylinders with D = 5.5 Å. All these conformers (14) are of the sts types, and they were found not to be inconvertible unless the cylinder was significantly expanded (30%).

Bruckner et al.[13] have performed a ^{2}H NMR study on isotactic TPPD when complexed to PHTP. They concluded that more than 20% of the C–D bonds are highly mobile, like TPBD, while the remainder of the C–D bond population exhibits increased rigidity, with a substantial portion exhibiting a Pakelike pattern associated with a rigid C–D bond orientation on a time scale of the order 10^{-5} s. They attributed this behavior to different local environments experienced by the TPPD chains inside the PHTP channels. However, they assumed that the TPPD chains are adopting only sts conformations by analogy to their crystalline conformation,[22,23] and did not consider the possibility of cis =CH—CH_2 or $C(CH_3)H$—CH= bonds. As seen in Table II, both of these bonds in the D = 5.5 Å conformers possess a substantial amount of cis character.

If the PHTP channel conformers of TPPD also possess some cis bonds, then its solid-state ^{13}C NMR spectrum should show resonances that are substantially shielded from those observed in the spectrum of pure crystalline TPPD, as was observed for TPBD. A recent ^{13}C NMR study[24] of pure TPPD and its inclusion compound with PHTP confirms this expectation. It may be possible that the rigid C–D bonds belong to those channel conformers that are not able to interconvert, while the mobile C–D bonds are part of the rapidly interconverting channel conformers. If these two populations of conformers have different numbers of cis =C—C— bonds (compare D = 5.0 and 5.5 Å TPPD channel conformers in Table II), then we might expect to observe at least two resonances for each carbon type in the ^{13}C NMR spectrum of the TPPD–PHTP inclusion compound. This expectation is confirmed.[24]

Summary

Cylindrical conformations have been derived for the three *trans*-1,4-polydienes TPBD, TPIP, and TPPD as models for these chains when confined to the channels of their inclusion compounds with PHTP. In agreement with the solid-state ^{2}H and ^{13}C NMR studies of Sozzani et al.,[7,8,12,13,24] the conformational and motional behavior of the derived channel conformers may be characterized in the following ways: (i) all three polydienes are able to adopt conformations which fit onto cylinders with diameters (D = 5.5 Å) comparable to the channels they occupy in their inclusion compounds with PHTP; (ii) all channel conformers have trans —C—C— bonds; (iii) both TPBD and TPPD can adopt channel conformers with cis =C—C— bonds, while all TPIP channel conformers are of the sts type; (iv) TPBD and TPPD chains are able to interconvert between several of their channel conformers without any significant expansion of their constraining cylinders, while TPIP chains cannot.

References and Notes

(1) Farina, M. *Inclusion Compounds*; Atwood, J. L., Ed.; Academic Press: New York, 1984; Vol. 2, p 69; Vol. 3, p 297.
(2) White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5678.
(3) (a) Farina, M.; Pedretti, U.; Gramegna, M. T.; Audisio, G. *Tetrahedron* 1970, *26*, 1839. (b) Sozzani, P.; Di Silvestro, G.; Gervasini, A. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 815.
(4) Colombo, A.; Allegra, G. *Macromolecules* **1971**, *4*, 579.
(5) Ohomori, T.; Ichikawa, T.; Iwasaki, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1383.
(6) Chatani, Y.; Kuwata, S. *Macromolecules* **1975**, *8*, 12.
(7) Sozzani, P. E.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1989**, *22*, 4225.
(8) Sozzani, P. E.; Behling, R. W.; Schilling, F. C.; Bruckner, S.; Helfand, E.; Bovey, F. A.; Jelinski, L. W. *Macromolecules* **1989**, *22*, 3318.
(9) Möller, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1987, *28* (2), 395. Möller, M. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 107.
(10) Schilling, F. C.; Gomez, M. A.; Tonelli, A. E.; Bovey, F. A.; Woodward, A. E. *Macromolecules* **1987**, *20*, 2954.
(11) Stellman, J. M..; Woodward, A. E.; Stellman, S. D. *Macromolecules* 1973, *6*, 330.
(12) Schilling, F. C.; Bovey, F. A.; Sozzani, P. E. *Macromolecules*, in press.
(13) Bruckner, S.; Sozzani, P. E.; Boeffel, C.; Destri, S.; Di Silvestro, G. *Macromolecules* **1989**, *22*, 607.
(14) Bunn, C. W. *Proc. R. Soc. London, Ser. A* **1942**, *180*, 40.
(15) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 6829.
(16) De Rosa, C.; Napolitano, R.; Pirozzi, B. *Polymer* **1985**, *26*, 2039.
(17) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969.

(18) The RIS model for TPPD was derived following the discussion of the conformational characteristics of TPBD, TPIP, and vinyl polymers presented in Chapters V and VI of ref 17.

(19) Iwayanagi, S.; Sakurai, I.; Sakurai, T.; Seto, T. *J. Macromol. Sci., Phys.* **1968**, *B2* (2), 163.

