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Stereocontrolled Polymerization of Diene Monomers within a Tris(*o*-phenylenedioxy)cyclotriphosphazene Tunnel Clathrate

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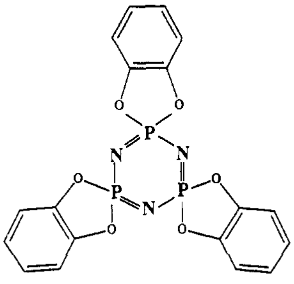
ABSTRACT: The inclusion and polymerization of the diene monomers 2,3-dimethylbutadiene, isoprene, *trans*-piperylene, *trans*-2-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, chloroprene, 1,3-cyclohexadiene, 2,3-dimethylbutadiene/isoprene, isoprene/*trans*-piperylene, and isoprene/butadiene within the tunnels of clathrates formed by tris(*o*-phenylenedioxy)cyclotriphosphazene have been achieved. The polymerizations were accomplished by ^{60}Co γ-irradiation. All the polymers obtained by this technique resulted from 1,4-addition. Specifically, 1,4-*trans*-poly(dimethylbutadiene), 1,4-*trans*-poly(isoprene), isotactic 1,4-*trans*-poly(*trans*-piperylene), isotactic 1,4-*trans*-poly(*trans*-2-methyl-1,3-pentadiene), 1,4-*trans*-poly(4-methyl-1,3-pentadiene), 1,4-*trans*-poly(chloroprene), atactic 1,4-poly(cyclohexadiene), 1,4-*trans*-poly(isoprene/dimethylbutadiene), 1,4-*trans*-poly(isoprene/*trans*-piperylene), and 1,4-*trans*-poly(isoprene/butadiene) were formed. The stereoregularity is explained in terms of monomer packing arrangements in the tunnels.

Introduction

The preparation of new stereoregular polymers is of prime interest in all areas of advanced polymer synthesis. Current and past methods for creating stereoregular polymers have primarily involved the use of organometallic-based catalysts. A drawback to these methods is that they are not applicable to the polymerization of all types of unsaturated monomers. An alternative approach that may be less dependent on monomer type is the use of clathrates as a means for producing stereoregular polymers. The first account of this approach appeared in 1956 in which Clasen[1] reported the polymerization of 2,3-dimethylbutadiene in a thiourea clathrate. This was followed by the work of Brown and White[2,3] with the inclusion and polymerization of various monomers clathrated within urea and thiourea matrices.

Here, we describe an extension of the clathrate-mediated method to provide a route to the selective stereocontrolled synthesis of diene polymers. Previously, we reported that a number of different types of molecules are trapped within the clathrate tunnels of tris(*o*-phenylenedioxy)cyclotriphosphazene (1).[4–11] Earlier work on the ^{60}Co γ-radiation-initiated polymerization of monomers within these tunnels has yielded polymers with enhanced stereoregularity or specific stereochemistry.[10,12] Here, we focus on the polymerization of unsaturated diene monomers and on the copolymers formed from several dienes within the tunnels of the host 1. The NMR characterization of the clathrate-formed polymers was used to monitor the stereochemistry that resulted from polymerization in the clathrate tunnels. A comparison between the products of bulk polymerizations of each monomer and the clathrate-formed polymers was also made.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Previous work in our group and by Wegner and Finter[13] has shown that the polymerization of 1,3-butadiene in host 1 yields only 1,4-*trans*-poly(butadiene).[10] Similarly, work involving thiourea[2] and perhydrotriphenylene (PHTP)[14] as host systems showed that the inclusion polymerization of various dienes yields polymers with only the 1,4-trans structure. Both of these hosts and phosphazene clathrate 1 have tunnel diameters in the region of 5 Å. Hence similarities might be anticipated. The copolymerization of dienes in PHTP to yield copolymers with a 1,4-trans structure has been reported by Farina.[15] The possible formation of 1,4-trans copolymers and homopolymers within the clathrate system 1 was thus of some interest.

In this paper we report the inclusion within the tunnels of crystalline 1 and polymerization of 2,3-dimethylbutadiene, isoprene, *trans*-piperylene, *trans*-2-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, chloroprene, 1,3-cyclohexadiene, isoprene/2,3-dimethylbutadiene, isoprene/butadiene, and isoprene/*trans*-piperylene monomers (Chart 1).

