Crystalline polymer inclusion compounds: potential models for the behaviour of polymer chains in their bulk, ordered phases

Alan E. Tonelli
Fiber and Polymer Science Program, College of Textiles, North Carolina State University, PO Box 8301, Raleigh, NC 27695-8301, USA
(Received 24 October 1992; revised 8 May 1993)

Several small-molecule hosts form clathrates or inclusion compounds (ICs) with polymers. In these polymer ICs the guest polymer chains are confined to occupy narrow channels in the crystalline matrix formed by the host. The walls of the IC channels are formed entirely from the molecules of the host, and they serve to create a unique solid-state environment for the included polymer chains. Each polymer chain included in the narrow, cylindrical IC channels (ca. 5.5 Å in diameter) is highly extended and also separated from neighbouring polymer chains by the host matrix channel walls. The net result is a solid-state environment where extended, stretched (as a consequence of being squeezed) polymer chains reside in isolation from their neighbours inside the narrow channels of the crystalline matrix provided by the small-molecule host. Comparison of the behaviour of isolated, stretched polymer chains in their crystalline ICs with observations made on ordered, bulk samples of the same polymer are beginning to provide some measure of the contributions made by the intrinsic nature of a confined polymer chain and the pervasive, cooperative, interchain interactions which can complicate the behaviour of bulk polymer samples. In the same way that dilute polymer solutions at the Θ temperature have been effectively used to model disordered, bulk polymer phases (both glasses and melts), polymer ICs may be utilized to increase our understanding of the behaviour of polymer chains in their ordered, bulk phases, such as those found in crystalline and liquid-crystalline samples.

(Keywords: inclusion compounds; conformations; molecular modelling)

INTRODUCTION

Many of the physical properties which are unique to polymers, and which serve to distinguish them from other classes of materials, are related to their sizes and shapes. Their long-chain natures (sizes), coupled with their ability to adopt an almost inexhaustible variety of different conformations (shapes and sizes), leads to a qualitative understanding of their behaviour. For example, viscoelastic phenomena and rubber elasticity, which are unique to polymers, are clearly attributable to the ability of large, flexible polymer chains to adjust their conformations in response to a stress. When cross-linked into three-dimensional networks, the flexible polymer chains between the cross-links respond elastically to the strain accompanying the stress by adopting more extended conformations, which return to their original distribution upon removal of the extensional stress. When the same large, flexible polymer chains are free from permanent cross-links they are capable of plastic deformation, but their irreversible flow is impeded by their inability to move freely past each other. Concentrated polymer solutions and polymer melts are highly cooperative, because each polymer chain is in contact with or influences many neighbouring polymer chains, solely because of their large sizes and pervasive, randomly coiling shapes.

In a polymer melt each chain is in contact with and able to influence roughly 100 other polymer chains. To understand the physical properties of such a polymer sample requires two distinct types of information: first, the inherent or intrinsic characteristics (conformations and motions) of the polymer chains, which depend solely upon intramolecular or intrachain interactions, and secondly, the effects of the cooperative interactions between polymer chains. By studying the behaviour of isolated polymer chains in dilute solutions at the Θ temperature[1], where the chains are free from both excluded-volume self-intersections and cooperative interchain interactions, it is possible to secure a useful description[2] of the inherent, intramolecular behaviour of disordered polymer chains. Comparison with the behaviour of the molten polymer, for example, can provide some measure of the nature of cooperative, interchain interactions occurring in a disordered, bulk polymer.

How then might we proceed to try and understand the properties of ordered, bulk polymers, such as those found in semicrystalline and liquid-crystalline samples? We have no dilute solution analogue for the conformationally, orientationally, and/or positionally ordered polymer chains found in liquid-crystalline and crystalline polymer samples. However, we believe that certain inclusion compounds (ICs) formed between polymers and small-molecule hosts may provide a solid-state analogue/model system/touchstone useful for separating the inherent, single-chain behaviour from the cooperative interactions

0032-3861/94/030573-07

occurring between chains in ordered, bulk polymer phases.

Certain small molecules such as urea and perhydrotriphenylene (PHTP), are observed[3–7] to form crystalline ICs with polymers. In these polymer ICs the guest polymer chains are included in and confined to occupy narrow channels provided by the crystalline matrix formed from the small-molecule host. Illustrations of two such polymer–urea[8,9] and polymer–PHTP[10] ICs are presented in *Figure 1* and are based on the results of X-ray diffraction analyses[10,11] performed on their single crystals. Two observations come almost immediately to mind: (i) the channels occupied by the included polymer chains are nearly cylindrical and quite narrow (D = channel diameter = 5.5 Å) and (ii) each included polymer chain is separated, and therefore decoupled, from all neighbouring chains by the walls of the IC channels, which are constructed exclusively of the host matrix molecules. Clearly, the polymer chains included in the narrow channels of their ICs with urea and PHTP hosts are highly extended[12] and isolated from neighbouring polymer chains. These two features of polymer ICs serve to recommend them as model systems whose study can lead to an assessment of the inherent, single-chain behaviour of ordered, bulk polymer solids.

