Macromolecules

Volume 22, Number 9 September 1989

Synthesis and Characterization of a Series of Alternating Copolymers (Oligomers) Containing Organo-λ^5-phosphazene Backbone Moieties

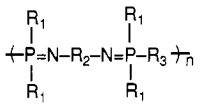
Martin Pomerantz* and Mark W. Victor

Center for Advanced Polymer Research, Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065. *Received November 7, 1988; Revised Manuscript Received January 31, 1989*

ABSTRACT: The Staudinger reaction of bis(diphenylphosphino)alkyl or -aryl compounds with 1,4-diazidobenzene at room temperature in benzene solution was shown to produce poly(organo-λ^5-phosphazenes), which are alternating copolymers (oligomers) with the general formula $(=P(Ph)_2RP(Ph)_2=NC_6H_4N=)_n$ where R = $(CH_2)_n$, n = 2–5, or R = p-C_6H_4. The CP/MAS ^{13}C and ^{31}P NMR spectra were consistent with the proposed structures and showed a small amount of P=O end groups in addition to the P=N ^{31}P resonances. The diffuse reflectance FT-IR spectra showed the typical P=N absorptions characteristic of λ^5-phosphazenes along with some azido end-group absorptions. The thermogravimetric analyses (TGA) of these polymers showed that they were reasonably thermally stable up to about 300 °C, and differential scanning calorimetry (DSC) provided the glass transition temperatures, T_g. The T_g's for the polymethylene-containing polymers were in the range 103–124 °C and appeared to decrease with increasing length of the polymethylene chain. Approximate molecular weights of these insoluble polymers were obtained by end-group analysis using the integrated areas from the ^{31}P NMR spectra (ratio of P=O and P=N groups) and assuming that P=O and N_3 were the end groups.

Introduction

Our interest in the preparation and study of λ^5-phosphazenes over the past several years[1-10] has led us to examine the synthesis and properties of alternating copolymers of the type 1 shown below. While it is well-

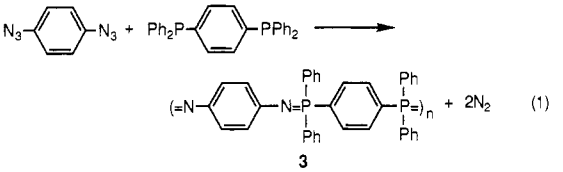


1

2

known that polymers of the type **2**, with completely inorganic backbones, have interesting and commercially useful properties, depending on the substituents, R,[11] the only way the properties of these polymers can be altered is by changing the R groups. In structures of type 1, however, not only can we retain the advantages of the phosphazene linkages and vary the phosphorus substituents, R_1, but also we can now vary the spacer groups R_2 and R_3. This should allow the altering of properties such as the glass transition temperature and the thermal stability. This means that we should be able to prepare polymers with more desirable and more readily controllable properties.

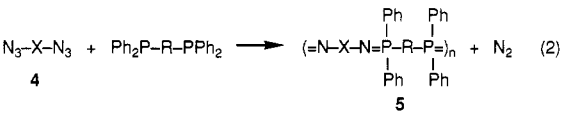
A search of the literature has revealed only a handful of references to polymers of this type and only one where the spacer groups R_2 and R_3 are organic. Herring[12] reported the synthesis of **3** from 1,4-bis(diphenylphosphino)benzene and 1,4-diazidobenzene via the Staudinger reaction (eq 1).[13] Unfortunately, only thermal stability data were presented for the product. The structure was not proven nor was a molecular weight obtained.



(1)

3

The only other reports of preparation of polymers of type 1 all involve the Standinger reaction of bis(phosphines) containing organic groups (R) between the phosphorus atoms and diazides (4) all of which contain inorganic groups and atoms (X) between the nitrogen atoms.[14-18] These produce polymers **5** with only one spacer group organic (R) and the other (X) containing inorganic groups and atoms (eq 2).