Results and Discussion

2,3-Dimethylbutadiene. The bulk-phase, γ-ray-induced polymerization of 2,3-dimethylbutadiene at 25 °C was carried out as a control as described in the Experimental Section. The bulk polymerization yielded a polymer that contained a mixture of both 1,4-cis and 1,4-trans sequences. This was indicated by the presence of the 1,4-cis addition resonances in the ^{13}C NMR spectrum at 18.60 (CH_3) and 33.54 (CH_2) ppm, together with the 1,4-trans addition resonances at 18.16 (CH_3) and 33.30 (CH_2) ppm.[14] The relative intensities of the methyl peaks for both the cis and trans arrangements indicated the presence of an equal mixture of both cis and trans configurations in the polymer. The molecular weight was estimated to be 3.7×10^3 (45 repeat units). The bulk polymerization of 2,3-dimethylbutadiene was also examined at −78 °C. The resultant polymer possessed essentially the same degree of polymerization and the same

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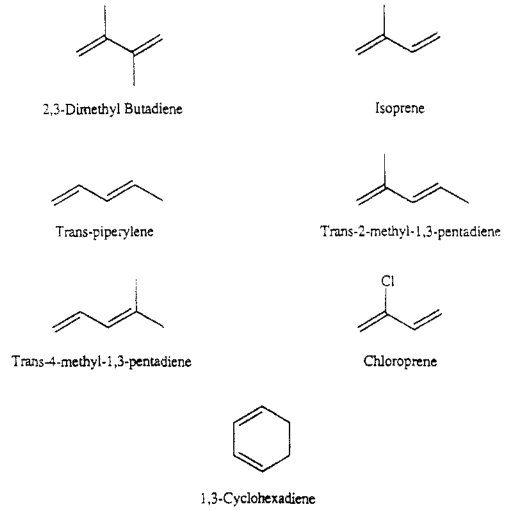
Chart 1



2,3-Dimethyl Butadiene

Isoprene

Trans-piperylene

Trans-2-methyl-1,3-pentadiene

Trans-4-methyl-1,3-pentadiene

Chloroprene

1,3-Cyclohexadiene

stereochemistry as the counterpart prepared at 25 °C.

γ-Ray-induced clathrate polymerization of a 2,3-dimethylbutadiene within the tunnels of 1 yielded 1,4-*trans*-oligo(2,3-dimethylbutadiene). The oligomer structure was established by ^{13}C NMR spectroscopy. Three resonances centered at 18.16 (CH_3), 33.30 (CH_2), and 128.33 (C) ppm indicated the presence of only the 1,4-trans species. The absence of 1,2-addition products for either the bulk or clathrated product was indicated by the absence of 1,2-addition resonances in the unsaturated region of the ^{13}C NMR spectrum. The molecular weight of the clathrate-mediated oligomer was estimated to be in the range of 1.0 × 10^3 (12 monomer units). Polymerization of clathrated 2,3-dimethylbutadiene was also examined at −78 °C. The resultant oligomer possessed essentially the same degree of polymerization and same stereochemistry as the clathrated polymer formed at 25 °C. No noticeable post-polymerization effects could be detected.

Isoprene. The γ-ray-induced polymerization of isoprene monomer in the bulk state yielded a high polymer that contained both 1,4-cis and 1,4-trans addition sequences. The 1,4-cis addition assignment was based on the appearance of a resonance at 22.90 (CH_3) ppm, which is indicative of cis addition. 1,4-Trans addition products were detected by the presence of a resonance at 16.03 (CH_3) ppm.[14] The peak intensities of the methyl substituents indicated that the trans addition predominated. The molecular weight of the polymer was estimated to be 1.4 × 10^5 (2000 repeat units). The polymerization of isoprene in the bulk state at −78 °C yielded a polymer essentially identical to that prepared at 25 °C.

Polymerization of isoprene clathrated within 1 yielded 1,4-*trans*-poly(isoprene) only. The 1,4-trans configuration was assigned based on the ^{13}C NMR spectrum of the isolated polymer. The spectrum of the polymer formed within the clathrate yielded resonances similar to those obtained from inclusion polymerizations carried out in perhydrotriphenylene (PHTP).[14] Thus, the spectrum of 1,4-*trans*-poly(isoprene) consisted of seven peaks at 134.92 (C), 124.19 (CH), 39.77 and 38.52 (CH_2), 28.29 and 26.71 (CH_2), and 16.03 (CH_3) ppm. The two methylene carbon atoms yielded two peaks each at (39.77 and 38.52) and (28.29 and 26.71) ppm, which suggest their presence in different chemical environments.[14] The absence of any 3,4-addition was indicated by the absence of a peak at 42.1 ppm.[16] The molecular weight of the 1,4-*trans*-poly(isoprene) was estimated to be 2.4 × 10^4. This corresponds to a polymer with roughly 350 repeat units. Polymerization of clathrated isoprene at −78 °C yielded a polymer with approximately the same degree of polymerization and the same stereochemistry as the species prepared at 25 °C, with no noticeable postpolymerization effects.

***trans*-Piperylene.** The bulk monomer yielded a polymer that contained a mixture of 1,4-cis and 1,4-trans addition environments. The identification of the cis and trans addition units was based on ^{13}C NMR spectroscopy of the polymer. The resonance at 17.98 (CH_3) ppm is characteristic of 1,4-cis addition, while the peak at 20.05 (CH_3) ppm was derived from 1,4-trans addition.[14] On the basis of the relative intensities of the methyl resonances, 1,4-cis addition appeared to predominate by a ratio of 2 to 1. The bulk polymer was found to have a molecular weight of ca. 5.7 × 10^3 (85 repeat units).

