Macromolecules **1991,** *24,* 1275–1278

Modeling the Conformations and Mobilities of Aliphatic Polyamides and Polyesters Confined to Channels

A. E. Tonelli

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

Received July 9, 1990; Revised Manuscript Received September 21, 1990

ABSTRACT: Polymers may be isolated from their neighboring chains in the solid state by formation of inclusion compounds with host clathrates, such as urea and perhydrotriphenylene (PHTP). Each polymer chain is confined to a cylindrical channel in the inclusion compound whose walls are formed exclusively from the host clathrate molecules. Each channel is well separated from neighboring channels, thereby isolating each included polymer chain from its neighbors. We have modeled the conformations and mobilities of isolated aliphatic polyamide (nylon-6) and polyester (poly-ϵ-caprolactone) chains when confined to the channels appropriate to the inclusion compounds formed between polymers and clathrates, such as urea and PHTP. This was achieved by a two-step procedure: (i) from all possible conformations available to the free polymer chain, those which fit into the channel found in inclusion compounds were defined, and (ii) a test was performed to determine whether or not it was possible to interconvert between these channel conformations while the polymer chain remained inside the channel. Both the nylon and polyester chains were able to adopt only five distinct conformations whose diameters are appropriate to the channels found in urea and PHTP inclusion compounds formed with other polymers (D = 5.25–5.50 Å). In addition to the all-trans, planar zigzag conformation, four kink conformers with $g^{\pm}tg^{\mp}$ sequences were found to fit in these channels. However, it was not possible to interconvert between these channel conformers without some portion of each polymer chain leaving the channel. It would appear that the experimental observation of the inclusion compounds of aliphatic polyamides and polyesters, which might be formed with channel clathrates, such as urea and PHTP, would be useful for determining their solid-state dynamic and conformational characteristics.

Introduction

It is possible to study the conformations and motions of polymer chains in the solid state when they are confined to channels and isolated from neighboring chains by the formation of inclusion compounds between small-molecule, host matrices and polymeric guest molecules. Two such host matrices are formed by the crystals of urea and perhydrotriphenylene (PHTP). Their inclusion compounds with *n*-hexadecane[1] and *trans*-1,4-polybutadiene,[2] respectively, are illustrated in Figure 1 as viewed down the channels of both complexes. Each channel is nearly cylindrical in shape with diameters in the range of 5.25–5.50 Å, though the channel interiors are polar for the urea complex and aliphatic and nonpolar for the PHTP complex. Some polymers may be prepared directly in the channels of their inclusion compounds by irradiation of the inclusion compounds formed by their monomers,[3] while others are obtained from solutions or melts of host matrix and guest polymer mixtures.[3–6]

Regardless of the method employed to prepare an inclusion compound between the host, small-molecule matrix and the guest polymer, it is the well-defined geometrical environment (narrow cylindrical channels, see Figure 1), which confines and separates the guest polymer chains, that makes these complexes useful for studying the motions and conformations of solid polymers. The motions and conformations of polymers confined to the channels of their crystalline inclusion compounds are free from interchain interactions. With comparison of the behavior exhibited in their bulk, solid state to polymer motions and conformations observed in their inclusion compounds, it may be possible to separate the effects of cooperative, interchain interactions from their intrinsic, intrachain mobilities and conformations. This approach has already been applied to the PHTP inclusion compounds with channel-entrained *trans*-1,4-polydienes,[7–11] polyethylene (PE),[12] and poly(oxyethylene) (POE).[12]

In the present work we model the conformations and mobilities of aliphatic polyamides and polyesters confined to cylinders with diameters in the range (5.25–5.50 Å) appropriate to the channels found in urea and PHTP inclusion compounds formed with other polymers. Recent ^{2}H, ^{13}C, and ^{15}N solid-state NMR and molecular dynamics studies[13–21] of the motions, conformations, and solid–solid phase transitions in aliphatic polyamides prompted our study. Modeling the conformations and motions of polymers in well-defined channels, which are free of the complications produced by cooperative, interchain interactions, is relatively simple. Furthermore, it is hoped that this work will lead to the experimental study of the formation of polyamide and polyester inclusion compounds and the motions and conformations characteristic of their isolated, entrained chains. We feel that these observations will significantly aid the analyses of polyamide and polyester dynamics as observed in their bulk, semicrystalline states.