(2)

4 5

In this paper we describe the preparation and properties of a series of polymers of type 1 where the groups attached to phosphorus, R, were phenyl, the group separating the nitrogen atoms, R_2, was p-phenylene, an organic group, and

0024-9297/89/2222-3511$01.50/0

Table I
Spectroscopic Properties of Polymers 12–16

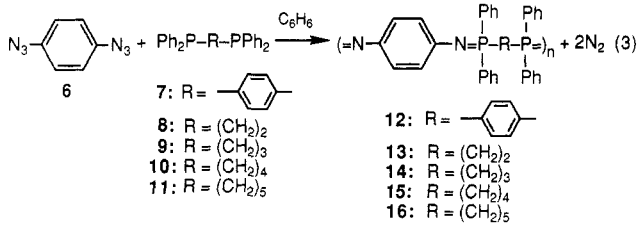
	IR,[a] cm^{-1}		CP/MAS NMR, ppm ^{31}P[b]		
polymer	P=N	N_3	P=N	P=O	^{13}C[c]
12	1312	2118, 2095	−2.7	24.4	143.4, 132.3, 129.1
13	1308	2121	5.4	31.1	143.3, 130.4, 121.1, 24.3
14	1304	2118	4.0	29.9	143.3, 131.6, 30.7, 23.0, 15.0
15	1304	2118	4.1, −3.0	30.8	143.3, 129.3, 23.5
16	1304	2118	1.4	30.8	142.2, 131.5, 30.1, 23.3

[a] Diffuse reflectance FT-IR; taken in KBr powder. [b] Downfield from external $NH_4H_2PO_4$. [c] Using external glycine as standard; $\delta_{C=O}$ 177.0.

the group between the phosphorus atoms was systematically varied.

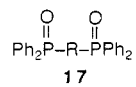
Results and Discussion

Reaction of 1,4-diazidobenzene (**6**)[12] with 1,4-bis(diphenylphosphino)benzene (**7**), 1,2-bis(diphenylphosphino)ethane (**8**), 1,3-bis(diphenylphosphino)propane (**9**), 1,4-bis(diphenylphosphino)butane (**10**), and 1,5-bis(diphenylphosphino)pentane (**11**) in benzene gave the alternating copolymers **12–16** respectively (eq 3). These polymers were insoluble in common organic solvents such as tetrahydrofuran, diethyl ether, dimethyl sulfoxide, dimethylformamide, and dimethylacetamide, and so spectroscopic analysis was done on solid samples.



Diffuse reflectance FT-IR spectroscopic analysis of the polymers **12–16** showed the P=N stretch as a broad peak at 1303–1311 cm^{-1} (Table I) as expected.[19] In addition all polymers showed a band at 2117–2125 cm^{-1} (Table I), which was indicative of an azide end group.[20] In the case of **12**, heating just below the decomposition point at 320 °C diminished the 2117 cm^{-1} absorption, but it was still present even after 15 min.

Solid-state CP/MAS ^{31}P NMR spectroscopy showed the P=N phosphorus at approximately δ +5 to −3 (relative to external $NH_4H_2PO_4$) similar to where it appears in monomeric λ^5-phosphazenes.[3,4] In all cases there was an additional small absorption at δ 24–31, which is where the corresponding oxides would appear,[21] and this functionality would of necessity be an end group. The chemical shift of polymer **12** at δ −2.7 is about 7 ppm upfield from the chemical shifts of the polymethylene polymers **13–16** and is most likely an electronic effect of the *p*-phenylene ring between the phosphorus atoms in **12**.[3,4,21] The same trend is observed in the oxide end groups where the ^{31}P shift of the P=O group in **12** appears about 6 or 7 ppm upfield of the other systems **13–16**. This is the same trend that is observed in the dioxides, **17**, where the compound with



17

the *p*-phenylene group between the phosphorus atoms (R = *p*-C_6H_4) shows $\delta_{^{31}P}$ shielded relative to the case where R = $(CH_2)_n$.[8,21] Also, compounds frequently show more than one solid-state NMR band because of "solid state effects"; that is, the atoms may appear in crystallographically nonequivalent sites or may show residual dipolar coupling of the spin $^1/_2$ nucleus to an adjacent quadrupolar nucleus such as ^{14}N.[22]

Table II
Thermogravimetric Analysis Data of 7–16

compd	onset of dec, °C	DTGA: T_{max}, °C (rate$_{max}$, %/min)	compd	onset of dec, °C	DTGA: T_{max}, °C (rate$_{max}$, %/min)
7	275	400 (18)	12	350	430 (25)
8	200	340 (27)	13	300	350 (30)
9	225	340 (30)	14	320	400 (16)
10	250	380 (30)	15	320	425 (40)
11	250	360 (27)	16	330	440 (30)