Inclusion and subsequent γ-ray polymerization of *trans*-piperylene in the clathrate formed by 1 yielded 1,4-poly(*trans*-piperylene) with 1,4-trans stereochemistry only. This polymer was identified by ^{13}C NMR spectroscopy. The spectrum of the polymer contained five peaks located at the following resonances: 137.27 (CH), 126.58 (CH), 40.35 (CH_2), 36.90 (CH), and 20.09 (CH_3) ppm. Further NMR analysis of the polymer identified an isotactic 1,4-*trans*-poly(*trans*-piperylene) structure.[14] The presence of 1,2-addition products for either the bulk or clathrated polymer was ruled out based on the absence of a chemical shift at 123.4 ppm. The molecular weight of 1,4-*trans*-poly(*trans*-piperylene) was estimated to be 1.3 × 10^4 (190 repeat units). This represents an increase of 100 additional monomer units over that of the polymer formed in the bulk state. Presumably, orientation of the monomer within the clathrate tunnels allows the formation of the higher molecular weight polymer.

***trans*-2-Methyl-1,3-pentadiene.** The bulk polymerization of *trans*-2-methyl-1,3-pentadiene was carried out as described in the Experimental Section. The polymer formed had a 1,4-trans structure. Further analysis of the ^{13}C NMR spectrum showed that the polymer was atactic in structure. Presumably, the presence of the methyl substituents prevents cis addition and allows randomization of the trans structure. The polymer had a molecular weight of 2.0 × 10^4 (240 monomer units).

The oligomer that resulted from the polymerization of the *trans*-2-methyl-1,3-pentadiene monomer in the clathrate yielded a macromolecule with the stereochemistry of 1,4-*trans*-poly(*trans*-2-methyl-1,3-pentadiene). The peaks in the ^{13}C NMR spectrum of the polymer are similar to those previously reported for the polymer formed in PHTP, which yielded an isotactic polymer structure.[14] The peaks appeared at 132.07 (CH), 130.66 (C), 47.18 (CH_2), 29.64 (CH), 19.95 (CH_3), and 14.95 (CH_3) ppm and were assigned to isotactic 1,4-*trans*-poly(*trans*-2-methyl-1,3-pentadiene). The absence of any 1,2-addition products was indicated by the absence of the characteristic NMR peak at 110 ppm.[17] The molecular weight was estimated to be 1 × 10^3 (12 monomer units).

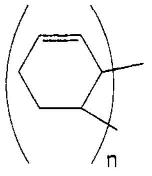
4-Methyl-1,3-pentadiene. The polymerization of 4-methyl-1,3-pentadiene in the bulk state by γ-radiation yielded a polymer consisting entirely of 1,4-trans addition units. Formation of a 1,4-cis addition polymer would involve considerable steric hindrance, and it is presumed that this favors the trans species. The molecular weight of the polymer was found to be 3.8 × 10^4 (470 monomer units).

The polymer recovered from the clathration polymerization of 4-methyl-1,3-pentadiene also possessed the stereochemistry of 1,4-*trans*-poly(4-methyl-1,3-pentadiene). The stereochemistry of the polymer was assigned based on ^{13}C NMR spectroscopy of the polymer and the appearance of five signals located at 142.63 (CH), 122.50 (CH), 46.40 (CH_2), 36.08 (C), and 27.20 (CH_3) ppm. Thus, the stereochemistry generated by the clathrate polymerization was identical to that formed in the bulk state. The existence of 1,2-addition was ruled out by the absence in the ^{13}C NMR spectrum of a peak at 127.4 ppm.[18] The molecular weight of the 1,4-*trans*-poly(4-methylpentadiene) formed under clathration conditions, 3.6×10^3 (45 monomer units), was ca. 1 order of magnitude less than for the bulk polymer.

Chloroprene. Polymerization of this monomer in the bulk state yielded a polymer formed by 1,4-trans addition only. The structure was determined by FT-IR spectroscopy of the polymer and by the appearance of an absorption peak at 1660 cm^{-1}.[19] No prior report could be found of the bulk homopolymerization of chloroprene by γ-radiation or of the assignment of any ^{13}C NMR shifts for 1,4-*trans*-poly(chloroprene). The ^{13}C NMR spectrum of 1,4-*trans*-poly(chloroprene) contained a total of six resonances. The shifts reported for 1,4-*trans*-poly(isoprene) were used as a starting point to estimate the carbon shift assignments for 1,4-*trans*-poly(chloroprene). The following shifts were assigned for this polymer: 134.90 (C), 124.01 (CH), 38.27 and 37.57 (CH_2), and 27.64 and 26.76 (CH_2) ppm. As noted previously for 1,4-*trans*-poly(isoprene), the two methylene carbon resonances are split into two signals representing their presence in different chemical environments. Presumably, in this case, the split is caused by the influence of the chlorine atoms on the methylene units. The 1,4-cis, 1,2, or 3,4 structures were ruled out by the absence of any peaks in the IR spectrum at 1520, 925, and 883 cm^{-1}, respectively. The molecular weight of the polymer was estimated to be 8.4×10^4 (950 repeat units) by GPC analysis.