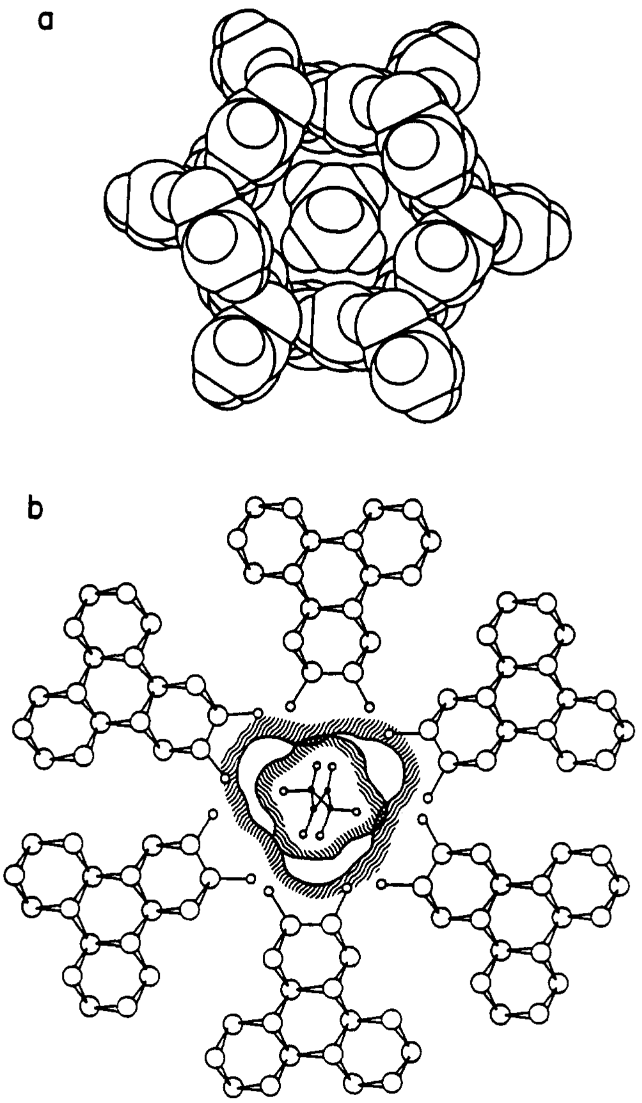
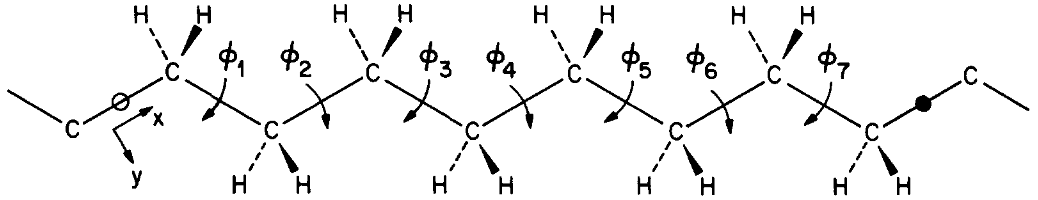


Figure 1 (a) Space-filling drawing of a channel in the urea–n-hexadecane clathrate[8,9] and (b) schematic drawing of a *trans*-1,4-polybutadiene chain in the channel of its inclusion compound with PHTP[10]

Recent studies of polymer ICs combine molecular modelling[12–19] with experimental observations[20–27] principally from solid-state n.m.r. spectroscopy. We attempt to define those conformations which are accessible to a polymer chain confined to occupy its narrow IC channels. In addition, the feasibility of interconverting between channel conformers is assessed. Information concerning the potential conformations and mobilities of polymer chains constrained to occupy the narrow channels of their ICs, which is derived from molecular modelling analyses, is used to interpret the experimental observations. Finally, we compare the observations, modelling results, and subsequent analyses performed on polymer ICs to identical observations recorded for ordered, bulk polymer samples of the same polymers. In this way we attempt to gauge the relative contributions made to the properties of ordered, bulk polymer samples by the inherent behaviour of single, isolated, stretched polymer chains and by the cooperative, interchain interactions. We illustrate this approach by way of its application to the polymer ICs formed by polyethylene, the *trans*-1,4-polydienes, poly(ethylene oxide), poly(L-lactic acid), and polypropylene.

Modelling polymer chains in IC channels

When modelling the behaviour of polymers confined to the channels of their ICs with urea and PHTP (see *Figure 1*), we simply consider only those conformations which fit into a cylinder with a diameter comparable[3–11] to the IC channels (ca. 5.5 Å). Consider the polyethylene



$$U = \begin{array}{c|ccc} & t & g^{+} & g^{-} \\ \hline t & 1 & .54 & .54 \\ g^{+} & 1 & .54 & .034 \\ g^{-} & 1 & .034 & .54 \end{array}$$

Figure 2 A four-repeat-unit fragment of PE used to derive[14] the conformations and motions of its channel-bound chains

