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# Synthesis of Purine- and Pyrimidine-Substituted Heptadienes. The Stereochemistry of Cyclization and Cyclopolymerization Products

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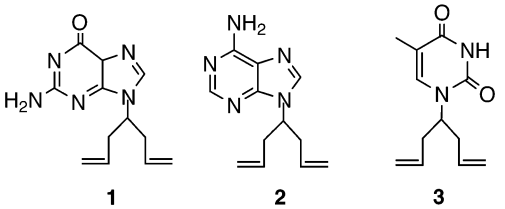
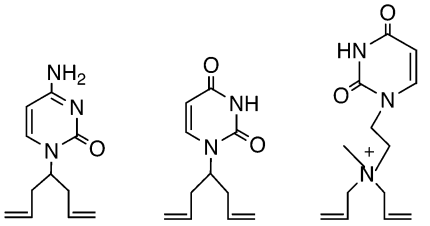
A series of 1,6-heptadienes, substituted in the 4 position with nucleic acid bases **1**−**6**, have been synthesized via Mitsunobu condensations. Guanine, adenine, thymine, and uracil derivatives can be prepared directly by coupling the protected base with 1,6-heptadien-4-ol (**7**). However, coupling protected cytosine and **7** gives an O-alkylated product. Thus, the cytosine derivative must be prepared from the uracil-substituted heptadienes via the triazole. The free-radical addition of $CCl_4$ and $BrCCl_3$ to these adducts was investigated. In all cases, both 1:1 and 1:2 adducts were obtained. The 1:1 adduct was identified as the cyclized product of the initially formed 5-hexen-1-yl radical. The cyclization takes place in a stereospecific manner, with only one of the four possible diastereomers resulting. NMR studies indicate that all substituents are cis in this product. In the case of the addition of $CCl_4$ to the uracil-substituted heptadiene, this conclusion was confirmed by an X-ray structure determination of the isolated cyclized product. The free-radical-initiated cyclocopolymerizations of **1**−**6** with $SO_2$ gave 1:1 copolymers with cis-linked five-membered rings. Two-dimensional NMR studies on poly(**2**−$SO_2$) showed predominately the cis−syn isomer while poly(**6**−$SO_2$) has an approximately equal amount of cis−syn and cis−anti isomers.

## Introduction

Interest in the chemistry of carbocyclic nucleotides and polymeric nucleic acid analogues has increased the need to develop synthetic routes to precursors of these species.[1] The 1,6-heptadienes **1**−**6** with a nucleic acid base substituted in the 4 position represent an interesting set of such molecules.

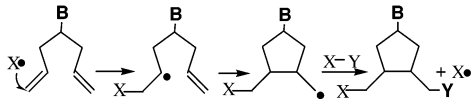


**1** **2** **3**



**4** **5** **6**

In these compounds, free-radical addition to the diene system followed by cyclization of the resultant 5-hexenyl radical has the potential of generating a variety of carbocyclic nucleotide analogues (eq 1). Although there



(1)

have been numerous studies of cyclizations of 5-hexenyl radicals derived from 1,6-heptadiene and from other sources,[2] we know of none where a nucleic acid base is substituted in the 4 position of the 1,6-heptadiene.

Modification of the process in eq 1 such that the intermediate cyclopentylmethyl radical is allowed to participate in a cyclocopolymerization may produce nucleic acid analogues. Because it is well-known that 1,6-heptadienes undergo a cyclocopolymerization with sulfur dioxide,[3] the reaction in eq 2 is a potential route to polysulfone nucleic acid analogues.

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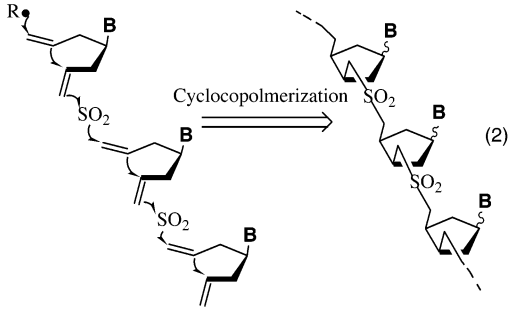



B = Adenine, Thymine, Guanine, Uracil, Cytosine

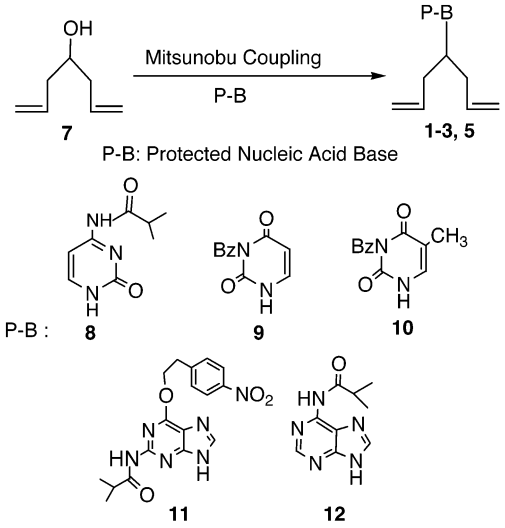
Polysulfone DNA has generated considerable interest recently.[4] Sulfones are nonionic, achiral, isoelectric analogues of phosphate diesters, which are stable to both chemical and biochemical degradation. Crystal structures have shown that dimethylene sulfone-bridged ribonucleotides can form A-type, Watson−Crick-paired duplexes[5] and, at elevated temperatures, extended single-stranded structures with only three torsion angles significantly different from A-type duplex RNA.[6] Therefore, it would be interesting to generate the polysulfone nucleic acid analogues by polymerization.

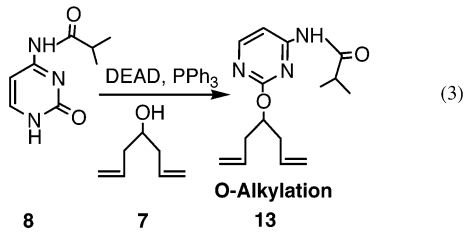
In this paper, we report the cyclization and copolymerization of $SO_2$ with 1,6-heptadienes substituted in the 4 position (**1**−**5**) with nucleic acid bases to generate carbocyclic analogues of nucleosides and polysulfone nucleic acid analogues. Unlike previously reported polysulfone nucleic acid analogues, those shown in eq 2 will have the methylenes at the 3 and 4 positions cis to one another.[7] Although this weakens the analogy with nucleic acids, these products are expected to have interesting properties.