The polymer isolated from the clathrate possessed the same stereochemistry as that of the bulk polymer but was of lower molecular weight. This assignment was again based on FT-IR analysis of the resultant polymer and the appearance of a peak at 1660 cm^{-1}.[19] The ^{13}C NMR spectrum of the clathration-generated polymer showed the same chemical shifts as did the bulk polymer. Other structures were ruled out based on the arguments stated previously for the bulk-phase-generated poly(chloroprene). The molecular weight was found to be ca. 2.9×10^3 (33 monomer units).

1,3-Cyclohexadiene. A mixture of both 1,2- and 1,4-addition products was obtained by the γ-ray-induced polymerization of 1,3-cyclohexadiene in the bulk state (**2** and **3**). The assignment of 1,2-addition structure was based on the presence of signals at 25.36 and 127.77 ppm in the ^{13}C NMR spectrum. These correspond to the unsubstituted α-CH_2 unit of cyclohexene and to the adjacent vinyl groups.[20] By using proton integration, it was estimated that 1,2-addition was favored 4:3 over 1,4-addition. GPC analysis of the polymer gave a molecular weight estimate of 4.5×10^3 (55 monomer units).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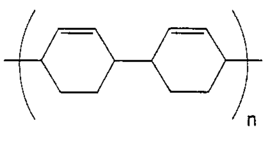
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The inclusion polymerization of 1,3-cyclohexadiene yielded a polymer that possessed a stereochemistry formed entirely by 1,4-addition. No ^{13}C NMR peaks associated with 1,2-addition were found. The peaks at 130.17 and 129.89 ppm represent the olefinic carbon atoms, and the four resonances at 38.46, 38.27, 38.18, and 37.96 ppm are from the α-carbon atom in different tacticities for atactic 1,4-poly(cyclohexadiene).[20] The four signals represent erythrodiisotactic, threodiisotactic, disyndiotactic, and isosyndiotactic. The relative intensities of the α-carbon resonances indicate that the polymer is essentially atactic. The molecular weight of 6.7×10^3 (85 monomer units) is slightly higher than that of the bulk polymer.

Isoprene/2,3-Dimethylbutadiene (Iso/DMB). A 50/50 (v/v) homogeneous mixture of Iso/DMB (corresponding to a 33/38 molar ratio of Iso/DMB) was polymerized in the bulk state to yield a polymer that contained both 1,4-cis and 1,4-trans units. It was not possible by ^{13}C NMR spectroscopy to determine the preferential mode of addition due to the large number of resonances that overlapped and appeared within the saturated carbon region of the spectrum. A GPC analysis of the polymer suggested a molecular weight of 5.0×10^4 (660 repeating units).

Irradiation of the clathrated 50/50 (v/v) mixture of Iso/DMB by γ-rays yielded 1,4-*trans*-poly(isoprene-*co*-2,3-dimethylbutadiene). Gas chromatography of the clathrated monomer adduct showed a preferential inclusion of 2,3-dimethylbutadiene over that of isoprene by a factor of 3 to 1. The stereochemistry of the resultant polymer was determined by ^{13}C NMR. On the basis of previous work by Farina,[15] in which 1,4-*trans*-poly(Iso/DMB) was obtained in PHTP by γ-radiation, it was possible to assign 12 of the 14 peaks observed. Peaks assigned to the 1,4-trans addition products occurred at 134.90, 129.29, 123.48, 39.77, 38.46, 38.22, 34.80, 33.75, 26.71, 18.66, 18.16, and 16.04 ppm. The peak assignments and their respective couplings can be found in the paper by Farina.[15] No 1,2-addition product was detected for either the bulk or internal polymers. The molecular weight was estimated at 1.6×10^3 (20 repeating units).

Isoprene/Butadiene (Iso/But). A 1/1 (mol/mol) mixture of Iso/But was polymerized in the bulk state to give a copolymer containing both 1,4-cis and 1,4-trans addition sequences. The assignment of the 1,4-cis addition was based on the resonances at 32.72, 31.92, 28.11, and 25.50 ppm, which have been assigned previously to the 1,4-cis copolymer of Iso/But.[21] Two resonances were detected at 114.12 and 113.77 ppm, which have been attributed to 1,2-addition products. This was the first detection of 1,2-addition in the polymerization of the diene monomers examined in this study. Previous work in our group that involved the polymerization of butadiene in the bulk state by γ-radiation showed a small amount of 1,2-addition in the polymer. Because no 1,2-addition is observed in the polymerization of isoprene, and the shifts reported here for the 1,2-addition coincided with those for 1,2-butadiene polymer, the 1,2-addition species was attributed to 1,2-butadiene sequences. On the basis of relative peak intensities present in the spectrum, it was concluded that the 1,4-trans addition species was the predominant form of the copolymer. The bulk polymer was found to have a molecular weight of ca. 3.0×10^3 (50 repeat units).