(20) Takahashi, Y.; Sato, T.; Tadokoro, H.; Tanaka, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 233.

(21) Patterson, D. J.; Koenig, J. L. *Polymer* **1988**, *29*, 240.

(22) Bassi, I. W.; Allegra, G.; Scordamaglia, R. *Macromolecules* **1971**, *4*, 575.

(23) Bruckner, S.; Di Silvestro, G.; Porzio, W. *Macromolecules* **1986**, *19*, 235.

(24) Schilling, F. C.; Bovey, F. A.; Sozzani, P. E.; Tonelli, A. E., work in progress.

Conformations and Motions of Polyethylene and Poly(oxyethylene) Chains Confined to Channels

A. E. Tonelli

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received November 10, 1989; Revised Manuscript Received January 17, 1990

ABSTRACT: Inclusion compounds formed by linear polymers and host clathrates, such as urea and perhydrotriphenylene (PHTP), provide a unique environment for the included polymer chains. We have investigated the conformations and mobilities of isolated polyethylene (PE) and poly(oxyethylene) (POE) chains when confined to the channels of their inclusion compounds. This was achieved by a two-step procedure: (i) from all possible conformations available to the free polymer chain, those conformations which fit into the channels of their inclusion compounds were defined; (ii) a test was performed to determine whether or not it was possible to interconvert between these channel conformations while the polymer chains remained inside their channels. Though several PE and POE conformers with diameters appropriate to the channels in their urea and PHTP inclusion compounds (D = 5.25–5.50 Å) were found, it was not possible to interconvert between them without some portion of each polymer chain leaving the channel. This is in marked contrast to the behavior of *trans*-1,4-polybutadiene and isotactic *trans*-1,4-poly(penta-1,3-diene), which were previously found capable of conformational interconversions in their inclusion compounds with the same host clathrates. On the basis of a comparison of the channel conformers derived for PE and POE with X-ray diffraction studies of their urea and PHTP inclusion compounds, we conclude the following: PE, as it does in its pure crystalline phase, assumes the all-trans, planar zigzag conformation in both clathrates. (ii) POE in the PHTP clathrate adopts several extended conformations, some with a few gauche bonds, in addition to the all-trans conformer. (iii) In its inclusion compound with urea, only more compact conformations with significant gauche bond contents are permitted. (iv) The POE chains in both clathrates adopt conformations that are more extended than the ...$g^{\pm}tt$... conformer found in POE crystals, which does not fit in either clathrate channel.

Introduction

Formation of inclusion compounds between small-molecule, host matrices and polymeric guest molecules permits the study of the conformations and motions of polymer chains confined to the channels of their inclusion compounds, where each chain is well-separated from neighboring chains by the host matrix. Two such host matrices are formed by the crystals of urea and perhydrotriphenylene (PHTP). In Figure 1, the inclusion compounds of urea with *n*-hexadecane[1] (a) and PHTP with *trans*-1,4-polybutadiene[2] (b) are illustrated as viewed down the channels of both complexes. Though the channel interiors are polar for the urea complex and nonpolar for the PHTP complex, each is nearly cylindrical in shape with diameters in the range 5.25–5.50 Å.

Though some polymers may be prepared directly in the channels of their inclusion compounds by irradiation of the inclusion compounds formed by their monomers,[3] the inclusion compounds of polyethylene (PE) and poly(oxyethylene) (POE) with both urea and PHTP are obtained[4-6] from solutions or melts of host matrix and guest polymer mixtures. X-ray diffraction studies[5,6] of the PE–urea and PE–PHTP clathrates reveal an extended, all-trans planar zigzag chain conformation was found in pure crystalline PE. In the POE clathrates with urea and PHTP, however, X-ray diffraction measurements[5,7] indicate unique chain conformations, both of which are different and more extended than the ...$g^{\pm}ttg^{\pm}tt$... chain conformation observed[8] for pure crystalline POE.

As an extension of our previous investigation, the preceding paper in this issue,[9] of the conformations and mobilities of *trans*-1,4-polydienes confined to the channels of their inclusion compounds with PHTP, we report here a similar modeling study for PE and POE chains in the channels of their urea and PHTP clathrates.

PE and POE in Clathrate Channels. Channel Conformers. To model PE and POE chains confined to the urea and PHTP clathrate channels illustrated in Figure 1, we simply consider only those PE and POE conformations which fit into a cylinder with a diameter comparable to these clathrate channels (5.25–5.50 Å). The portions of PE and POE considered in our model are drawn in Figure 2 and contain four and three repeat units, respectively. Below each drawing are the statistical weight matrices (U)[10] corresponding to the constituent bonds of PE and POE. These matrices embody the rotational isomeric state (RIS) descriptions of the conformations of PE[11] and POE[12] chains, and their elements are appropriate to room temperature.

0024-9297/90/2223-3134$02.50/0