Aliphatic Polyamides and Polyesters in Clathrate Channels

Channel Conformers. Nylon-6 (N-6) and poly-ϵ-caprolactone (E-6) (see Figure 2) were selected as the model polyamide and polyester. To simulate the environment found in the urea and PHTP complexes illustrated in Figure 1, we simply consider only those N-6 and E-6 conformations that fit into a cylinder with a diameter comparable to these clathrate channels (5.25–5.50 Å). The portion of N-6 and E-6 chains considered in our modeling is drawn in Figure 2, below which are presented the statistical weight matrices (U)[22] corresponding to the constituent bonds of both N-6 and E-6. These matrices embody the rotational isomeric states (RIS) description[23] of the conformations of N-6 and E-6, and their elements (statistical weight Boltzmann factors) are appropriate to room temperature.

Each bond in both polymers, except the predominantly trans, planar amide and ester bonds, was assumed[22,23] to adopt only the trans (t = 0) and gauche ($g^{\pm}$ = ±120) conformations. The following bond lengths and valence

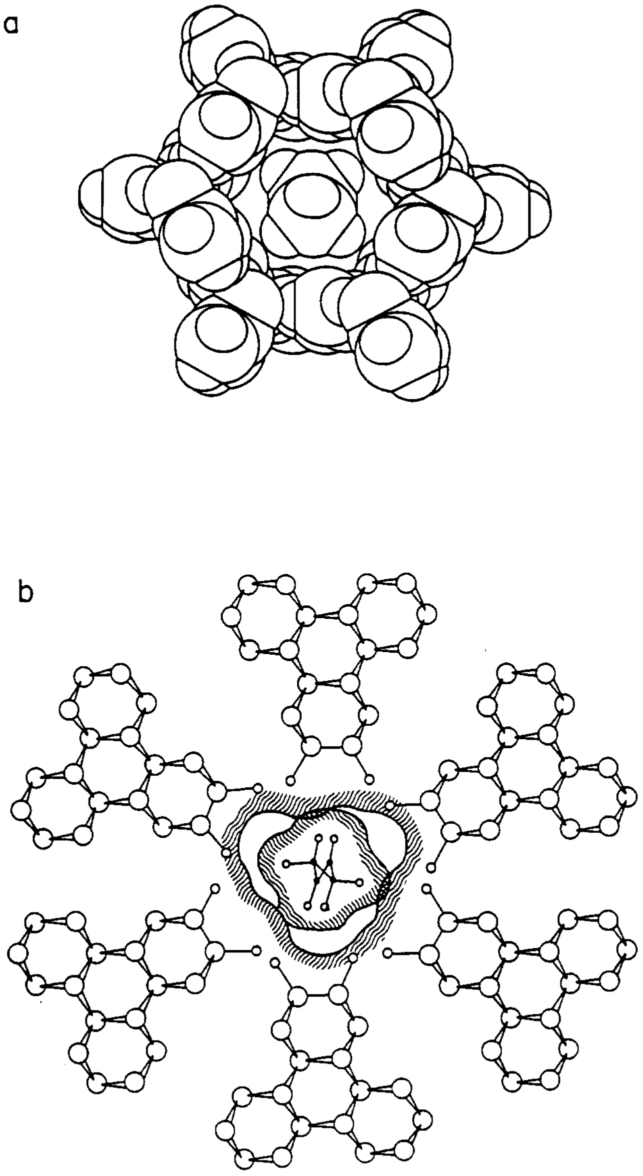
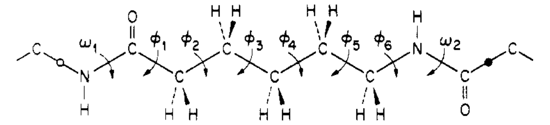


Figure 1. (a) Space-filling drawing of a channel in the urea-*n*-hexadecane clathrate.[1] (b) Schematic drawing of a *trans*-1,4-polybutadiene chain in the channel of its inclusion compound with PHTP.[2]