Gas chromatographic analysis of the clathrated isoprene/butadiene monomers showed that no selective inclusion of one monomer over the other had occurred. Irradiation of the clathrated comonomer mixture gave 1,4-*trans*-poly(isoprene-*co*-butadiene). The ^{13}C NMR spectrum of the isolated oligomer yielded a spectrum similar to that obtained by Lobach,[21] with confirmation of the 1,4-trans polymer structure indicated by the resonances at 39.74 and 16.01 ppm. The spectrum suggested that no 1,2-

Table 1. Characterization of the Polymers

monomer	physical state	stereochemistry	mol wt (PDI)
2,3-dimethyl-1,3-butadiene	bulk	1,4-cis and 1,4-trans	3.7×10^3 (2.8)
2,3-dimethyl-1,3-butadiene	clathrated	1,4-trans	1.0×10^3 (2.0)
isoprene	bulk	1,4-cis and 1,4-trans	1.4×10^5 (1.4)
isoprene	clathrated	1,4-trans	2.4×10^4 (2.9)
trans-piperylene	bulk	1,4-cis and 1,4-trans	5.7×10^3 (1.7)
trans-piperylene	clathrated	1,4-trans	8.3×10^4 (1.2)
trans-2-methyl-1,3-pentadiene	bulk	atactic 1,4-trans	2.0×10^4 (2.1)
trans-2-methyl-1,3-pentadiene	clathrated	isotactic 1,4-trans	1.0×10^3 (1.5)
4-methyl-1,3-pentadiene	bulk	1,4-trans	3.8×10^4 (1.5)
4-methyl-1,3-pentadiene	clathrated	1,4-trans	3.6×10^3 (1.8)
chloroprene	bulk	1,4-trans	8.4×10^4 (1.9)
chloroprene	clathrated	1,4-trans	2.9×10^3 (1.4)
1,3-cyclohexadiene	bulk	1,2 and 1,4	4.5×10^3 (1.5)
1,3-cyclohexadiene	clathrated	atactic 1,4	6.7×10^3 (1.7)
isoprene/2,3-dimethylbutadiene	bulk	1,4-cis and 1,4-trans	5.0×10^4 (1.6)
isoprene/2,3-dimethylbutadiene	clathrated	1,4-trans	1.6×10^3 (2.9)
isoprene/butadiene	bulk	1,2; 1,4-cis and 1,4-trans	3.0×10^3 (1.8)
isoprene/butadiene	clathrated	1,4-trans	1.0×10^3 (1.4)
isoprene/*trans*-piperylene	bulk	1,4-cis and 1,4-trans	3.9×10^3 (1.5)
isoprene/*trans*-piperylene	clathrated	1,4-trans	4.0×10^3 (2.1)

addition product was present (in contrast to the bulk polymerization) and that the oligomer was entirely 1,4-*trans*-poly(Iso/But) with an approximate molecular weight of 1.0×10^3 (15 repeat units).

Isoprene/*trans*-Piperylene. A 1:1 (mol/mol) ratio mixture of isoprene and *trans*-piperylene was polymerized in the bulk state to give a polymer that contained both 1,4-cis and 1,4-trans structures. The cis and trans configurations were assigned on the basis of the characteristic peaks associated with each region of the polymer. Trans addition was based on the peaks at 16.01 (CH_3) and 39.74 (CH_2) ppm for the isoprene segment and at 20.08 (CH_3) ppm for the *trans*-piperylene segments. Cis addition was assigned based on peaks at 23.46 (CH_3) and 32.86 (CH_2) ppm for isoprene addition and 17.96 (CH_3) ppm for *trans*-piperylene addition. GPC analysis of the polymer suggested a molecular weight of ca. 3.9×10^3 (55 repeat units).

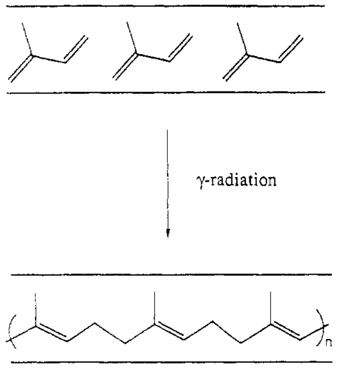
The ^{13}C NMR spectrum of the clathrate copolymer formed from isoprene/*trans*-piperylene was similar to that reported previously by Farina for the copolymerization of the monomers within PHTP.[14] The reported shifts for the copolymer were all within 1 ppm of those found for the polymer formed in 1. The molecular weight was ca. 4.0×10^3 (55 repeat units). The presence of other addition modes was ruled out by the absence of their peaks in the ^{13}C NMR spectrum.