## Result and Discussion

**Synthesis of Dienes.** Mitsunobu conditions[8] were used to synthesize the 1,6-heptadienes **1**−**5** as shown in Scheme 1. Thus, the protected guanine,[9] adenine,[10] thymine,[11] uracil,[11] and cytosine[11] were coupled with 1,6-heptadien-4-ol (**7**) under Mitsunobu conditions and subsequent deprotection. The guanine, adenine, thymine, and uracil derivatives can be prepared directly by coupling the protected base with **7**. However, coupling the protected cytosine, **8**, and **7** gave predominantly the O-alkylated product as shown in eq 3. The regiochemistry

**SCHEME 1. Synthesis of Dienes by Mitsunobu Coupling**




(3)

of **13** was indicated by the downfield shift (75.1 ppm) of the carbon attached to the $O_2$ position of cytosine as compared to the literature values of 50−60 ppm for carbons on the $N_1$ position in the corresponding N-alkylated compounds.[12,13] Cytosine protected at $N_4$ usually acts as an ambient nucleophile in Mitsunobu reactions with cyclopentanols, producing either the N- or O-alkylated product or a mixture of both, depending on the stereochemistry of the substituents on the carbocyclic ring.[14] Although the O-alkylated product is thermodynamically stable, the N-alkylated product is often the kinetically controlled product.[15] The distribution of the products in the Mitsunobu coupling of cytosines is usually explained as arising from the inherent nucleophilicities of the $N_1$ and $O_2$ in the attacking bases and the steric hindrance in the competing $S_N2$ transition states. This steric hindrance is caused by an interaction either between the incoming deprotonated base and the substrate or between the oxyphosphonium leaving group and the substituents on the substrate. In most cases, the $N_1$

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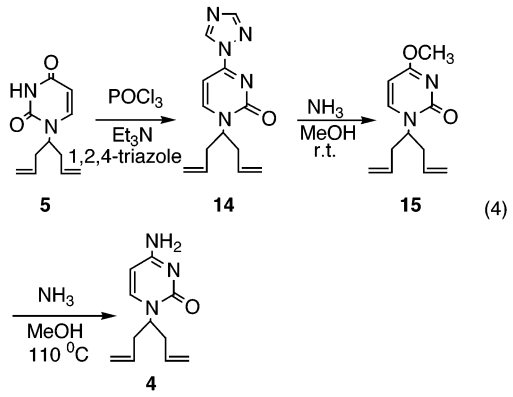
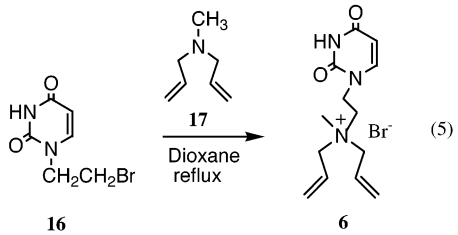
is more nucleophilic than the $O_2$ and the kinetically controlled product predominates. In the present case, steric effects may favor the O-alkylation product.

Because **4** could not be generated directly by Mitsunobu coupling, we first prepared the uracil derivative 4-[(1*H*,3*H*)-pyrimidine-2,4-dion-1-yl]-1,6-heptadiene (**5**) and converted it to **4** by established procedures (eq 4).[16]




Treatment of **5** with $POCl_3$ and 1,2,4-triazole in acetonitrile gave the triazole **14**. The attempted ammonolysis of the triazole with a methanolic ammonia solution at room temperature gave 1-(1,6-heptadien-4-yl)-4-methoxypyrimidin-2(1*H*)-one (**15**). Ammonolysis was achieved by heating **15** with methanolic ammonia at 110 °C to give **4** in 51% overall yield from **5**. A comparison of the $^{13}C$ NMR spectra of **4** with that of **13** indicates the formation of a C−O bond (O-alkylation) in the Mitsunobu reaction of the latter. Thus, the signal of $C_4$ in **13** is at 75.1 ppm, while the corresponding carbon signal in **4** is at 54.9 ppm.

The water-soluble heptadiene derivative **6** was synthesized by reacting 1-(2-bromoethyl)uracil (**16**)[17] with methyldiallylamine (**17**) in refluxing dioxane (eq 5).




**Free-Radical Cyclization of Nucleic Acid Base-Substituted Heptadienes.** To assess the potential of these substituted heptadienes to undergo free-radical cyclopolymerization, we have investigated the addition of $CCl_4$ to **5**. This reaction has the possibility of generating diastereomers **18**−**21**. Molecular mechanics calculations (MM2-calculated steric energies are shown with the structures)[18] gave the expected trends in energies with the two trans 3,4 diastereomers, **20** and **21**, more stable products than the two cis 3,4 diastereomers, **18** and **19**.

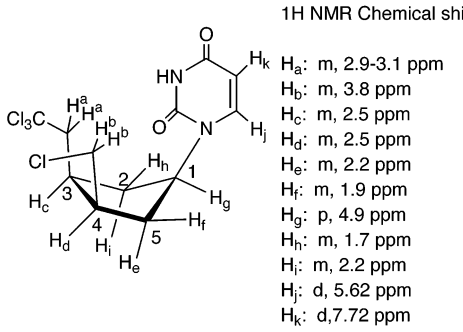
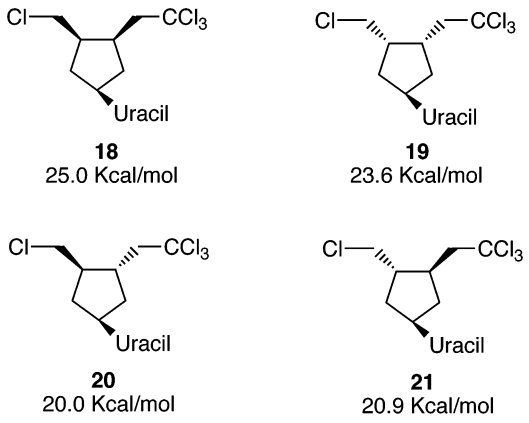


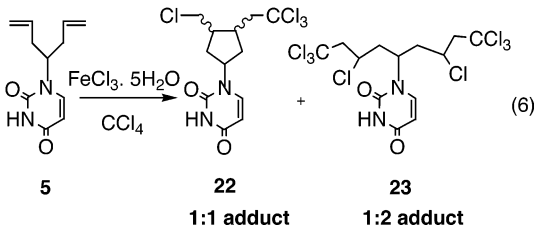

**FIGURE 1.** $^1H$ NMR chemical shifts of **22**.

Because this is a kinetically controlled reaction, there is no reason to expect that these energies will reflect the experimental product ratios.