Table III
Glass Transition Temperatures (T_g) and Molecular Weights (M_n) of 12–16

polymer	T_g,[a] °C	mol wt[b]	polymer	T_g,[a] °C	mol wt[b]
12	*c*	1830	15	112[e]	2570
13	119[d]	2100	16	103[e]	2030
14	124[b]	2580			

[a] Obtained by DSC. [b] Obtained by integration of the ^{31}P NMR spectrum and assuming P=O and N_3 end groups. [c] T_g not observed. [d] Obtained by method A (see text). [e] Average of results obtained by methods A and B.

CP/MAS ^{13}C NMR spectra of **12–16** showed the aryl carbon atoms in the range of δ 121–143 (Table I). In all cases there was a peak downfield at ca. δ 142–143 (Table I), and this must be due to the ipso carbon to which the nitrogen is attached.[4] Polymers **13–16** showed the aliphatic carbon resonances at δ 14–30 (Table I), which is within the expected range.

Thermogravimetric analysis (TGA) indicated that the polymers were reasonably thermally stable to temperatures above 300 °C in a nitrogen atmosphere. Table II shows the thermal data including the temperature for the onset of decomposition (the procedural decomposition temperature),[23] and the temperature and rate for the maximum in the decomposition rate, obtained from the derivative TGA trace. The weight loss for **12–16** was a single step with no observable plateaus (no other peaks in the DTGA trace) with <5% residue at 1000 °C. The residue, if any, was not analyzed. Also shown, for comparison, are the procedural decomposition temperatures for the starting phosphines **7–11**. The diazide starting material, **6**, had a procedural decomposition temperature of 100 °C. As expected, the polymer with the two *p*-phenylene units in the backbone, **12**, is the most thermally stable. Further, thermal stability appears to increase with increasing chain length in polymers **13–16**.

In order to obtain glass transition temperatures (T_g) for these polymers (**12–16**) duplicate samples were heated in an oven at 280 °C (320 °C for **12**) and allowed to equilibrate. One of the duplicate samples of each was cooled autogenously to room temperature (method A) while the other was rapidly cooled in liquid nitrogen (method B). Differential scanning calorimetry (DSC) was run on each of the samples from −90 to 280 °C (320 °C for **12**) at 20 °C/min. Table III shows the average values for T_g. We were not able to observe a glass transition for polymer **12** while for polymers **13** and **14** a clear T_g could only be observed using method A. There is an error of about ±5 °C in T_g and even so, it appears that the polymer with the longest, most flexible spacer, **16**, has the lowest T_g. As the spacer group gets shorter T_g appears to increase modestly, which is what one would expect.[24]

Table IV
Additional IR Bands for Polymers 12–16[a]

polymer	IR bands, cm⁻¹
12	3051, 1589, 1497, 1435, 1107, 829, 748, 717, 694
13	3051, 2919, 1599, 1493, 1435, 1111, 834, 818, 725, 694
14	3051, 2941, 1601, 1489, 1435, 1281, 1111, 829, 740, 714, 694
15	3051, 2943, 1600, 1493, 1435, 1285, 1111, 829, 745, 714, 694
16	3051, 2940, 1600, 1493, 1435, 1111, 829, 745, 718, 694

[a] Bands not shown in Table I.

For none of the polymers could a T_m be observed since they began decomposing before a melting temperature could be reached.

Because of the insolubility of these systems in common organic solvents the molecular weights could not be obtained by solution methods such as GPC. With several assumptions, the molecular weights (M_n) could be calculated using end-group analysis. By assuming one end group was the azide and the other was phosphine oxide and then integrating the CP/MAS ^{31}P NMR spectrum, we could get the ratio of end to internal phosphorus atoms. This provided the molecular weights shown in Table III, and these range from ca. 1800 to 2600. The modest molecular weights are most likely due to the insolubility of these compounds since they precipitate out of solution before they can achieve a larger molecular weight.