(PE)[14] chain fragment depicted in *Figure 2*. The statistical weight matrix U drawn below the PE fragment embodies the rotational isomeric state (RIS) conformational description of the PE chain[28], and its elements are appropriate to room temperature. We adopt C–C and C–H bond lengths of 1.53 and 1.10 Å, respectively, with the angle C–C–C = 112° and the angle H–C–H = 110°. A Cartesian coordinate system is affixed to the middle of the first C–C bond at O and is used to express the x, y, and z coordinates of each C and H atom in the PE chain fragment. These atomic coordinates depend on the set of 7 ϕ-rotation angles, resulting in 3^7 (=2187) total PE fragment conformers when each backbone bond is restricted to adopt only the staggered *trans* (t) ($\phi = 0°$) and *gauche* ($g^{\pm}$) ($\phi = \pm 120°$) rotational states. For each of these conformations the x, y, and z coordinates of all of the atoms are calculated and then transformed to the Cartesian coordinate system (x', y', z') whose z'-axis connects the mid-points of the terminal bonds in the PE fragment (○ and ● in *Figure 2*). The radius of the corresponding cylindrical coordinate system with a coincident z'-axis is $r = (x'^2 + y'^2)^{1/2}$.

In our selection of channel conformations, we simply 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 PE fragment passes this test, then the conformation is considered to be a channel conformer.

Matrix multiplication techniques[2] are used to calculate various properties of the PE chain fragment, averaged over all conformations and also averaged over just the set of channel conformers found. This is made possible by the RIS conformational model developed for PE[28]. Average probabilities, or populations, of channel conformers and fragment bond conformations averaged over all 2187 conformations, and for just the set of channel conformers, are obtained in this manner for channels (cylinders) of various radii.

Summation of the elements in the matrix product $(U)^7$ yields the configurational partition function Z(PE) of the PE fragment in *Figure 2*. The probability that the PE fragment adopts the ttg^+tg^-tt conformation, for example, is obtained from $[U(1)U(1,1)U(1,2)U(2,1)U(1,3)U(3,1)U(1,1)]/Z(\mathrm{PE})$, where $U(1)$ is the statistical weight matrix U of *Figure 2* with all elements in columns 2 and 3 replaced by zeros. To determine the probability of finding the fourth C–C bond of the PE fragment in the $\phi = g^-$ rotational state (or conformation), we simply divide the matrix product $(U)^3U(g^-)(U)^3$ by Z(PE), where $U(g^-)$ is the statistical weight matrix U with the first and second column elements, which correspond to the t and g^+ conformations, replaced by zeros.

As a measure of the mobility of the PE chains confined to occupy the channels of its ICs with urea and PHTP, we have attempted to determine the feasibility of interconverting between the channel conformers without any part (atom) of the chain fragment leaving the channel during any step in the interconversion process. One of the channel conformers is selected as the starting conformation. As each rotation angle is incremented ($|\Delta\phi| = 20°$), the x', y', and z' coordinates of each atom in the PE fragment are calculated and checked to see that all atoms remain inside the cylinder of the starting channel conformer. This procedure is repeated until one or more atoms passes through the cylinder wall, or another channel conformer is reached. If the former occurs, then another channel conformer is selected as the starting conformer, and the interconversion procedure is repeated. After reaching another channel conformer, all rotational angles are reinitialized to the values of the new starting channel conformer, and the interconversion process is restarted. The test for interconversion between channel conformers is complete after each channel conformer has been used as the starting conformation.

Recently, Mattice and co-workers[29–32] have begun to model the mobilities and conformations of polymers that are confined to their ICs with urea and PHTP by means of a molecular dynamics simulation technique. They place a polymer chain fragment inside a single IC channel formed by the host clathrate crystalline lattice, whose molecules are positioned according to their X-ray determined structures[10]. As an example, in their modelling[29] of the IC formed with PHTP and *trans*-1,4-polybutadiene (TPBD), a 10-repeat-unit fragment of TPBD was placed in the clathrate channel which is formed by 6 stacks containing 15 PHTP molecules each (see *Figure 1b*), which results in a channel that is roughly 60% longer than the fully extended TPBD fragment. Each of the 4422 atoms in this portion of the PHTP lattice channel which contained a 10-repeat-unit TPBD fragment was explicitly considered. Their dynamic simulation was carried out for a 70-ps trajectory using the Verlet algorithm in integration steps of 0.5 fs, with the CHARMm potential function employed to calculate the energy of the system.

It should be mentioned that there is potentially a serious drawback in simulating the conformations and mobilities of included polymer chains solely by the molecular dynamics approach. For those polymers that are unable to interconvert between channel conformers (see below), the results of the molecular dynamics trajectories will depend on the choice of the starting channel conformer. This inability to interconvert between channel conformers will prevent sampling of all of the possible channel conformers. The optimum approach would seem to be afforded by combining a complete conformational search for channel conformers, as described here, with molecular dynamics trajectories which begin from all of those channel conformers that are unable to interconvert.

RESULTS AND DISCUSSION

Polyethylene

The channel conformers found[14] for PE are partially characterized in *Table 1*, where their numbers, probabilities, and bond rotational state probabilities are presented for cylinders of various diameters (D). Because in the search for channel conformers each atom is considered to be a volumeless point, a channel conformer found to fit into 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 a radius of 0.5 Å are assigned to each hydrogen atom. The steric requirements of 0.5 Å-van der Waals spheres placed on each hydrogen atom are reflected in the cylinder diameters that are given in *Table 1*.