Conclusions

The use of 1 as a template system for producing stereoregular polymers has been expanded to the field of diene monomer–clathrate polymerization. Irradiation of diene adducts within the tunnels of 1 yielded stereoregular polymers or oligomers that have exclusively a 1,4-trans structure, except in the case of 1,3-cyclohexadiene, which yielded atactic 1,4-addition products. The formation of 1,4-trans stereochemistry by inclusion polymerization can be viewed as a result of stereoregular packing of the diene monomers in the tunnels of the clathrate 1. A possible packing arrangement sequence that would yield 1,4-trans polymer is shown in Scheme 1.

In the case of 1,3-cyclohexadiene, the absence of any 1,2-addition product from the polymerization can be rationalized in terms of the steric constraints imposed by the clathrate tunnel diameter. Any 1,2-addition to the ring would produce an oligomer or polymer that would be too large to fit within the tunnel of the clathrate. Thus 1,4-addition may be preferred because of steric constraints imposed by the tunnel diameter and perhaps not by the monomer packing arrangement within the tunnels. This provides a method for the formation of exclusively 1,4-poly(cyclohexadiene).

Scheme 1



The molecular weights of the clathrate-generated polymers fell in the range from 1.0×10^3 for 1,4-*trans*-poly(2,3-dimethylbutadiene) to 2.4×10^4 for 1,4-*trans*-poly(isoprene). Variations in molecular weight detected by GPC analysis were also found in the previous polymerizations of various monomers in 1.[10] The polymers formed in this work tend to possess polydispersities that are typically not related to those of the corresponding polymers formed during bulk polymerization. These variations in polymer molecular weights and polydispersities can possibly be attributed to the effect of unfilled sites between the included monomers or to variations in tunnel lengths as a result of different crystal dimensions. Both of these possibilities would lead to variations in polymer chain length and to higher polydispersities. The yields of the clathrate-mediated polymers ranged between 30 and 50%. Logical correlations between polymer yield, polydispersity, and monomer size could not be found. Variations in polymerization temperature did not affect the degree of polymerization or the stereochemistry of the resulting polymers. For example, the polymerization of isoprene and 2,3-dimethylbutadiene in 1 at −78 °C with a 4-Mrad radiation dose yielded polymers essentially identical to those prepared at 25 °C.

Thus, the clathrate system of 1 provides an environment that is favorable for the exclusive formation of 1,4-*trans*-polydienes and 1,4-poly(cyclohexadiene).[22] It is also possible to produce copolymers with a 1,4-trans structure in clathrate systems derived from 1. This added ability to produce copolymers with a 1,4-trans addition structure offers a route to polymers with unique structures and new physical properties by selective variations in the initial monomer ratio. However, the main advantage for using clathrate systems based on 1 is the access it provides to 1,4-trans addition products at ambient temperatures.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) was recrystallized from heptane, followed by vacuum sublimation (0.002 mmHg, 40 °C). Catechol (Aldrich) was purified by vacuum sublimation (0.002 mmHg, 40 °C). Triethylamine (J. T. Baker) was dried over and distilled from calcium hydride. Tetrahydrofuran (Omnisolv) was dried and distilled from sodium benzophenone. Benzene (Aldrich), 1,3-butadiene (Aldrich), and methylene chloride were used as received. The monomers, 2,3-dimethylbutadiene (Aldrich), isoprene (Aldrich, Fluka), *trans*-piperylene (Aldrich), *trans*-2-methyl-1,3-pentadiene (Aldrich), 1,3-cyclohexadiene (Aldrich), chloroprene (Alfa), and 4-methyl-1,3-pentadiene (Fluka), were vacuum distilled.

Synthesis of Tris(*o*-phenylenedioxy)cyclotriphosphazene (1). The following procedure represents an improvement over previous methods.[23,24] A solution of catechol (19.0 g, 0.173 mol) and triethylamine (48.1 mL, 34.9 g, 0.345 mol) in THF (60 mL) was added dropwise to a stirred solution of $(NPCl_2)_3$ (20.0 g, 0.058 mol) in THF (450 mL). Dropwise addition took place over a 2-h period under an inert atmosphere of argon. The solution was stirred for a further 20 h at room temperature. The mixture was then filtered through a sintered glass funnel and washed with ~5% hydrochloric acid (200 mL), followed by distilled water (600 mL). The white solid was vacuum dried for 24 h at 25 °C, recrystallized from benzene, and sublimed (0.002 mmHg, 180 °C) to give crystals of 1 (25.2 g, 95.2% yield), mp 244–245 °C.