angles were adopted:[22,23] $l_{CH_2-CH_2} = 1.53$ Å; $l_{CH_2-N,O} = 1.46$, 1.44 Å; $l_{CH_2-C(=O)} = 1.51$ Å; $l_{N,O-C(=O)} = 1.33$ Å; $l_{C-H} = 1.1$ Å; $l_{N-H} = 1.04$ Å; $l_{C=O} = 1.22$ Å; ∠H–C–H = 110°; ∠O=C–N,O = 125°; ∠H–N–CH$_2$ = 118.5°; ∠C–C–C = 112°; ∠C–N–C(=O) = 123°; ∠C–O–C(=O) = 113°; and ∠C–C(=O)–N,O = 114°. Amide bonds were permitted to deviate ±20° away from the planar, trans conformation, while ±30° deviations were allowed for the ester bonds. Considering the 2-fold barriers to rotation about the amide and ester bonds, with respective heights[24,25] of 20 and 10 kcal/mol, ±20° and ±30° deviations away from ω_1 and $\omega_2 = 0°$ (see Figure 2) occur with probabilities $s\omega = 0.0193$ and 0.0147 in N-6 and E-6, respectively. Consequently amide and ester group rotation angles ω_1 and ω_2 were permitted three values; 0° (t) and ±20° (N-6) or ±30° (E-6).

A Cartesian coordinate system was affixed to the middle of the first CH$_2$–N (N-6) or CH$_2$–O (E-6) bond (see Figure 2) and was used as a reference frame for expressing the x, y, z coordinates of each of the atoms in both N-6 and E-6 chain fragments. Of course these atomic coordinates depend on the set of 8 (2ω and 6ϕ) rotation angles resulting in $(3)^8 = 6561$ total conformations for the free N-6 and E-6 chain fragments considered here. For each of these conformations the x, y, z coordinates of all atoms were calculated and then transformed to the Cartesian coordinate system x', y', z' whose z' axis connects the midpoints (○, ●) of the terminal bonds. The radius, r, of the corresponding cylindrical coordinate system with coincident z' axis is $r = (x'^2 + y'^2)^{1/2}$.



$$U_{\omega_1} = \begin{array}{c} \begin{array}{ccc} t & \Delta\omega_1 & -\Delta\omega_1 \end{array} \\ \begin{bmatrix} 1 & s\omega & s\omega \end{bmatrix} \end{array}; \quad U_{\phi_1} = \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \end{array}; \quad U_{\phi_{2,5,6}} = \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & .1 \\ 1 & .1 & 1 \end{bmatrix} \end{array}$$

$$U_{\phi_3} = \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & .43 & .43 \\ 1 & .43 & .043 \\ 1 & .043 & .43 \end{bmatrix} \end{array}; \quad U_{\phi_4} = \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & .43 & .43 \\ 1 & .43 & .015 \\ 1 & .015 & .43 \end{bmatrix} \end{array}; \quad U_{\omega_2} = \begin{array}{c} \begin{array}{ccc} t & \Delta\omega_2 & -\Delta\omega_2 \end{array} \\ \begin{bmatrix} 1 & s\omega & s\omega \\ 1 & s\omega & s\omega \\ 1 & s\omega & s\omega \end{bmatrix} \end{array}$$

Figure 2. Fragment of N-6 used to derive conformations of its channel-bound chains. (For E-6 replace –NH– with –O–). Statistical weight matrices corresponding to the bonds in the N-6 (E-6) fragment have elements appropriate to room temperature, where $s\omega = 0.0193$ (N-6) and 0.0147 (E-6).

In selecting channel conformations, we simply determined 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 N-6 or E-6 fragment passed this test, then the conformation was considered a channel conformer.