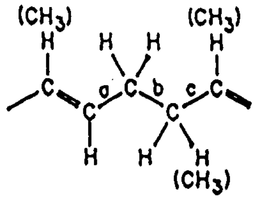
It should be noted that only ca. 1% of the 2187 total PE fragment conformers are slim enough to fit into those cylinders ($D = 5.5$ Å) corresponding to the channels in the polymer ICs with urea and PHTP. Among these channel conformers is the lowest-energy, all-*trans*, planar zigzag conformation which is found in bulk PE crystals. Furthermore, it is not possible to

Table 1 Characteristics of the polyethylene channel conformers[14]

D (Å)	Number of channel conformers	Probability of channel conformers	n in $P(\phi_n=t)$ 1.7	2.6	3.5	4.0
4.0	1	0.012	1.0	1.0	1.0	1.0
4.5	3	0.014	0.855	1.0	0.855	1.0
5.0	5	0.016	0.746	1.0	0.746	1.0
5.2	11	0.032	0.591	1.0	0.591	1.0
5.5	25	0.058	0.575	0.750	0.640	0.870
6.0	101	0.164	0.481	0.756	0.648	0.751
7.0	365	0.349	0.519	0.618	0.695	0.650
8.0	805	0.659	0.522	0.605	0.663	0.674
9.0	1597	0.865	0.525	0.608	0.617	0.641
11.0	2165	0.998	0.539	0.605	0.596	0.599
Free chain	2187	1.0	0.540	0.605	0.596	0.598

Table 2 Structures and conformations of *trans*-1,4-polydienes[13]

			Number of channel conformers		$P(\phi_a=c)$		$P(\phi_b=t)$		$P(\phi_{C=C}=c)$	
Polymer	Abbreviation	Structure	Free chain	$D=5.5$ Å	Free chain	$D=5.5$ Å	Free chain	$D=5.5$ Å	Free chain	$D=5.5$ Å
trans-1,4-Polybutadiene	TPBD	$-\overset{H}{C}=\underset{H}{C}-CH_2-CH_2-$	531441	109	0.210	0.32–0.33	0.47	1.0	0.210	0.31–0.34
trans-1,4-Polyisoprene	TPIP	$-\overset{CH_3}{C}=\underset{H}{C}-CH_2-CH_2-$	104976	14	0.0	0.0	0.55	0.99	0.226	0.0
trans-1,4-Poly(penta-1,3-diene)	TPPD	$-\overset{H}{C}=\underset{H}{C}-CH_2-\overset{CH_3}{CH}-$	531441	39	0.204	0.376	0.45	1.0	0.206	0.327



interconvert between these channel conformers until the cylinder diameter is increased to $D>6.5$ Å. The inability of PE channel conformers to interconvert parallels the behaviour observed when modelling poly(ethylene oxide)[14], aliphatic polyesters and polyamides[15], polypropylenes[16], and *trans*-1,4-poly(isoprene) (TPIP)[13], also confined to cylinders with $D=5.5$ Å. On the other hand, two other *trans*-1,4-polydienes, namely *trans*-1,4-poly(butadiene) (TPBD) and isotactic *trans*-1,4-poly(penta-1,3-diene) (TPPD), do exhibit[13] the ability to interconvert between channel conformers when confined to occupy cylinders with $D=5.5$ Å (see below).

Sozzani *et al.*[25] have recently reported the high resolution ^{13}C n.m.r. spectra of the PE–PHTP inclusion compound and bulk crystalline PE. The ^{13}C chemical shifts of the methylene carbons were identical for the included and the crystalline, bulk PE chains, but their spin-lattice relaxation times, T_1, differed widely, with values of 6.4 s (IC) and 320 s (bulk). The spin-lattice relaxation times measured for the PHTP carbons in its IC with PE were more than an order of magnitude longer than those observed for the included PE chains, approaching those observed for the crystalline chains in the bulk PE sample.

We suggest[33–37] that PE chains assume the all-*trans*, planar zigzag conformation in both samples, and the marked increase in the mobility of the PE chains in the PHTP inclusion compound is not a consequence of *trans–gauche* conformational interconversion. Both of these findings are in accord with the results discussed above and are obtained from the conformations of PE chains confined to occupy narrow cylinders[14], thus, mimicking the channels in polymer–PHTP ICs, i.e. with $D=5.5$ Å. Molecular dynamics simulations of PE in its IC with PHTP, performed by Zhan and Mattice[32], are completely consistent with the results of our modelling[14] and the observations of Sozzani *et al.*[24]. It is also noteworthy that the PHTP matrix in the PE–PHTP inclusion compound is considerably more rigid than the included PE chains ($T_1 = 70$–150 s (PHTP) *versus* $T_1 = 6.4$ s (PE)). This observation[24] lends support to the assumption that the channels in polymer ICs may be considered as rigid, cylindrical constraints when modelling the behaviour of the included polymer chain.

Sozzani *et al.*[24] suggest that the motions responsible for the short T_1 (6.4 s) observed at room temperature for PE in its PHTP IC might be similar to those thought to occur in the crystalline portions of bulk PE at elevated temperatures just prior to melting, which are termed as the α_c relaxation process[38]. This conclusion was made possible by their direct observation of the mobility of PE chains isolated in the narrow and rigid channels of its IC with PHTP.