Summary and Conclusions

A series of poly(organo-λ⁵-phosphazenes), **12–16**, which are alternating copolymers (oligomers) with the general formula $(=P(Ph)_2RP(Ph)_2=NC_6H_4N=)_n$, has been synthesized from the corresponding bis(phosphines), **7–11**, and 1,4-diazidobenzene (**6**). These insoluble polymers have been characterized by CP/MAS ^{13}C and ^{31}P NMR and FT-IR spectroscopy and by thermal analysis including TGA and DSC. They appear to be reasonably thermally stable, and all showed temperatures for the onset of decomposition of 300 °C or greater. Glass transition temperatures were observed for polymers **13–16**. They were all between 103 and 124 °C and appeared to decrease with increasing chain length in the spacer group, R. Since the IR spectra showed residual azide groups and the ^{31}P NMR spectrum showed some P=O groups, the molecular weights (M_n) were calculated by end-group analysis, assuming N_3 and P=O end groups. The modest molecular weights, which were in the range 1800–2600, were probably the result of the insolubility of the polymers in the reaction solvent.

Work on other, more soluble polymers containing both λ⁵-phosphazene and organic groups in the backbone is continuing.

Experimental Section

General Methods. IR Spectra were recorded on a Biorad-Digilab FTS-40 FT-IR spectrometer using a resolution of 8 cm⁻¹. Diffuse reflectance spectra were done in KBr powder using a SpectraTech DRIFTS accessory. CP/MAS NMR spectra were obtained on a Bruker MSL-300 NMR spectrometer at 75.5 and 121.5 MHz for ^{13}C and ^{31}P, respectively, using a Doty Scientific probe with 5-mm silicon nitride rotors and a spinning speed of 11.1–11.4 kHz. The magic angle was checked with glycine and the ^{13}C chemical shifts were referenced against the carbonyl carbon of glycine ($\delta_{C=O}$ 177.0),[25] which was in turn referenced against the methylene carbon of adamantane (δ_{CH_2} 29.5).[26] The ^{31}P chemical shifts were referenced against $NH_4H_2PO_4$ (δ 0.00). The TGA and DSC analyses were done on a Du Pont 9900 thermal analysis system. 1,4-Diazidobenzene (**6**) was prepared by literature methods[12] as was the bis(phosphine) **7**.[27] Bis(phosphines) **8–11** were commercial samples (Organometallics, Inc). All were checked for purity by melting point and ^{31}P NMR spectroscopy prior to use.

Synthesis of Polymers 12, 13, 15, and 16. In a 100-mL round-bottomed, three-necked flask, equipped with a magnetic stirrer, argon inlet, addition funnel, reflux condenser, and drying tube, was put 1–2 mmol of the bis(phosphine) dissolved in 30 mL of benzene. Note: benzene is a cancer suspect agent. To this was added 1 equiv (1–2 mmol) of 1,4-diazidobenzene (**6**) in 30 mL of benzene dropwise, over a period of about 10 min. During the addition the solution became colored and a gas was evolved. The reaction mixture was stirred overnight. The solid that formed was filtered, extracted with boiling benzene, and filtered hot. It was vacuum dried and stored in a desiccator until used. Yields: **12**, 0.26 g, 46%, orange powder; **13**, 0.48 g, 91%, greenish yellow powder; **15**, 0.62 g, 90%, yellow powder; **16**, 0.74 g, 43%, yellow powder. Additional infrared bands, not shown in Table I, for **12**, **13**, **15**, and **16** are presented in Table IV.

Synthesis of Polymer 14. The synthesis of polymer **14** was the same as for the other polymers except that after stirring overnight the reaction mixture was refluxed for 3 h prior to extracting with boiling benzene and hot filtration. It, too, was vacuum dried and stored in a desiccator, yield 0.11 g (18%, olive green powder). Additional IR bands are presented in Table IV.

Acknowledgment. Financial support through grants from The Defense Advanced Research Projects Agency monitored by The Office of Naval Research and The Robert A. Welch Foundation is gratefully acknowledged. We also thank Professors Timothy D. Shaffer and John R. Reynolds for helpful discussions and Drs. Sanjay Basak and Peter Rooney for help in obtaining the FT-IR spectra.

Registry No. (**6**)(**7**) (copolymer), 120545-22-4; (**6**)(**7**) (SRU), 120545-27-9; (**6**)(**8**) (copolymer), 120545-23-5; (**6**)(**8**) (SRU), 120545-28-0; (**6**)(**9**) (copolymer), 120545-24-6; (**6**)(**9**) (SRU), 120545-29-1; (**6**)(**10**) (copolymer), 120545-25-7; (**6**)(**10**) (SRU), 120545-30-4; (**6**)(**11**) (copolymer), 120545-26-8; (**6**)(**11**) (SRU), 120545-31-5.