8

The free-radical cyclization of **5** was investigated using the redox-transfer reaction of $Fe^{2+}/Fe^{3+}$ and $CCl_4$ to generate the trichloromethyl radical (eq 6).[19] The $^{13}C$ NMR spectrum of the product mixture showed only two peaks for the $CCl_3$ carbons, indicating the formation of two major products. These were shown to be the cyclized 1:1 adduct **22** and the open-chain 1:2 adduct **23**. **22** precipitated in 28% yield when the crude product was triturated with chloroform. **23**, contaminated with some **22**, was collected in 61% yield. The fact that the 1:2 adduct was formed suggests that Cl abstraction from $CCl_4$ competes with cyclization in the 5-hexen-1-yl radical **24**.




Surprisingly, only one isomer of the cyclization product **22** was detected in this reaction. Decoupled $^1H$ NMR spectra were helpful in assigning the $^1H$ NMR chemical shifts of this isomer that are listed in Figure 1.

(16) Divakar, K. J.; Reese, C. B. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1171−1176.

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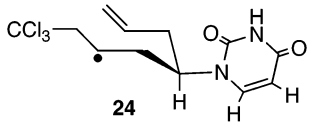
(19) Asscher, M.; Vofsi, D. *Org. Synth.* **1965**, *45*, 104−107.

Difference NOE (DNOE) was utilized to assign the stereochemistry of **22**. Thus, the irradiation of $H_b$ resulted in a 2% enhancement of $H_a$, indicating that the substituents at $C_3$ and $C_4$ are cis to one another. The same irradiation resulted in a 1% enhancement of $H_j$, indicating that the uracil ring is cis to the $CH_2Cl$ group. Other DNOE enhancements included as Supporting Information are consistent with an all-cis structure for **22**. The structure of **22** was confirmed by X-ray crystallography.

The generation of only one cyclized product in this reaction may be rationalized by assuming a transition-state geometry similar to that of **24** in which the uracil assumes a pseudoequatorial position, as has been established,[7] leading to the all-cis product.




**24**

Preliminary studies of the AIBN-catalyzed addition of $BrCCl_3$ to **2** and **3** lead to the isolation of a single 1:1 adduct and a 1:2 adduct in each case. Although the gross structure of these adducts was established by $^1H$ NMR and mass spectrometry, the stereochemistry has not been determined.

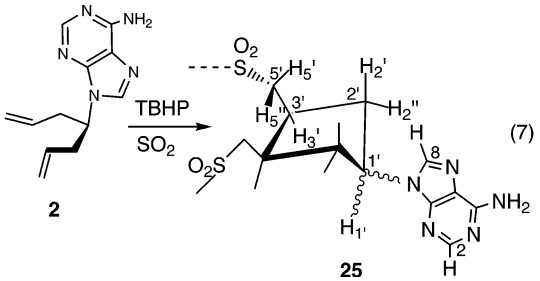
**Cyclocopolymerization of Dienes with $SO_2$.** Attempts to carry out homocyclopolymerizations of dienes **1**−**5** were unsuccessful, probably as a result of the termination by abstraction of allylic hydrogens on the diene. Allylic monomers often exhibit such degradative chain-transfer behavior.[20] To circumvent this problem, we have investigated the copolymerization of our substituted heptadienes with $SO_2$. In this case, the cyclopentylmethyl radical, rather than abstracting an allylic hydrogen, will react with $SO_2$ to generate a sulfinyl radical. The weak S−H bond in sulfinic acids precludes H abstraction, and the sulfinyl radical adds to another diene to continue the copolymerization. Attempts to copolymerize **1**−**5** with $SO_2$ at 81 °C with AIBN as an initiator were only successful in the presence of high concentrations of the monomer (>0.3 M). We attribute this concentration effect on the elevated-temperature polymerizations to the fact that, as in many addition polymerizations, there is a ceiling temperature at which the rate of addition of the monomer to the growing polymer chain is equal to the rate of the reverse reaction.[21] As this ceiling temperature is approached, high concentrations of the monomer are required to drive the polymerization. This effect has been observed in other copolymerizations involving $SO_2$.[22]

To avoid the complications associated with the elevated-temperature polymerizations, we have used *tert*-butyl hydroperoxide to initiate the copolymerizations at 20 °C in acetonitrile.[23] Although dienes **1**−**6** could all be copolymerized to generate copolymers with satisfactory NMR spectral properties, only the copolymers of **2** and **6** were examined in detail, and these will be discussed.

**TABLE 1. $^1H$ and $^{13}C$ NMR Spectra of 25**

| $^1H$ | $\delta$ (ppm) | $^{13}C$ | $\delta$ (ppm) |
|---|---|---|---|
| $H_2'$ | 1.95 | $C_2'$ | 36.9 |
| $H_2''$ | 2.36 | | |
| $H_5$ and $H_5'$ | 3.17 | $C_5$ and $C_5'$ | 55.0 |
| $H_3'$ | 2.60 | $C_3'$ | 35.2 |
| $H_1'$ | 4.82 | $C_2'$ | 60.1 |
| $H_2$ | 8.95 | $C_1$ | 148.9 |
| $H_8$ | 8.21 | $C_8$ | 143.2 |

In analogy with the well-known stereochemistry of 5-hexenyl radical cyclizations[7] and with that of other cyclopolymerizations,[24,25] we believe that the two methylene groups linking the cyclopentane rings in the copolymers are cis to one another as shown in eq 7 for copolymer **25**.