Trans-1,4-polydienes

Table 2 partially summarizes the results of modelling[13] the conformations accessible to three *trans*-1,4-diene polymers (TPBD, TPIP, and TPPD (isotactic)) in the 5.5 Å channels of their ICs with PHTP. Four-repeat-unit fragments of each polymer were modelled[13] resulting in the large overall numbers of conformations available to their free-chain fragments, as listed in the fourth column of *Table 2*. In addition to the numbers of channel conformers found for each of the *trans*-1,4-polydiene fragments, the probability of finding the olefinic-to-paraffinic and paraffinic-to-paraffinic C–C bonds in the *cis* (*c*) and *trans* (*t*) conformations[2], respectively, are contrasted for the free and channel-bound chains.

What is not presented in *Table 2* is information regarding the mobility of the channel-bound fragment conformers. It was found[13] that interconversion between all 109 TPBD channel conformers is possible, while only a portion of the 39 TPPD channel conformers, and none of the 14 TPIP channel conformers, are able to interconvert without penetrating the channel walls.

^{13}C n.m.r. studies[21,22] of TPBD and TPIP inclusion compounds with PHTP and of their bulk, crystalline polymorphs can be summarized as follows: (i) chemical shifts and T_1s for the TPBD and TPIP ICs are closely similar to those observed in their bulk, crystalline form II and β-form polymorphs, respectively, and (ii) T_1s for the TPIP–PHTP inclusion compound are longer by nearly an order of magnitude than the spin-lattice relaxation times observed for TPBD chains in both its PHTP IC and in its form II bulk crystals. In addition, ^{2}H n.m.r. observations[20] of TPBD in its IC and form II bulk phases are closely similar. Each of these observations is consistent with the conformational modelling[13] of their channel-bound fragments.

In the form I, bulk crystal TPBD chains are rigidly fixed in the $Ts^{\pm}ts^{\mp}$ conformation, where T corresponds to the *trans* double bond and $s^{\pm}ts^{\mp}$ indicate *skew* (*s*) and *trans* conformations about the single C–C bonds (a, b, and c) of the repeat unit (see *Table 2*), while in the form II polymorph $Tcts^{\pm}$ and $Ts^{\pm}tc$ conformers are rapidly interconverting with the form I conformation ($Ts^{\pm}ts^{\mp}$). Note that TPBD fragment conformers which can be accommodated and can interconvert in the IC channels ($D = 5.5$ Å) have =CH–CH$_2$ and –CH$_2$–CH= bonds in both the $s^{\pm}$ and c conformations[2], while the CH$_2$–CH$_2$ bond is always t. Clearly, the conformations accessible to TPBD chains in the channels of their PHTP IC, and their mobility, are consistent with the n.m.r. observations[20,21] recorded both for the IC and the bulk, form II samples. It would appear that the conformations and motions of TPBD chains are primarily governed by geometrical constraints provided either by the IC matrix walls or by the neighbouring TPBD chains in its form II crystals, and are not, therefore, significantly modified by cooperative interchain interactions.

In bulk, α- and β-form crystals of TPIP the chains adopt the $Tcts^{\pm}$ and $Ts^{\pm}ts^{\mp}$ conformations[2], respectively. None of the rigid, non-interconverting channel conformers found for TPIP has a *cis* (*c*) =CH–CH$_2$ or =CCH$_3$–CH$_2$ bond, but rather only conformers of the β-form type ($Ts^{\pm}ts^{\mp}$) fit into the $D = 5.5$ Å channels. It is not surprising that the TPIP chains in PHTP IC and the bulk, β-form phases are behaving similarly[22].

To date, only ^{2}H n.m.r. observations[39] have been reported on TPPD–PHTP inclusion compounds, and are consistent with the presence of two populations of relaxing deuterium nuclei: 20% of the C–D bonds are highly mobile, as are all of the C–D bonds in the TPBD IC and form II crystals, while the remaining 80% are increasingly rigid with 'Pake-like' quadrupolar coupling patterns which are associated with rigid C–D bond orientations on a time scale of the order of 10^{-5} s. This observation is not at odds with our modelling of channel-bound TPPD fragments that has led to two populations of channel conformers, namely those conformers that are able to interconvert and those that could not.

Bruckner *et al.*[39] attributed the bimodal motional behaviour they observed for the TPPD chains in its IC with PHTP to different local environments experienced by the TPPD chains inside the PHTP channels. However, they assumed that the TPPD chains were adopting only *Tsts* conformations by analogy with their bulk crystalline conformation[39–41], and did not consider the possibility of *cis* =CH–CH$_2$ or C(CH$_3$)H–C= bonds. As can be seen from *Table 2*, both of these bonds possess a substantial amount of *cis* character in the 39 channel conformers ($D = 5.5$ Å) found here for the TPPD–PHTP inclusion compound. Based on the potential for TPPD chains to adopt different conformations in their PHTP IC and also in their bulk crystals, we would suggest a detailed comparison of ^{2}H and ^{13}C n.m.r. studies performed on both of these TPPD samples.