References and Notes

(1) Bittner, S.; Assaf, Y.; Pomerantz, M. *J. Org. Chem.* **1982**, *47*, 99.
(2) Bittner, S.; Assaf, Y.; Krief, P.; Pomerantz, M.; Ziemnicka, B. T.; Smith, C. G. *J. Org. Chem.* **1985**, *50*, 1712.
(3) Pomerantz, M.; Ziemnicka, B. T.; Merchant, Z. M.; Chou, W.-N.; Perkins, W. B.; Bittner, S. *J. Org. Chem.* **1985**, *50*, 1757.
(4) Pomerantz, M.; Marynick, D. S.; Rajeshwar, K.; Chou, W.-N.; Throckmorton, L.; Tsai, E. N.; Chen, P. C. Y.; Cain, T. *J. Org. Chem.* **1986**, *51*, 1223.
(5) Pomerantz, M.; Chou, W.-N.; Witczak, M. K.; Smith, C. G. *J. Org. Chem.* **1987**, *52*, 159.
(6) Tsai, E. W.; Witczak, M. K.; Rajeshwar, K.; Pomerantz, M. *J. Electroanal. Chem.* **1987**, *236*, 219.
(7) Pomerantz, M.; Chou, W.-N.; Witczak, M. K.; Smith, C. G. *Phosphorus and Sulfur* **1987**, *30*, 799.
(8) Bittner, S.; Pomerantz, M.; Assaf, Y.; Krief, P.; Xi, S-K.; Witczak, M. K. *J. Org. Chem.* **1988**, *53*, 1.
(9) Pomerantz, M.; Xi, S.-K.; Bittner, S. *Phosphorus and Sulfur* **1988**, *37*, 13.
(10) λ⁵-Phosphazene is the nomenclature used to indicate a phosphorus with 4σ and π bond, bound to a nitrogen (σ and π bond). This nomenclature is normally not used for the phosphazene homopolymers, which should be referred to as λ⁵-phosphazene homopolymers by the IUPAC rules. Powell, W. H. *Pure Appl. Chem.* **1984**, *56*, 769.
(11) Allcock, H. R. *Phosphorus-Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*; Academic: New York, 1972. Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1981. Allcock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22.
(12) Herring, D. L. *J. Org. Chem.* **1961**, *26*, 3998.
(13) Gololobov, Y. G.; Zhmurova, I. N.; Kashukhin, L. F. *Tetrahedron* **1981**, *37*, 159.
(14) Schroeder, H.; Reiner, J. R.; Knowles, T. A. *Inorg. Chem.* **1963**, *2*, 393.

(15) Bilbo, A. J.; Sharts, C. M. *J. Polym. Sci., Part A-1* **1967**, *5*, 2891.
(16) Horn, H.-G. *Makromol. Chem.* **1970**, *138*, 163.
(17) Horn, H.-G.; Steger, W. *Makromol. Chem.* **1974**, *175*, 1777.
(18) Washburn, R. M.; Baldwin, R. A. U.S. Patents 3341477 and 3341478, 1967; *Chem. Abstr.* **1967**, *67*, 100585w, 100586x.
(19) Wiegräbe, W.; Bock, H. *Chem. Ber.* **1968**, *101*, 1414. Thomas, L. C. *Interpretation of the Infrared Spectra of Organophosphorus Compounds*; Heyden: London, 1974; Chapter 10.
(20) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, G. R. *Introduction to Organic Spectroscopy*; Macmillan: New York, 1987; Chapter 7.
(21) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. In ^{31}P Nuclear Magnetic Resonance. *Topics in Phosphorus Chemistry*; Crutchfield, M. M., Dungan, C. H., Letcher, J. H., Mark, V., Van Wazer, J. R., Eds.; Interscience: New York, 1967; Vol. 5, Chapter 4.
(22) Fyfe, C. A. *Solid State NMR for Chemists*; CFC Press: Guelph, ON, Canada, 1983; Chapter 6. Komoroski, R. A. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Chapter 2.
(23) Wendlandt, W. W. *Thermal Analysis*, 3rd ed.; Wiley: New York, 1986; p 10.
(24) Shalaby, S. W. In *Thermal Characterization of Polymeric Materials*; Turi, E. A., Ed.; Academic: New York, 1981; Chapter 3.
(25) Kricheldorf, H. R.; Müller, D. *Macromolecules* **1983**, *16*, 615.
(26) Earl, W. L.; Vanderhart, D. L. *J. Magn. Reson.* **1982**, *48*, 35.
(27) Baldwin, R. A.; Cheng, M. T. *J. Org. Chem.* **1967**, *32*, 1572.