Average Properties of Channel Conformers. Matrix multiplication techniques[22] were used to calculate various properties of the N-6 and E-6 chain fragments, averaged over all conformations and averaged over just the set of channel conformers found. This averaging was made possible by the RIS model developed[22,23] for N-6 and E-6. Average probabilities, or populations, of channel conformers and bond conformations averaged over all conformations and just the set of channel conformers were obtained in this manner for channels (cylinders) of various radii r_c. The product of statistical weight matrices ($\mathbf{U}_{\omega_1}\mathbf{U}_{\phi_1}\mathbf{U}_{\phi_2}\mathbf{U}_{\phi_3}\mathbf{U}_{\phi_4}\mathbf{U}_{\phi_5}\mathbf{U}_{\phi_6}\mathbf{U}_{\omega_2}$) led to the partition functions ($z_{N\text{-}6}$ and $z_{E\text{-}6}$) of each fragment where $z_{N\text{-}6}$ and $z_{E\text{-}6}$ are simply the sum of elements of this matrix product. Let us suppose our N-6 fragment adopts the (ω_1=0°)-ttg$^+$tg$^-$t(ω_2=20°) conformation. Its probability of occurrence was obtained from $[\mathbf{U}_{\omega_1}(1,1)\mathbf{U}_{\phi_1}(1,1)\mathbf{U}_{\phi_2}(1,1)\mathbf{U}_{\phi_3}(1,2)\text{-}\mathbf{U}_{\phi_4}(2,1)\mathbf{U}_{\phi_5}(1,3)\mathbf{U}_{\phi_6}(3,1)\mathbf{U}_{\omega_2}(1,2)]/z_{N\text{-}6}$. To determine the probability of finding the second CH$_2$–CH$_2$ bond in our N-6 fragment in the ϕ_3 = g$^-$ rotational state, or conformation, we simply divided $[\mathbf{U}_{\omega_1}\mathbf{U}_{\phi_1}\mathbf{U}_{\phi_2}\mathbf{U}_{\phi_3}(g^-)\mathbf{U}_{\phi_4}\mathbf{U}_{\phi_5}\mathbf{U}_{\phi_6}\mathbf{U}_{\omega_2}]$ by $z_{N\text{-}6}$, where $\mathbf{U}_{\phi_3}(g^-)$ is the statistical weight matrix $\mathbf{U}_{\phi_3}$ (see Figure 2) with first and second columns, which correspond to the ϕ_3 = t and g$^+$ conformers, replaced by zeros.

Mobility of Channel Conformers. As a measure of the mobilities of N-6 and E-6 chains confined by cylindrical channels, we attempted to determine the possibility of interconverting between channel conformers without any part of the chain leaving the channel during any step of the interconversion process. As each rotation angle was incremented ($\Delta\phi = 20°$, $\Delta\omega = 20°$ or 30°), the x', y', z' coordinates of each atom in the N-6 and E-6 chain fragments 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

Table I
N-6 Channel Conformers

D, Å	no. of channel conformers	probability of channel conformers	$P(\phi_n$=t) 1	2	3	4	5	6
4.0	0	0						
4.5	9 (1)[a]	0.008	1.0	1.0	1.0	1.0	1.0	1.0
5.0	9 (1)	0.008	1.0	1.0	1.0	1.0	1.0	1.0
5.25	15 (3)	0.011	1.0	0.711	1.0	0.711	1.0	1.0
5.5	35 (5)	0.018	1.0	0.627	0.814	0.627	0.814	1.0
6.0	94 (16)	0.034	1.0	0.427	0.718	0.427	0.718	0.707
7.0	513	0.249	0.590	0.488	0.635	0.636	0.542	0.421
8.0	1318	0.442	0.373	0.556	0.674	0.714	0.553	0.414
9.0	3009	0.750	0.370	0.534	0.685	0.677	0.526	0.386
10.0	4496	0.899	0.387	0.495	0.666	0.682	0.497	0.392
11.0	6065	0.990	0.409	0.468	0.661	0.664	0.468	0.406
12.0	6505	1.0	0.409	0.467	0.660	0.5660	0.467	0.409
free chain	6561	1.0	0.409	0.467	0.660	0.660	0.467	0.409

[a] No. of conformers with different ϕ-bond conformations (see Figure 2).

Table II
E-6 Channel Conformers

D, Å	no. of channel conformers	probability of channel conformers	$P(\phi_n$=t) 1	2	3	4	5	6
4.0	0	0						
4.5	9 (1)[a]	0.008	1.0	1.0	1.0	1.0	1.0	1.0
5.0	9 (1)	0.008	1.0	1.0	1.0	1.0	1.0	1.0
5.25	13 (4)	0.008	1.0	0.994	0.994	0.994	0.994	1.0
5.5	29 (5)	0.014	1.0	0.769	0.769	0.769	0.769	1.0
6.0	127 (36)	0.059	0.701	0.545	0.671	0.671	0.545	0.701
7.0	597	0.248	0.423	0.555	0.660	0.673	0.553	0.437
8.0	1454	0.500	0.405	0.537	0.720	0.714	0.537	0.390
9.0	3197	0.755	0.379	0.533	0.675	0.678	0.533	0.375
10.0	5024	0.940	0.397	0.477	0.677	0.676	0.478	0.396
11.0	6184	0.997	0.409	0.469	0.661	0.661	0.467	0.409
12.0	6501	1.0	0.404	0.467	0.660	0.660	0.467	0.409
free chain	6561	1.0	0.409	0.467	0.660	0.660	0.467	0.409

[a] No. of conformers with different ϕ-bond conformations (see Figure 2).

another channel conformer was selected as the starting conformer and the channel conformer interconversion procedure was repeated. After successfully reaching another channel conformer, 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 N-6 and E-6 are partially characterized in Tables I and II, where their numbers, probabilities, and bond rotation populations are presented for cylinders of various diameter D. 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 D given in Tables I and II reflect the steric requirements of 0.5-Å van der Waals spheres placed on each proton.