Mattice and co-workers[29–31] have modelled the conformations and motions of TPBD[29] and TPIP[31] in their ICs with PHTP via the molecular dynamics approach outlined above. With one notable exception, they have generally arrived at the same conclusions that were obtained in our modelling studies of the ICs formed between PHTP and the *trans*-1,4-polydienes. However, Dodge and Mattice[29] and Zhan and Mattice[30] found chains of TPBD, both in its PHTP IC and in both of its bulk crystalline polymorphs (forms I and II), to be restricted to $Ts^{\pm}ts^{\mp}$ conformations, with *cis* =CH–CH$_2$ bonds only permitted for free, isolated TPBD chains. This result is clearly at odds with our modelling[13] of the TPBD–PHTP inclusion compound and the ^{13}C n.m.r. observations recorded on it, which strongly indicate flexible TPBD chains undergoing interconversions between $Ts^{\pm}ts^{\mp}$ and *cis*-bond containing $Tcts^{\pm}$ conformations in its PHTP IC, as well as in its form II bulk crystals[42] and amorphous phase.

Other polymers

Several other PHTP and urea ICs that have been formed include polymer chains in conformations that are distinct from those observed in their bulk crystals. Poly(ethylene oxide) (PEO)[14], poly(L-lactic acid)[17,26,27], and isotactic and syndiotactic polypropylenes[16] all form PHTP and/or urea ICs that fall into this class. Molecular modelling of their fragments indicate that the conformations assumed by the chains in their bulk crystals are not slim enough to fit into the narrow IC channels.

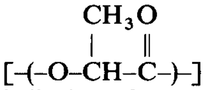
PEO forms ICs with both PHTP and urea. The fibre repeat distance per monomer of the included PEO chains were found by X-ray diffraction to be 3.43 Å (PHTP)[43] and 2.313 Å (urea)[44]. By contrast, a repeat distance of 2.77 Å per monomer is observed[45] for bulk crystalline PEO chains, and PEO in the fully extended all-*trans* conformation has a per-monomer fibre repeat distance of 3.6 Å. Farina *et al.*[43] suggest a conformation with *trans* C–C bonds and C–O bonds that alternate ±40° away from *trans* when PEO is included in PHTP. Chenite and Brisse[44] find a C–C(*g*), C–O(*t*) conformation for PEO in its urea IC, which is similar to, but more compact than the bulk crystalline conformation.

Our modelling[14] indicated that all-*trans*, 'kink' ($ttg^{\pm}tg^{\mp}tt$), and 'jog' ($ttg^{\pm}tttg^{\mp}tt$) conformers all fit into cylinders that mimic the channels in urea and PHTP clathrates. We are unable, however, to interconvert between these channel conformers, and noted that the bulk crystalline conformation of PEO would not fit into a cylinder with $D = 5.5$ Å.

As mentioned above, Chenite and Brisse[44] found PEO in its clathrate with urea to adopt a distorted *gtt* conformation, where, as indicated by our modelling, the distortions away from perfecly staggered *t* and *g* conformations are made necessary by the narrow channel diameter. Furthermore, a third of the urea molecules in the PEO–urea inclusion compound are found to reside inside the clathrate channels and are directly hydrogen bonded to the oxygen atoms of the included PEO.

PEO chains clearly adopt different conformations in their urea and PHTP ICs, and a third of the urea molecules are non-matrix forming and instead are hydrogen bonded to the PEO chains in the urea clathrate channels. Thus it would seem that solid-state n.m.r. studies of the motions of the PEO chains in these two unique ICs and in their bulk crystalline and amorphous phases hold considerable promise for characterizing the relative contributions made by inherent PEO chain flexibility, geometrical constraints, and strong directional forces (hydrogen bonds) to the solid-state chain dynamics of PEO.

Modelling[17] poly(lactic acids) in a search for conformations slim enough to reside in the narrow channels of a potential urea clathrate indicated that only the all-L polymer (PLLA), when adopting a nearly all-*trans* conformation, would fit. We have since made the PLLA–urea inclusion compound[26,27] and ^{13}C n.m.r. observations[27] of this IC, and bulk crystalline PLLA point to different conformations and/or packing environments for the PLLA chains in these two solid samples. PLLA



$[\!-\!(\!-O-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\!)\!-\!]$ adopts a g^+tt (O–$\overset{\overset{CH_3}{|}}{CH}$, $\overset{\overset{CH_3}{|}}{CH}$–$\overset{\overset{O}{\|}}{C}$, $\overset{\overset{O}{\|}}{C}$–O) helical conformation in its bulk crystals[46–48], and our modelling[17] suggests an all-*trans* conformation for the PLLA chains in its urea IC. Our preliminary ^{13}C n.m.r. observations[27] appear consistent with these conformational differences.

Our modelling[16] of polypropylene (PP) tetramer fragments indicated that neither isotactic (i)- nor syndiotactic (s)-PP chains could assume their bulk crystalline conformations, 3_1-helical ...*tgtgtg*..., and 4_1-helical ...*ttggttggttgg*..., respectively, and be expected to reside in the $D = 5.5$ Å channels of their PHTP ICs. Instead, s-PP with an all-*trans* conformation and i-PP with a relatively high energy (...(t^* or g^*) $\bar{g}$ (t^* or g^*)$\bar{g}$...) nonstaggered bond conformation were found to fit, and also appear to be consistent with preliminary ^{13}C n.m.r. observations[16] of both PHTP ICs.