^{60}Co γ-Irradiations. Samples were placed in a thick-walled glass ampule and subjected to two freeze–pump–thaw cycles. The samples were then sealed under vacuum, placed in an aluminum-jacketed Dewar flask, and irradiated with 4 Mrad (dose rate 180 krad/h) of ^{60}Co γ-radiation at 25 or −78 °C (acetone/CO_2) as specified. The irradiation of the ampules was carried out at the Breazeale Nuclear Reactor facility at The Pennsylvania State University.

Equipment. ^{13}C NMR spectra were recorded using a Bruker WM-360 spectrometer operating at 90.0 MHz. The solvent used for all the polymers was $CDCl_3$ (MSD Isotopes). The chemical shifts were referenced to $CDCl_3$. Molecular weights were determined using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1037A refractive index detector and a Polymer Laboratories PL Gel 10-μm column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF. The PL Gel column was calibrated with narrow molecular weight polystyrene standards. Infrared spectra were obtained using a Perkin-Elmer 1710 FT-IR interfaced with a Perkin-Elmer 1700 data station.

Polymerizations. (a) 2,3-Dimethylbutadiene. Tris(*o*-phenylenedioxy)cyclotriphosphazene (1) was vacuum sublimed (0.002 mmHg, 180 °C) to remove any residual solvent present in the clathrate tunnels. Twice-sublimed 1 (5 g) was placed in a thick-walled ampule, and 2,3-dimethylbutadiene (10 mL) was added to form a slurry. The mixture was then allowed to stand for 24 h at 25 °C. Excess monomer external to 1 was removed in vacuo. The ampule was then degassed by two freeze–pump–thaw cycles. The ampule was flame sealed and irradiated with 4 Mrad of ^{60}Co γ-radiation at 25 °C. This procedure was followed for all the polymerizations unless stated otherwise.[25]

After irradiation, unreacted monomer was removed *in vacuo*, and any polymer formed on the surface of the crystallites was removed by washing with benzene using a mechanical shaker (24 h). The filtered clathrate was then placed in refluxing benzene until all of the clathrate was dissolved (48 h) to extract the "internal" poly(2,3-dimethylbutadiene). Benzene was then removed from this extract by rotatory evaporation. The polymer was subsequently dissolved in methylene chloride and was isolated by solvent evaporation; yield 0.103 g.[24]

(b) Isoprene. The inclusion of isoprene in 1 was carried out in a manner similar to that described previously for (a). After irradiation, unreacted monomer was removed *in vacuo*. Polymer formed on the surface of the clathrate crystals was removed by washing in methylene chloride using a mechanical shaker (24 h). The clathrate was recovered by filtration and was added to refluxing benzene (48 h) to remove the clathrated poly(isoprene). The benzene was removed by rotatory evaporation, and the clathrate-generated polymer was extracted using methylene chloride. The poly(isoprene) was recovered by evaporation of the methylene chloride; yield 0.108 g.

(c) *trans*-Piperylene, *trans*-2-Methyl-1,3-pentadiene, and 1,3-Cyclohexadiene. The inclusion of the monomers in 1 was carried out in a manner similar to that described for 2,3-dimethylbutadiene. After irradiation, any unreacted monomer was removed *in vacuo*. Polymer external to the clathrate was subsequently removed by washing with THF for 24 h. The solution was filtered to isolate the clathrate, which was subsequently placed in refluxing benzene (48 h) to extract the clathrated polymer. Removal of the benzene by rotatory evaporation yielded the polymer. Extraction of the residue with THF and evaporation allowed isolation of the polymer; yield for the polymers respectively 0.124, 0.177, and 0.201 g.

(d) 4-Methyl-1,3-pentadiene. 4-Methyl-1,3-pentadiene was included in 1 using the method described above. The sample was irradiated. Unreacted monomer was removed, and any polymer adhering to the clathrate surface was dissolved by washing in THF (24 h). The clathrate was recovered and added to benzene (800 mL, 50 °C) to release the internal polymer. The benzene was removed, and the poly(4-methyl-1,3-pentadiene) was extracted with THF; yield 0.126 g.

(e) Chloroprene. The monomer adduct was formed in the manner described previously. The sample was irradiated in the dark and was maintained in low-light conditions during isolation to prevent any possible photo-cross-linking. Unreacted monomer was removed *in vacuo*, and the surface of the crystals was washed with THF to remove any polymer formed external to the tunnels. The crystals were filtered off and added to 700 mL of benzene (50 °C), and the mixture was stirred for 24 h to dissolve the crystals and release the polymer. The benzene was removed, leaving behind the polymer and host. Subsequent extraction with THF yielded the host-freed polymer; yield 0.132 g.

(f) Isoprene/2,3-Dimethylbutadiene. A homogeneous 50/50 (v/v) mixture of 2,3-dimethylbutadiene/isoprene was used to form an adduct of 1 in a similar manner to that described previously. The sample was irradiated with γ-rays. Following irradiation, the unreacted monomer was removed *in vacuo*, and any "external" polymer was removed by washing with methylene chloride using a mechanical shaker (24 h). The "internal" polymer was then extracted by dissolving the filtered clathrate in refluxing benzene (48 h). The benzene was removed by rotatory evaporation, and the clathrate-recovered polymer was extracted using methylene chloride; yield 0.024 g.