**2** **25** (7)

The $^{13}C$ NMR spectrum of **25** in Table 1 shows six signals for the proton-attached carbons that were assigned by a DEPT experiment. A $^{13}C-^1H$ heteroscalar correlation (HETCOR) experiment was used to assign the protons attached to these carbons (Table 1). To determine the stereochemistry of the adenine ring with respect to the two $-CH_2SO_2-$ groups, the NOESY spectrum was obtained (Supporting Information). This spectrum allows us to identify $H_2'$ by means of its large cross-peak with the unresolved $H_5'$ and $H_5''$. The fact that there is a large NOE cross-peak between $H_1'$ and $H_2''$ indicates that the adenine ring is cis to $H_2'$ and thus cis to $H_5'$ and $H_5''$.[26]

Although these considerations clearly indicate that this copolymer consists predominately of cis-linked rings in which the adenine is cis to the backbone, the $^{13}C$ dimension in the HETCOR spectrum of **25** shows the splitting of $C_1'$ and $C_2'$, indicating the presence of at least one other isomer. The NOESY spectrum of **25** taken at high sensitivity (Supporting Information) clearly shows two other minor correlations for $H_1'$, indicating the presence of two additional stereoisomeric linkages. Although the resolution of these NMR experiments does not allow us to assign the stereochemistry of these linkages, it is reasonable to assume that they correspond to cis-linked rings with the base trans and to trans-linked rings (eq 8). Integration of the $H_1'$ protons for the three linkages allows us to estimate that 65% of the linkages in **25** are cis with the adenine cis and that the other

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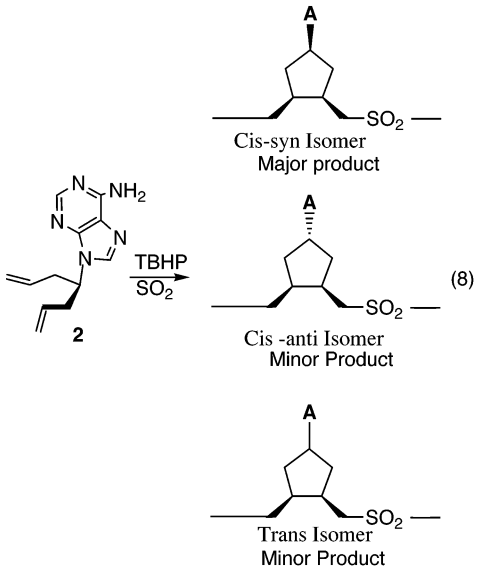
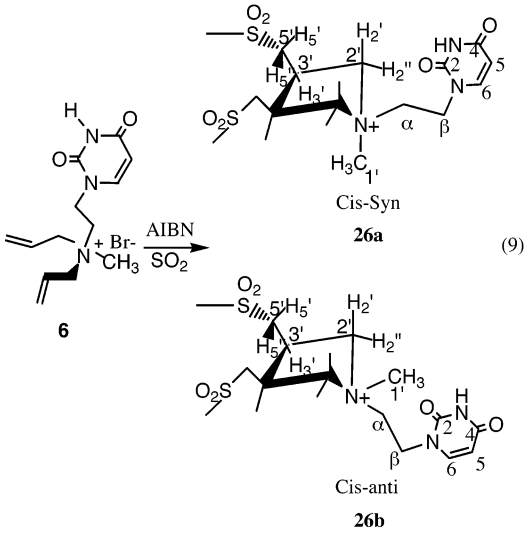



(8)

stereoisomeric linkages are 19.4 and 15.6%. The predominance of an all-cis link in copolymer **25** is analogous with the free-radical cyclization of **5** in which the all-cis product is isolated.

Unlike dienes **1**−**5**, the copolymerization of **6** with $SO_2$ can be conveniently carried out at 81 °C with AIBN initiation to generate the copolymer **26** as shown in eq 9.[27] If **26** has the expected cis-linked pyrrolidine rings




(9)

as do the homopolymers of diallylammonium salts,[28] we may expect that the steric demands of the groups attached to the quaternary nitrogen (methylene and methyl) would be similar and that the linkages **26a** and **26b** would be present in the copolymer. The $^{13}C$ NMR spectra of **26**, listed in Table 2, confirm this expectation, showing two signals for $C_1'$, C$\alpha$, C$\beta$, $C_3'$, $C_5$, and $C_6$. A $^1H$-detected heteronuclear multiple-quantum coherence experiment allows us to assign the protons in **26**, whose chemical shifts are listed in Table 2. The two $H_1'$, H$\alpha$, H$\beta$, and $H_3'$ signals correspond to those of the two isomeric linkages. In principle, a NOESY study could determine which of these signals corresponds to $H_2'$ and which to $H_2''$. However, resolution problems make this determination problematic.

**TABLE 2. $^1H$ and $^{13}C$ NMR Spectra of 26a and 26b**

| $^1H$ | **26a** $\delta$ (ppm) | **26b** $\delta$ (ppm) | $^{13}C$ | **26a/26b** $\delta$ (ppm) |
|---|---|---|---|---|
| $H_2'$ and $H_2''$ | 3.76, 4.18 | 3.77, 4.31 | $C_2'$ | 67.5 (br) |
| $H_5'$ and $H_5''$ | 3.86, 3.62 | 3.86, 3.62 | $C_5'$ | 51.8 (br) |
| $H_3'$ | 3.65 | 3.59 | $C_3'$ | 32.3, 31.6 |
| $H_1'$ | 3.36 | 3.42 | $C_1'$ | 49.4, 51.7 |
| H$\alpha$ | 3.94 | 3.86 | C$\alpha$ | 59.5, 63.1 |
| H$\beta$ | 4.40 | 4.37 | C$\beta$ | 42.8, 43.1 |
| $H_5$ | 5.95 | 5.95 | $C_5$ | 102.6, 102.8 |
| $H_6$ | 7.75 | 7.75 | $C_6$ | 146.4, 146.3 |

Although we are unable to assign NMR signals to a particular linkage, the integration of the two signals for $H_1'$ gave a ratio of isomeric linkages of 1.2:1. Thus, **26** is formed with less stereoselectivity than is **25**. Possible reasons for this reduced stereoselectivity include less difference in the steric demand of the groups attached to the 4 position on the heptadiene and the fact that the polymerization of **6** is carried out at 81 °C as compared to 20 °C for **2**.