PEO, PLLA, and i- and s-PP all form ICs in which they reside in channels too narrow to accommodate their bulk crystalline conformations. This raises the question of what factors are contributing to the thermodynamic stabilities of these polymer ICs? Expressed another way, what forces are compensating for the loss of conformational entropy[12,49,50] suffered by the extended, stretched chains occupying the IC channels, especially when in some instances their lowest energy, bulk crystalline conformations are not accessible in these channels?

Stability of polymer ICs

It is possible to estimate[12] the free energy increase (ΔA) and stored elastic force (f_A) in those polymer chain fragments that are confined to narrow IC channels. This is achieved[12,51] by evaluation of the fragment configurational partition function Z^2, and the end-to-end distances averaged over all conformations accessible to the free, unconstrained and channel-bound chain fragments. The results of such an analysis[12], performed at 50°C, are displayed in *Table 3* for the PE, TPBD, and PEO chain fragments employed in the conformational modelling of their channel conformers. Note that the free-energy change required to stretch these chain fragments from their multitude of randomly coiling conformers to the relatively small numbers of channel-bound conformers (see *Tables 1* and *2*) ranges from 225–341 cal (942–1427 J) per mole of bonds.

To provide some perspective, it may be mentioned that the observed[53] enthalpy of melting for bulk, crystalline PE is ~1000 cal (4184 J) per mole of bonds, which is more than sufficient to balance the higher intramolecular free energy of all-*trans*, planar zigzag PE chains in the crystal when compared to the randomly coiling PE chains in the melt. In bulk PE crystals it is the precise crystallographic packing of neighbouring chains, and the consequent favourable interchain van der Waals interactions, which provide the crystalline stability below

Table 3 Free energy change and elastic force stored in polymer chain fragments stretched by squeezing them into narrow IC channels[12]

Polymer	$\Delta\langle r\rangle$ (Å)	ΔE^a	$-T(\Delta S)^a$	ΔA^a	$f_E{}^b$	$f_S{}^b$	$f_A{}^b$
PE	1.685	−65	290	225	−39	172	133
PEO	2.785	17	266	283	6	95	101
TPBD	6.719	−43	384	341	−6	57	51

[a] Units are calories per mole of backbone bonds (1 cal = 4.184 J)
[b] Units are calories per Å, per mole of backbone bonds (1 cal Å^{-1} = 4.184 × 10^{10} J m^{-1})

the melting temperature. However, in polymer ICs no such interchain packing is possible, and even the van der Waals interactions between the walls of the PHTP channels and the included PE chains, for example, cannot be too favourable, because there is considerable motion permitted to the included PE chains[24]. In addition, the disparity in the relaxation behaviour and mobilities between the included polymer chains (T_1(PE) = 6.4 s) and the crystalline, host lattice (T_1(PHTP) = 70–150 s) implies that the included PE chains are not interacting very strongly with the PHTP clathrate walls, but instead are somewhat decoupled.

A likely explanation for the thermodynamic stability of polymer ICs would seem to lie in an increase in the stability of the host clathrate structure, which is only formed by including polymer chains in the matrix channels, relative to the stability of pure clathrate molecular crystals, which possess no channel structure[3]. Apparently PHTP and urea molecules pack more efficiently, interact more strongly, and/or are more mobile, with greater entropy, when they form the channelled matrix structure to host the included polymer chains.

Independent of the preceding conjecture on polymer IC stability, is the fact that polymer ICs provide an extremely useful model system or touchstone with which to probe and explore the more complex behaviour of polymer chains in their ordered, bulk phases, where they can be strongly coupled.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

2 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969

3 Fetterly, L. C. in 'Non-Stoichiometric Compounds' (Ed. L. Mandelcorn), Academic, New York, 1965, Ch. 8

4 Farina, M. in 'Proceedings of the International Symposium on Macromolecules, Rio de Janeiro, 1974' (Ed. E. B. Mano), Elsevier, New York, 1975, p. 21

5 Farina, M. in 'Inclusion Compounds' (Eds J. L. Atwood *et al.*), Vol. 2, Academic, New York, 1984, p. 69

6 Farina, M. in 'Inclusion Compounds' (Eds J. L. Atwood *et al.*), Vol. 2, Academic, New York, 1984, p. 297

7 Di Silvestro, G. and Sozzani, P. in 'Comprehensive Polymer Science' (Eds G. C. Eastman *et al.*), Vol. 4, Pergamon, Oxford, 1988, Ch. 18, p. 303