Any differences in the numbers of channel conformers found for N-6 and E-6 are directly attributable to the absence of an amide proton and the smaller valence angle at the ester oxygen in E-6. Different numbers of channel conformers and slightly different statistical weights for ω_1 and ω_2 rotations [0.0193 (N-6) vs 0.0147 (E-6)] produce some differences between the probabilities of channel conformers found for N-6 and E-6.

For channels with $D \leq 5.5$ Å the all-trans bond conformer ($\phi_{1,2,3,4,5,6} = 0°$) accounts for at least 40% of all channel conformers found for both polymers. The remaining conformers found to fit in a 5.5-Å cylinder are characterized by the following kink structures: $\phi_{1,2,3,4,5,6}$ = tg$^\pm$tg$^\mp$tt and ttg$^\pm$tg$^\mp$t. Both N-6 and E-6 crystallize[25,26] in the all-trans conformation, which is the most stable conformation for their isolated chains (see Figure 2); however, the CH_2–O bonds in E-6 crystals deviate somewhat from 0°. Once the cylinder is expanded to $D \geq 6.0$ Å other gauche-bond-containing, nonkink N-6 and E-6 conformers, such as those containing adjacent gauche bonds, are found to fit in the channel.

Mobility of N-6 and E-6 Channel Conformers. For channels with $D \leq 5.5$ Å we did not find interconversions between those N-6 and E-6 conformers that fit in a cylinder of this size. Only when the channel diameter was expanded beyond 7.0 Å did we find interconversion between the kink conformers that fit into a D = 5.5-Å cylinder. However, interconversions between the all-trans and kink conformers were not observed even in the expanded cylinder. The inability of N-6 and E-6 conformers to interconvert in cylinders of a size comparable to the channels found in urea and PHTP inclusion compounds with other polymers is similar to the behavior found for PE and POE chains[12] in their urea[26] and PHTP clathrates but stands in marked contrast to the facile interconversion of channel conformers found for *trans*-1,4-polybutadiene[8-12] confined to the channels of its inclusion compound with PHTP.

It therefore seems likely that the aliphatic polyamides and polyesters confined by the channels in inclusion compounds with clathrate hosts like urea[26] and PHTP will not exhibit trans ↔ gauche bond conformational interconversion but be restriced to the all-trans, planar zigzag conformation. Similar behavior has been reported recently[16-18] for bulk, crystalline aliphatic polyamides, where it was found that the all-trans, planar zigzag conformation is retained until the crystals are melted. Though no trans ↔ gauche interconversion of bond conformations was found right up to the melting point, substantial libration about the trans conformation was observed for several of the C–C bonds. The amide nitrogen atoms were observed to be immobile until melting occurred, suggesting retention of interchain hydrogen bonding.

The mobilities of aliphatic polyamide chains in their crystalline phases have usually been interpreted in terms of the effects produced by the anchoring of amide groups through interchain hydrogen bonds. However, in our modeling of the conformations and motions of an isolated N-6 chain in cylindrical channels, we also found the all-trans conformer to be preferred and unable to interconvert into gauche-bond-containing conformers. Because hydrogen bonding of amide groups played no role in our modeling of isolated N-6 chains confined to channels, we suggest that interamide group hydrogen bonding in crystalline aliphatic polyamides may not play as pivotal a role in their chain dynamics as has been suggested. Instead, nondirectional, steric interactions of the van der Waals type probably govern the dynamics of nylons and the polyesters in their crystals.

Summary

We have attempted to model the conformations and motions of aliphatic polyamides and polyesters when isolated and confined in cylindrical channels. For cylinders with diameters similar ($D \leq 5.5$ Å) to the channels found in the urea and PHTP inclusion compounds formed with other polymers, all-trans, planar zigzag, and kink ($g^{\pm}tg^{\mp}$) conformers are found to fit. Because the all-trans conformer is energetically preferred and interconversion between the kink and all-trans conformers is prohibited in channels with $D \leq 7.0$ Å, we suggest that both the aliphatic polyamides and polyesters will assume the all-trans conformation in their inclusion complexes with clathrates, such as urea[26] and PHTP.