## Conclusions

These studies demonstrate that 1,6-heptadienes substituted in the 4 position with a nucleic acid base can be conveniently synthesized via Mitsunobo condensations. The free-radical cyclization of the adenine-substituted diene generates a carbocyclic nucleoside analogue in which all three substitutents are cis. The copolymerization of these dienes with $SO_2$ generates copolymers with cis-linked cyclopentanes in the backbone. Although the fact that both the free-radical cyclization products and the copolymers have cis links in the 3′,4′ position diminishes the biological relevance of these species, they may exhibit interesting self-binding and replication properties. These possibilities are currently under study.

## Experimental Section

The NMR spectral measurements for poly(**1**−, **2**−, **3**−, **4**−, and **5**−$SO_2$) were determined in 85:15 $D_2O/D_2SO_4$ with TMS as the external standard. For poly(**6**−$SO_2$), the solvent was $D_2O$ with $H_2O$ as the internal standard.

**Materials.** 1,6-Heptadien-4-ol (**7**),[29] $N^6$-isobutyrylcytosine (**8**),[11] $^3N$-benzoyluracil (**9**),[11] $^3N$-benzoylthymine (**10**),[11] $N^2$-isobutyryl-$O^6$-[2-(*p*-nitrophenyl)ethyl]guanine (**11**),[9] $N^6$-isobutyryladenine (**12**),[10] and 1-(2-bromoethyl)uracil (**16**)[17] were prepared according to literature procedures.

**General Procedure for Mitsunobu Condensations.** A 500-mL flask was charged with protected base (1 equiv), **7** (1.2 equiv), triphenylphosphine (1 equiv), and dioxane (300 mL). A solution of diethyldiazodicarboxylate (1 equiv) in dioxane (100 mL) was added dropwise under a nitrogen stream over 0.5 h. The reaction was stirred at room temperature overnight to yield a clear solution. The solvent was removed, and the residue was purified by column chromatography (9:1 $CH_2Cl_2$/$CH_3COCH_3$) to give a white solid. For the condensation products of **9**, **10**, and **12** with **7**, the deprotection was carried out with sodium methoxide. For the condensation product of

(27) For an explanation for the lack of degradative chain transfer on the monomer **6**, see: Kabanov, V. A.; Topchiev, D. A.; Nazhmetdinova, G. T. *Vysokomol. Soedin., Ser. B* **1984**, *26* (1), 51−53.

(28) Lancaster, J.; Baccei, L.; Panzer, H. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 549−554.

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**11**, the 2-(*p*-nitrophenyl)ethyl group was first removed by DBU,[8] followed by ammonolysis to remove the isobutyl group.

**4-(Guanin-9-yl)-1,6-heptadiene (1):** $^1$H NMR (250 MHz) $\delta$ 2.57 (m, 4 H), 4.37 (p, 1 H), 4.96 (m, 4 H), 5.58 (m, 2 H), 7.75 (s, 1 H), 10.55 ($NH_2$, br); $^{13}$C NMR (250 MHz) $\delta$ 38.01, 53.45, 116.50, 117.93, 134.16, 136.13, 151.24, 153.23, 156.86; MS (EI) *m*/*z* (relative intensity) 245 ($M^+$, 29.16), 204 (57.83), 151 (100), 109 (59.85), 41 (55.75). HRMS calcd for $C_{12}H_{15}N_5O_1$, 245.1277; found, 245.1271. 36.5% from **11** and **7**.

**4-(6-Amino-9*H*-purin-9-yl)-1,6-heptadiene (2):** $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 2.73 (m, 4 H), 4.65 (m, 1 H), 5.0 (m, 4 H), 5.6 (m, 2 H), 6.6 (br s, 2 H), 7.79 (s, 1 H), 8.35 (s, 1 H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 38.4, 55.4, 118.0, 119.9, 133.0, 139.2, 150.1, 152.7, 155.9; MS (VG 7070E, CI) *m*/*z* (relative intensity) 230 ($M^+$, 100), 215 (6.9), 204 (22.3). HRMS (CI, $M^+$) calcd for $C_{12}H_{15}N_5$, 230.1405; found, 230.1407. 33.2% from **12** and **7**.

**4-[(1*H*,3*H*)-5-Methylpyrimidine-2,4-dion-1-yl]-1,6-heptadiene (3):** $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 1.93 (s, 3 H), 2.43 (m, 4 H), 4.72 (m, 1 H), 5.06 (m, 4 H), 5.7 (m, 2 H), 6.92 (s, 1 H), 9.3 (br s, 1 H); $^{13}$C NMR (250 MHz, DMSO-$d_6$) $\delta$ 12.6, 37.8, 54.7, 110.6, 118.9, 133, 136.6, 151.5, 163.7; MS (EI) *m*/*z* (relative intensity) 220 ($M^+$, 4.18), 179 (66.64), 136 (100), 127 (15.29), 109 (7.35). HRMS calcd for $C_{12}H_{16}N_2O_2$, 220.1212; found, 220.1216. 22.5% from **10** and **7**.

**4-[(1*H*,3*H*)-Pyrimidine-2,4-dion-1-yl]-1,6-heptadiene (5):** $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 2.3−2.5 (m, 4 H), 4.75 (p, 1 H), 5.0−5.12 (m, 4 H), 5.6−5.75 (m, 2 H), 5.72 (d, 1 H), 7.12 (d, 1 H), 7.79 (s, 1 H), 8.35 (s, 1 H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 37.75, 54.96, 102.15, 119.2, 132.7, 141.1, 151.4, 163.4; MS (EI) *m*/*z* (relative intensity) 206 ($M^+$, 5), 165 (76), 122 (100), 113 (13), 95 (41.5). HRMS (EI, $M^+$) *m*/*e* calcd for $C_{11}H_{14}N_2O_2$, 206.1055; found, 206.1056. 46% from **9** and **7**.