Synthesis and Solution Properties of Extended Chain Poly(2,6-benzothiazole) and Poly(2,5-benzoxazole)

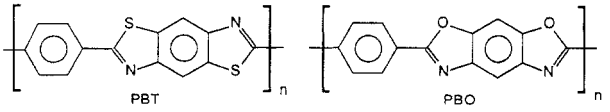
Andrea W. Chow,* Steven P. Bitler, Paul E. Penwell, Dyan J. Osborne, and James F. Wolfe*,†

Chemistry Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025. *Received October 25, 1988; Revised Manuscript Received February 27, 1989*

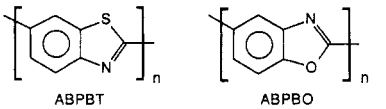
ABSTRACT: The P_2O_5 adjustment method allows polymerization of poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO) in poly(phosphoric acid) at high concentrations up to 21 wt %. ABPBO can also be prepared in methanesulfonic acid by adding up to 45 wt % P_2O_5. When polymerized at concentrations above ~14 wt %, the reacting mixture became liquid crystalline and the molecular weight of the resulting polymer was significantly higher than that of mixtures polymerized in the isotropic phase (below ~14 wt %). Addition of monofunctional end-capping agents to the starting mixture depressed the final molecular weight of the polymeric products, and Flory's theory for condensation polymerization appeared to predict the degree of molecular weight depression. Dilute solution characterization of these poly(benzazole) polymers indicated stiff-chain conformations, and comparison with the Yamakawa–Fujii wormlike chain model suggested that they have persistence lengths of 90–130 Å. The Mark–Houwink–Sakurada constants for these semirigid polymers were also determined.

Introduction

Our studies of aromatic heterocyclic polymers of the poly(benzazole) family are motivated by the need for lightweight, high-strength, high-modulus, environmentally resistant materials for use in structural applications. Within the Air Force's Ordered Polymers Research Program, our original approach focused on the rigid-rod polymer structures poly(*p*-phenylenebenzo[1,2-*d*:4,5-*d'*]-bisthiazole) (PBT)[1] and poly(*p*-phenylenebenzo[1,2-*d*:5,4-*d'*]bisoxazole) (PBO),[2] which formed liquid-crystalline phases during polymerization at concentrations above 5 wt %.[3] The catenation angle, which is the angle between exocyclic bonds of the rigid backbone units, is 180° for both PBT and PBO. These structures thereby provide some of the most rodlike configurations in the poly(benzazole) family.



While developing the synthesis methods for preparing PBT in poly(phosphoric acid) (PPA), we discovered that polymerization proceeded at polymer concentrations as high as 21 wt % if the P_2O_5 content of PPA was increased to account for the greater relative amount of water of condensation.[4] The ability to polymerize at such high concentrations led to the discovery that polymers with catenation angles much less than 180°, such as poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO), also formed the liquid-crystalline phase during polymerization.



ABPBT and ABPBO are characterized by catenation angles of 162° and 150°, respectively. Because of the unrestricted rotation between repeat units,[5] these backbone diads can assume either an extended chain conformation (trans) or a coil-like conformation (cis), as illustrated in Figure 1. In dilute solution, these polymers are likely to assume a random distribution of cis and trans conformations if neither conformation is statistically favored. At high concentrations, the liquid-crystalline phase is favored energetically, and the trans conformation is believed to dominate to allow this phase change.

We report the synthesis method for polymerizing these poly(benzazoles) with controlled molecular weights and the determination of their dilute solution properties by low-angle light-scattering and viscometry measurements. We

* To whom correspondence should be addressed.
† Current address: Lockheed Missiles & Space Co., 3251 Hanover St., Palo Alto, CA 94304.

0024-9297/89/2222-3514$01.50/0