(g) Isoprene/Butadiene (Iso/But). Equimolar amounts of isoprene and butadiene were mixed in the presence of 1 to form an adduct. The temperature of the Iso/But mixture was kept between −55 and −78 °C to ensure that the butadiene monomer remained in the liquid state. The inclusion adduct of 1 was then irradiated with 4 Mrad of γ-radiation at −78 °C. After irradiation, unreacted monomer was removed *in vacuo* and the clathrate was washed with THF (24 h). The clathrate was isolated by filtration and then placed in refluxing benzene (48 h) to release the polymer. The internal polymer was then recovered by extraction and evaporation of the THF to give poly(isoprene/butadiene); yield 0.071 g.

(h) Isoprene/*trans*-Piperylene. An equal 50/50 (mol/mol) mixture of isoprene and *trans*-piperylene was mixed and added to 1 to form an adduct as described previously. The sample was then irradiated. Following irradiation, the unreacted monomer was removed *in vacuo*, and any external polymer was removed by washing with THF using a mechanical shaker (24 h). The filtered clathrate was placed in refluxing benzene (48 h) to extract the internal polymer. The benzene was removed by rotary evaporation, and the clathrate polymer was extracted using THF; yield 0.069 g.

(i) Bulk, Unclathrated Polymerizations. Glass ampules were charged with the monomers and were subjected to two freeze–thaw degassing cycles before being sealed. The bulk monomers were irradiated at temperatures and dosages that correspond to the clathrated monomers. After irradiation unreacted monomer was removed *in vacuo* and the polymer was characterized by solution-state ^{13}C NMR spectroscopy.

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References and Notes

(1) Clasen, H. *Z. Elecktrochem.* **1956**, *60*, 982.
(2) Brown, J. F.; White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5671.
(3) White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5698.
(4) Allcock, H. R. *Acc. Chem. Res.* **1978**, *11*, 81.
(5) Allcock, H. R.; Siegel, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 5140.
(6) Siegel, L. A.; van der Hende, J. H. *J. Chem. Soc. A* **1967**, 817.
(7) Allcock, H. R.; Teeter-Stein, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 49.
(8) Allcock, H. R.; Teeter-Stein, M. J.; Bissel, E. C. *J. Am. Chem. Soc.* **1974**, *96*, 4795.
(9) Allcock, H. R.; Allen, R. W.; Bissell, E. C.; Smeltz, L. A.; Teeter, M. *J. Am. Chem. Soc.* **1976**, *98*, 5120.
(10) Allcock, H. R.; Ferrar, W. T.; Levin, M. L. *Macromolecules* **1982**, *15*, 697.
(11) Allcock, H. R. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 1.
(12) Allcock, H. R.; Levin, M. L. *Macromolecules* **1985**, *18*, 1324.
(13) Wegner, G.; Finter, J. *Makromol. Chem.* **1979**, *180*, 1093.
(14) Sozzani, P.; Silvestro, G. D.; Grassi, M.; Farina, M. *Macromolecules* **1984**, *17*, 2532.
(15) Sozzani, P.; Silvestro, G. D.; Grassi, M.; Farina, M. *Macromolecules* **1984**, *17*, 2538.
(16) Gronski, W.; Murayama, N.; Cantow, H. *Polymer* **1976**, *17*, 358.
(17) Cabassi, F.; Porzio, W.; Ricci, G. *Makromol. Chem.* **1988**, *189*, 2135.
(18) Aambelli, A.; Ammendola, P.; Proto, A. *Macromolecules* **1989**, *22*, 2126.
(19) Garret, R. R.; Hargreaves, H. C. A., II; Robinson, D. N. *J. Macromol. Sci., Chem.* **1970**, *A4* (8), 1679.
(20) Shraby, Z.; Martan, M.; Jagur-Grodzinski, J. *Macromolecules* **1982**, *15*, 1167.
(21) Lobach, M. I.; Poletayeva, I. A.; Khatchaturov, A. S.; Druz, N. N.; Kormer, V. A. *Polymer* **1977**, *18*, 1196.
(22) Occasionally, traces of the phosphazene host were detected in the ^{13}C NMR of the polymers but these were removed by standard polymer purification techniques. No attempt was made to identify the end groups for the polymers studied.
(23) Allcock, H. R. *J. Am. Chem. Soc.* **1964**, *86*, 2591.
(24) Allcock, H. R.; Walsh, E. J. *Inorg. Chem.* **1971**, *10*, 1643.
(25) Inclusion of the monomers within the clathrate resulted in a general decrease of the melting point of the host by at least 10 °C. Polymers formed within the clathrate raised and broadened the melting point of the host by at least 10 °C.