**2-(1,6-Heptadien-4-yl)-*O*$^2$-isobutyrylcytosine (13):** $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 1.20 (d, 6 H), 2.41 (m, 4 H), 2.58 (m, 1 H), 4.98 (m, 2 H), 5.16 (m, 1 H), 5.76 (m, 4 H), 7.72 (d, 1 H), 8.26 (br s, 1 H), 8.31 (d, 1 H); $^{13}$C NMR (250 MHz, $CDCl_3$) $\delta$ 19.1, 36.3, 37.5, 75.1, 103.9, 117.6, 133.5, 159.9, 160.4, 164.2, 176.4; MS (EI) *m*/*z* (relative intensity) 276 ($M^+$, 6.47), 235 (53.26), 181 (100), 165 (42.22), 150 (63.03). HRMS calcd for $C_{15}H_{21}O_2N_5$, 275.1634; found, 275.1631.

**4-(1,2,4-Triazol-1-yl)-1-(1,6-heptadien-4-yl)pyrimidin-2(1*H*)-one (14).** Triethylamine (1.16 mL, 8.36 mmol) was added dropwise to a stirred, cooled (ice−water bath) mixture of 1,2,4-triazole (603.4 mg, 8.74 mmol), phosphoryl chloride (0.17 mL, 1.87 mmol), and acetonitrile (20 mL). To the resulting mixture was added a solution of **5** (0.2 g, 0.97 mmol) in acetonitrile (30 mL), and the reaction mixture was stirred at room temperature overnight. Triethylamine (0.74 mL, 5.26 mmol) and water (0.19 mL, 10.5 mmol) were then added. After 10 min, the solvent was evaporated under reduced pressure. The residue was partitioned between chloroform (50 mL) and saturated aqueous sodium hydrogen carbonate (30 mL). The organic layer was separated and the aqueous layer extracted with chloroform (2 × 30 mL). The combined organic layers were dried ($MgSO_4$), and the residue was purified by column chromatography (9:1 $CH_2Cl_2$/acetone) to yield a white solid (0.189 g, 76%): $^1$H NMR (250 MHz) $\delta$ 2.56 (m, 4 H), 5.04−5.13 (m, 5 H), 5.69 (m, 2 H), 7.05 (d, 1 H), 7.89 (d, 1 H), 8.14 (s, 1 H), 9.28 (s, 1 H); $^{13}$C NMR (250 MHz) $\delta$ 37.69, 57.31, 94.43, 119.7, 132.48, 143.1, 147.98, 154.04, 155.53, 158.46; MS (ES) *m*/*z* (relative intensity) 257 ($M^+$, 3.81), 94 (75.63), 79 (100), 53 (54.12), 39 (45.46), 28 (31.22). HRMS calcd for $C_{13}H_{15}N_5O_1$, 257.1277; found, 257.1283.

**1-(1,6-Heptadien-4-yl)-4-methoxypyrimidin-2(1*H*)-one (15)**. Aqueous ammonia (0.30 g) was added to a solution of **14** (0.14 g, 0.55 mmol) in dioxane (10 mL) at room temperature. After 6 h, the reaction mixture was concentrated under reduced pressure and the residue dissolved in methanolic ammonia (half-saturated at 0 °C, 16.5 mL). After 16 h, the solution was evaporated to dryness. The residue was purified by column chromatography (9:1 $CH_2Cl_2$/acetone) and gave **15** as a white solid (78 mg, 75%): $^1$H NMR (250 MHz) $\delta$ 2.56 (m, 4 H), 4.04 (s, 3 H), 5.04 (m, 1 H), 5.19 (m, 4 H), 5.74 (m, 2 H), 5.99 (d, 2 H), 7.43 (d, 2 H); $^{13}$C NMR (250 MHz) $\delta$ 37.79, 54.27, 55.59, 95.30, 118.93, 133.10, 143.79, 156.95, 170.80; MS (EI) *m*/*z* (relative intensity) 220 ($M^+$, 6.85), 179 (48.98), 147 (22.70), 127 (100), 79 (75.31), 41 (44.37). HRMS calcd for $C_{12}H_{16}N_2O_2$, 220.1211; found, 220.1206.

**4-(Cytosin-1-yl)-1,6-heptadiene (4).** A 50-mL high-pressure reaction vessel was charged with **15** (0.7 g, 3.18 mmol) and 30 mL of a saturated methanolic ammonia solution. The vessel was sealed and heated at 110 °C for 48 h. The solvent was removed and the residue purified by column chromatography (8:2 $CH_2Cl_2$/acetone) to give **4** (0.58 g, 90%): $^1$H NMR (250 MHz) $\delta$ 2.43 (m, 4 H), 4.82 (m, 1 H), 5.04 (m, 2 H), 5.65 (m, 4 H), 5.93 (d, 1 H), 7.15 (d, 1 H); $^{13}$C NMR (250 MHz) $\delta$ 37.85, 54.97 (br), 95.14, 118.47, 133.48, 141.71, 157.20, 165.46; MS (EI) *m*/*z* (relative intensity) 205 ($M^+$, 5.41), 164 (54.92), 121 (19.59), 112 (100), 94 (43.78), 79 (61.83), 41 (30.38). HRMS calcd for $C_{11}H_{15}O_1N_3$, 205.1215; found, 205.1217.

**[2-(Uracil-1-yl)ethyl]methyldiallylammonium Bromide (6).** A mixture of **16** (2.2 g, 0.01 mol) and **17** (2.8 g, 0.025 mol) in dioxane (40 mL) was refluxed overnight. After the removal of the solvent, the residue was washed with diethyl ether and recrystallized from ethanol to give 2.88 g (87%) of **6** as colorless crystals: $^1$H NMR ($D_2O$/dioxane, 250 MHz) $\delta$ 2.92 (s, 3 H), 3.35−3.41 (m, 2 H), 3.81 (d, $J$ = 7.2 Hz, 4 H), 4.07−4.13 (m, 2 H), 5.52−5.66 (m, 5 H), 5.69−5.95 (m, 2 H), 7.43 (d, $J$ = 7.9 Hz, 1 H); $^{13}$C NMR ($D_2O$/dioxane, 62.9 MHz) $\delta$ 42.1, 47.8, 57.0, 64.6, 102.6, 123.8, 129.7, 146.6, 151.9, 166.5; MS (ES) *m*/*z* (relative intensity) 250 (M − Br, 100).