Our results, which are based solely upon the steric requirements of polymer chains confined by narrow cylinders, suggest that motions of polyamides in their crystals may also be significantly influenced by interchain steric interactions in addition to the network of interchain hydrogen bonds formed between amide groups. As a consequence, we might expect the motions of crystalline, aliphatic polyamides and polyesters to evidence similarities.

References and Notes

(1) Harris, K. D. M. Ph.D. Thesis, University of Cambridge, 1988. Harris, K. D. M.; Jonsen, P. *Chem. Phys. Lett.* **1989**, *154* (6), 593.
(2) Colombo, A.; Allegra, G. *Macromolecules* **1971**, *4*, 579.
(3) Farina, M. *Inclusion Compounds*; Atwood, J. L., Ed.; Academic Press: New York, 1984; Vol. 3, p 297.
(4) Parrod, J.; Kohler, A. *Compt. Rend.* **1958**, *246*, 1046.
(5) Farina, M.; Natta, G.; Allegra, G.; Loffelholz, M. *J. Polym. Sci., Part C* **1967**, *16*, 2517.
(6) Monobe, K.; Yokoyama, F. *J. Macromol. Sci., Phys. Ed.* **1973**, *B8*, 277.
(7) Bruckner, S.; Sozzani, P. E.; Boeffel, C.; Destri, S.; Di Silvestro, G. *Macromolecules* **1989**, *22*, 607.
(8) Sozzani, P. E.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1989**, *22*, 4225.
(9) Sozzani, P. E.; Behling, R. W.; Schilling, F. C.; Bruckner, S.; Helfand, E.; Bovey, F. A.; Jelinski, L. W. *Macromolecules* **1989**, *22*, 3318.
(10) Schilling, F. C.; Bovey, F. A.; Sozzani, P. E. *Macromolecules*, in press.
(11) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3129.
(12) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3134.
(13) Powell, D. G.; Mathias, L. J. *Macromolecules* **1989**, *22*, 3814.
(14) Okada, A.; Kawasumi, M.; Tajima, I.; Kurauchi, T.; Kamigaito, O. *J. Appl. Polym. Sci.* **1989**, *37*, 1363.
(15) Kubo, K.; Yamanobe, T.; Komoto, T.; Ando, I.; Shiibashi, T. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 929.
(16) Angelo, R. J.; Miura, H.; Gardner, K. H.; Chase, D. B.; English, A. D. *Macromolecules* **1989**, *22*, 117.
(17) Wendoloski, J. J.; Gardner, K. H.; Hirschinger, J.; Miura, H.; English, A. D. *Science* **1990**, *247*, 431.
(18) Mathias, L. J.; Powell, D. G.; Autran, J.-P.; Porter, R. S. *Macromolecules* **1990**, *23*, 963.
(19) Hatfield, G. R.; Glans, J. H.; Hammond, W. B. *Macromolecules* **1990**, *23*, 1654.
(20) Powell, D. G.; Mathias, L. J. *Polym. Commun.* **1990**, *31*, 58.
(21) Powell, D. G.; Mathias, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 669.
(22) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969; Chapters I–V.
(23) Flory, P. J.; Williams, A. D. *J. Polym. Sci., Polym. Phys. Ed.* **1967**, *5*, 417.
(24) Robin, M. B.; Bovey, F. A.; Basch, H. *The Chemistry of the Amides*; Zabicky, J., Ed.; Wiley: New York, 1970.
(25) Mueller, R. P.; Hollenstein, H.; Huber, J. R. *J. Mol. Spectrosc.* **1983**, *100*, 95.
(26) Brisse and Chenite[27] have recently reported the successful formation of inclusion compounds of aliphatic polyesters with urea. In addition, we[28] have DSC evidence that an inclusion compound is formed between urea and poly-ε-caprolactone when they are cosolidified from a common melt.
(27) Brisse, F.; Chenite, A. 33rd IUPAC International Symposium on Macromolecules, July 8–13, 1990, Montreal, Canada.
(28) Gomez, M. A.; Tonelli, A. E., unpublished observations.

Registry No. N-6, 25038-54-4; E-6 (SRU), 25248-42-4; E-6 (homopolymer), 24980-41-4.