8 Harris, K. D. M. *PhD Thesis*, University of Cambridge, 1988

9 Harris, K. D. M. and Joneson, P. *Chem. Phys. Lett.* 1989, **154**, 593

10 Colombo, A. and Allegra, G. *Macromolecules* 1971, **4**, 579

11 Smith, A. E. *Acta Crystallogr.* 1952, **5**, 224

12 Tonelli, A. E. *Comp. Polym. Sci.* 1991, **1**, 22

13 Tonelli, A. E. *Macromolecules* 1990, **23**, 3129

14 Tonelli, A. E. *Macromolecules* 1990, **23**, 3134

15 Tonelli, A. E. *Macromolecules* 1991, **24**, 1275

16 Tonelli, A. E. *Macromolecules* 1991, **24**, 3069

17 Tonelli, A. E. *Macromolecules* 1992, **25**, 3581

18 Tonelli, A. E. *Makromol. Chem. Symp. Ser.* 1993, **65**, 133

19 Tonelli, A. E. unpublished results

20 Sozzani, P., Behling, R. W., Schilling, F. C., Bruckner, S., Helfand, E., Bovey, F. A. and Jelinski, L. W. *Macromolecules* 1989, **22**, 3318

21 Sozzani, P., Bovey, F. A. and Schilling, F. C. *Macromolecules* 1991, **24**, 4369

22 Schilling, F. C. and Sozzani, P. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1992, **33**, 80

23 Bovey, F. A. and Schilling, F. C. *Macromolecules* 1992, **25**

24 Sozzani, P., Schilling, F. C. and Bovey, F. A. *Macromolecules* 1991, **24**, 6764

25 Choi, C., Davis, D. D. and Tonelli, A. E. *Macromolecules* 1993, **26**, 1468

26 Howe, C., Hancock, M., Sankar, S., Simonsen, I., MacClamrock, C. and Tonelli, A. E. unpublished results

27 Howe, C., Sankar, S. and Tonelli, A. E. *Polymer* 1993, **34**, 2674

28 Abe, A., Jernigan, R. L. and Flory, P. J. *J. Am. Chem. Soc.* 1966, **88**, 631

29 Dodge, R. and Mattice, W. L. *Macromolecules* 1991, **24**, 2709

30 Zhan, Y. and Mattice, W. L. *Macromolecules* 1992, **25**, 1554

31 Zhan, Y. and Mattice, W. L. *Macromolecules* 1992, **25**, 3439

32 Zhan, Y. and Matice, W. L. *Macromolecules* 1992, **25**, 4078

33 See refs. 34–37 for a discussion of the connection (γ-effect) between the local polymer chain conformation and the resultant ^{13}C chemical shifts observed both in high-resolution solution and solid-state ^{13}C n.m.r. spectra

34 Tonelli, A. E. *J. Am. Chem. Soc.* 1980, **102**, 7635

35 Tonelli, A. E. and Schilling, F. C. *Acc. Chem. Res.* 1981, **14**, 233

36 Tonelli, A. E. *Biopolymers* 1984, **23**, 819

37 Tonelli, A. E. 'NMR Spectroscopy and Polymer Microstructure: The Conformational Connection', VCH, New York, 1989

38 Mansfield, M. and Boyd, R. H. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 1227

39 Brucker, S., Sozzani, P. E., Boeffel, C., Destry, S. and Di Silvestro, G. *Macromolecules* 1989, **22**, 607

40 Bassi, I. W., Allegra, G. and Scordamaglia, R. *Macromolecules* 1971, **4**, 575

41 Bruckner, S., Di Silvestro, G. and Prozio, W. *Macromolecules* 1986, **19**, 235

42 Schilling, F. C., Gomez, M. A., Tonelli, A. E., Bovey, F. A. and Woodward, A. E. *Macromolecules* 1987, **20**, 2954

43 Farina, M., Natta, G., Allegra, G. and Loffelholz, M. *J. Polym. Sci. Part C* 1967, **16**, 2517

44 Chenite, A. and Brisse, F. *Macromolecules* 1991, **24**, 2221

45 Tadokoro, H., Chantani, Y., Yoshirhara, T., Tahara, S. and Murahashi, S. *Makromol. Chem.* 1969, **73**, 109

46 Desantis, P. and Kovacs, A. J. *Biopolymers* 1968, **6**, 299

47 Ikada, Y., Jamshichi, K., Tsuji, H. and Hyon, S.-H. *Macromolecules* 1987, **20**, 904

48 Okihara, T., Tsuji, M., Kuwaguchi, A. and Katayama, K.-I. *J. Macromol. Sci.–Phys.* (*B*) 1991, **30**, 119

49 Tonelli, A. E. *J. Chem. Phys.* 1970, **52**, 4749

50 Tonelli, A. E. in 'Analytical Calorimetry' (Eds R. S. Porter and J. L. Johson), Vol. 3, Plenum, New York, 1983, p. 89

51 From the configurational partition functions Z for each polymer chain fragment, the free energy (A) and the end-to-end distance $\langle r \rangle$ are calculated by averaging over all possible conformations of the free chain and over just the set of channel-bound conformers. Then $f_A = \Delta\langle A \rangle / \Delta\langle r \rangle$: f_E and f_S are the energetic and entropic components of $\Delta\langle A \rangle(\Delta\langle E \rangle - T\Delta\langle S \rangle)$, i.e. $f_E = \Delta\langle E \rangle / \Delta\langle r \rangle$ and $f_S = -T\Delta\langle S \rangle / \Delta\langle r \rangle$

52 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964