**Free-Radical Cyclization of 4-(6-Amino-9*H*-purin-9-yl)-1,6-heptadiene (2) with $BrCCl_3$ and AIBN.** A 50-mL round-bottom flask was charged with **2** (0.5 g, 2.18 mmol), AIBN (0.043 g, 0.217 mmol), and bromotrichloromethane (8.84 mL, 108.89 mmol). The flask was purged with nitrogen gas and heated at 70 °C for 16 h. The solvent was evaporated under reduced pressure, and diethyl ether was added to dissolve the brownish residue. Upon standing overnight, a white powder precipitated and was identified as the 1:1 adduct (0.1 g, 13%): $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ 2−3.3 (m, 8 H), 4.28 (d, 1 H), 4.89 (d, 1 H), 5.22 (m, 1 H), 8.4 (s, 1 H), 8.72 (s, 1 H), 9.2 (br d, 2 H); $^{13}$C NMR (250 MHz, DMSO-$d_6$) $\delta$ 35.97 (d), 37.3 (t), 54.3 (d), 54.7 (d), 58.9 (t), 100.5 (d), 120.4 (d), 139.8 (s), 141.1 (s), 148.8 (d), 156.6 (s); MS (CI) *m*/*z* (relative intensity) 348 (M + 2 − Br, 2.5), 346 (M − Br, 1.9), 312 (15.3), 310 (17.8), 244 (15.9), 242 (19.6), 136 (100); MS (EI) *m*/*z* (relative intensity) 393 (M + 4 − HBr, 0.41), 391 (M + 2 − HBr, 1.08), 389 (M − HBr, 0.61), 136 (59.86), 135 (100). The mother liquor was evaporated under reduced pressure to give 0.72 g of crude mixture (71%), where the major product was identified as the 1:2 adduct: MS (CI) *m*/*z* (relative intensity) 635 (M + 14, 0.4), 633 (M + 12, 0.8), 631 (M + 10, 3.9), 629 (M + 8, 12.6), 627 (M + 6, 22.8), 625 (M + 4, 26.7), 623 (M + 2, 15.7), 621 ($M^+$, 4.1), 188 (5.4), 162 (16), 136 (100), 135 (26.4).

**Free-Radical Cyclization of 4-[(1*H*,3*H*)-Pyrimidine-2,4-dion-1-yl]-1,6-heptadiene (5) with $CCl_4$ by Redox Transfer.** A 10-mL round-bottom flask was charged with **5** (1.0 g, 4.85 mmol), benzoin (0.1 g, 0.47 mmol), $FeCl_3 \cdot 6H_2O$ (0.1 g, 0.37 mmol), $CCl_4$ (2.5 mL, 25.8 mmol), acetonitrile (1.0 mL, 18.9 mmol), and $Et_2NH_2Cl$ (0.05 g, 0.46 mmol). The flask was freeze thawed, degassed twice, purged with nitrogen gas, and heated at 80 °C for 22 h. Chloroform (10 mL) was added, and the mixture was washed with aqueous HCl (10%, 10 mL), dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure to give a mixture of products. One isomer was crystallized from methanol (0.5 g, 28.6%), and the mother liquor was evaporated under reduced pressure to give 1.07 g of crude mixture (61%). The crystalline product was identified as the 1:1 adduct **22**: $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ 1.84 (m, 1 H), 1.99 (q, 1 H), 2.36 (m, 2 H), 2.59 (m, 1 H), 2.68 (m, 1 H), 3.04 (m, 1 H), 3.78 (m, 2 H), 4.82 (p, 1 H), 5.65 (d, 1 H), 7.48 (d, 1 H), 11.11 (br s, 1 H); $^{13}$C NMR (250 MHz, DMSO-$d_6$) $\delta$ 33.19 (d), 36.47 (t), 33.59 (d), 40.8 (d),

47 (t), 54.37 (t), 55 (d), 100 (s), 102.4 (d), 141.34 (d), 151.2 (s), 163.5 (s); MS (EI) *m*/*z* (relative intensity) 360 (M + 2, 0.85), 358 ($M^+$, 0.69), 325 (0.82), 323 (M − Cl, 0.83), 113 (100), 112 (56.89); HRMS (EI, $M^+$) *m*/*e* calcd for $C_{12}H_{14}N_2O_2Cl_4$, 357.9809; found, 357.9808. Crystals were obtained by crystallizing the 1:1 adduct from dioxane. The major product in the crude mixture was identified as the 1:2 adduct **23**: $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ 1.84 (m, 1 H), 1.99 (q, 1 H), 2.4 (m, 4 H), 3.76 (m, 2 H), 4.38 (m, 1 H), 5.18 (d, 1 H), 8.5 (d, 1 H); $^{13}$C NMR (250 MHz, DMSO-$d_6$) $\delta$ 39.4, 41.3, 54.1, 59.2, 96.2, 101.4, 142.6.

**Free-Radical Cyclization of 4-[(1*H*,3*H*)-5-Methylpyrimidine-2,4-dion-1-yl]-1,6-heptadiene (3) with $BrCCl_3$ by Redox Transfer**. A 50-mL round-bottom flask was charged with **3** (6.35 g, 28.8 mmol), benzoin (0.127 g, 0.6 mmol), $FeCl_3 \cdot 6H_2O$ (0.18 g, 0.67 mmol), $BrCCl_3$ (4.5 mL, 45.7 mmol), acetonitrile (3.0 mL, 56.7 mmol), and $Et_2NH_2Cl$ (0.1 g, 45.7 mmol). The flask was freeze thawed, degassed twice, purged with nitrogen gas, and heated at 80 °C for 4 days. Chloroform (5 mL) was added, and the mixture was washed with aqueous hydrochloric acid (10%, 3 mL), dried with anhydrous magnesium sulfate, and filtered. The solvent was evaporated under reduced pressure to give a mixture of products. One isomer was crystallized from methanol (2.72 g, 23%) and was identified as the 1:1 cyclized product: $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ 1.7 (m, 1 H), 1.79 (s, 3 H), 1.96 (q, 1 H), 2.2 (m, 2 H), 2.5 (m, 1 H), 2.6 (m, 1 H), 2.9−3.2 (m, 2 H), 3.7 (d, 2 H), 4.73 (p, 1 H), 7.6 (s, 1 H), 11.2 (br s, 1 H); $^{13}$C NMR (250 MHz, DMSO-$d_6$) $\delta$ 11.97 (q), 34.6 (t), 35.4 (t), 37.25 (t), 37.5 (d), 41.5 (d), 53.7 (t), 54.4 (d), 99.95 (s), 109.0 (d), 137.8 (s), 150.76 (s), 163.6 (s); MS (EI) *m*/*z* (relative intensity) 422 (M + 6, 0.14), 420 (M + 4, 0.61), 418 (M + 2, 0.88), 416 ($M^+$, 0.42), 127 (27.89), 126 (100). The mother liquor was evaporated under reduced pressure to yield the 1:2 adduct contaminated with some 1:1 adduct: $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ 1.72 (s, 3 H), 2.3−2.5 (m, 2 H), 3.3−3.5 (m, 1 H), 4.0 (m, 1 H), 4.3 (m, 2 H), 7.25 (s, 1 H), 11.0 (br s, 1 H); $^{13}$C NMR (250 MHz, DMSO-$d_6$) $\delta$ 11.67 (q), 97.3 (s), 107.5 (d), 137.6 (s), 151.3 (s), 164.8 (s); MS (EI) *m*/*z* (relative intensity) 620 ($M^{+8}$, 0.12), 618 ($M^{+6}$, 0.18), 616 ($M^{+4}$, 0.24), 614 ($M^{+2}$, 0.13), 126 (100), 55 (83.79).

**General Procedure for the Copolymerization of Dienes 1−5 with $SO_2$.** The monomers **1**−**5** (0.873 mmol) and the initiator (TBHP, 4.74 mg, 0.043 mmol) were placed in a long-stemmed glass tube. Acetonitrile was added as the solvent to maintain the monomer concentration at 0.1 M. The tube was attached to a vacuum line, and sulfur dioxide (55.87 mg, 0.873 mmol) was distilled in at 77 K. The tube was then degassed and sealed off. The reaction vessel was placed at −23 °C ($CCl_4$−liquid $N_2$ slurry) for 24 h. The solvent was evaporated and the residue washed with methanol to remove the monomer, giving the polymer as an insoluble residue. The molecular weight of the polymer was not measured. The poly(**1**−, **2**−, **3**−, **4**−, and **5**−$SO_2$) were slightly soluble in DMSO and soluble in $H_2SO_4$.

**Poly[4-(adenin-9-yl)-1,6-heptadiene−$SO_2$] (25):** $^1$H NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 1.95, 2.36, 2.60, 3.17, 4.82, 8.21, 8.95; $^{13}$C NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 35.2, 36.9, 55.0, 60.1, 143.2, 148.9; IR (KBr) 3101, 1699, 1284, 1137 cm$^{-1}$. 70% yield.

**Poly[4-(guanin-9-yl)-1,6-heptadiene−$SO_2$]:** $^1$H NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 1.23, 1.77, 2.43, 2.82, 2.94, 3.17, 3.65, 4.45, 7.75, 8.49; IR (KBr) 1140, 1290, 1403, 1690, 3143 cm$^{-1}$. 40% yield. Because poly(**5**−$SO_2$) has a very low solubility in any common organic solvent or acidic or basic aqueous solution, the $^{13}$C NMR spectrum was not measured.

**Poly[4-(thymin-1-yl)-1,6-heptadiene−$SO_2$]:** $^1$H NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 1.80, 2.27, 2.62, 3.12, 4.05, 4.42, 7.74; $^{13}$C NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 11.9, 35.2, 36.9, 55.0, 60.1, 109, 137.9, 150.7, 163.3; IR (KBr) 1137, 1284, 1403, 1684, 3143 cm$^{-1}$. 64% yield.

**Poly[4-(cytosin-1-yl)-1,6-heptadiene−$SO_2$]:** $^1$H NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 1.60, 2.05, 2.53, 3.06, 4.35, 5.88, 7.44; $^{13}$C NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 31.1, 32.25, 52.4, 58.7, 95.1, 146.1; IR (KBr) 1120, 1280, 1542, 1679, 2350, 3103 cm$^{-1}$. 74% yield.

**Poly[4-(uracil-1-yl)-1,6-heptadiene−$SO_2$]:** $^1$H NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 1.70, 2.28, 2.60, 3.24, 3.66, 4.43, 6.23, 7.88; $^{13}$C NMR (400 MHz, 85:15 $D_2O/D_2SO_4$) $\delta$ 36.7, 38.15, 52.3, 55.38, 105.5, 146.20, 161.2, 176.9; IR (KBr) 1137, 1284, 1403, 1684, 3143 cm$^{-1}$. 48% yield.

**Poly{[2-(uracil-1-yl)ethyl]methyldiallylammonium-$SO_2$} Bromide (26).** A solution of **6** (0.11 g, 0.33 mmol), AIBN (1.64 mg, 0.01 mmol), and 3.3 mL of methanol was placed in the long-stemmed glass tube, which was attached to a vacuum line, and sulfur dioxide (21.1 mg, 0.33 mmol) was distilled in at 77 K. The tube was degassed, sealed off under vacuum, and heated at 81 °C (the boiling point of acetonitrile) for 5 h. At the conclusion of the reaction, the volatiles were removed under reduced pressure. A small amount of water was added, and the mixture was dialyzed against water (cellulose membrane, MW cutoff 1000) for 48 h to give 105 mg (80%) of **26** after evaporation of the water: $^1$H NMR (400 MHz, $D_2O$) $\delta$ 1.43, 3.15, 3.23, 3.36, 3.42, 3.59, 3.62, 3.65, 3.76, 3.86, 3.94, 4.13, 4.31, 4.37, 4.40, 5.95, 7.75; $^{13}$C NMR (400 MHz, $D_2O$) $\delta$ 31.6, 32.3, 42.8, 43.1, 49.4, 51.7, 51.8 (br), 59.5, 63.1, 67.5 (br), 102.6, 102.8, 146.3, 146.4, 152.0, 166.5; IR (KBr) 495, 515, 1126, 1261, 1684, 3040, 3427 cm$^{-1}$.

**Supporting Information Available:** DNOE results and the ORTEP figure for the adduct **22**, and two-dimensional NOESY NMR spectrum of copolymer **25** in high and low contour levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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