Chirality Assignment of Amines and Amino Alcohols Based on Circular Dichroism Induced by Helix Formation of a Stereoregular Poly((4-carboxyphenyl)acetylene) through Acid−Base Complexation

Eiji Yashima, Teruyuki Matsushima, and Yoshio Okamoto*

Contribution from the Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

Received December 31, 1996[⊗]

Abstract: An optically inactive polyacetylene, poly((4-carboxyphenyl)acetylene) (poly-**1**), exhibits an induced circular dichroism (ICD) in the UV−visible region upon complexation with chiral amines and amino alcohols in DMSO and in the film, the sign of which reflects the stereochemistry including bulkiness, type (primary, secondary, or tertiary), and absolute configuration of the amines. Therefore, the polyacetylene can be used as a novel probe for determining the chirality of amines. Most primary amines and amino alcohols of the same configuration gave the same sign for the induced Cotton effect; however, secondary and/or tertiary amines used in the present study tended to show Cotton effect signs opposite to those of the primary amines and amino alcohols of the same configuration. The magnitude of the ICD likely increases with an increase in the bulkiness of the chiral amines. The complexation dynamics during the formation of the helical structure of poly-**1** with chiral amines were investigated on the basis of the spin−spin relaxation behavior and ^{1}H NMR, CD, and optical rotatory dispersion (ORD) titrations. The complex formation of poly-**1** with chiral amines such as 1-(1-naphthyl)ethylamine and 2-amino-1-propanol exhibits a positive nonlinear effect between the enantiomeric excess of the chiral amines and amino alcohols and the observed ellipticity of the Cotton effects. The excess enantiomer bound to poly-**1** may induce an excess of a single-handed helix (right- or left-handed helix), which may result in a more intense ICD than that expected from the ee of the amine. Moreover, it was found that the coexistence of achiral amines such as 1-aminoethanol also induced an excess of one helical sense of poly-**1**.

Introduction

Chiral recognition is of particular importance in living systems which often show different pharmacokinetics and pharmacodynamics activities toward a pair of enantiomeric drugs.[1] Therefore, detection and assignment of the chirality of molecules have been extensively studied by using chiral host molecules capable of discriminating chiral guests.[2] The most extensively studied chiral host molecules are cyclodextrins,[3] cyclophanes,[4] crown ethers,[2a,b,5] and calixarenes[6] which are cyclic compounds with a specific cavity and/or functional groups capable of interacting with particular guests through inclusion via hydrogen

bonding, $\pi-\pi$ interaction, or ionic interactions.[7] The chiral recognition phenomena in solution have often been studied by NMR, UV, fluorescence, and circular dichroism (CD) spectroscopies. Among them, CD may be the most powerful probe of the chiral binding interactions in small bimolecular systems[8] and also in biological systems, including the conformational

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) (a) Waldeck, B. *Chirality* **1993**, *5*, 350−355. (b) Millership, J. S.; Fitzpatrick, A. *Chirality* **1993**, *5*, 573−576. (c) White, C. A. *A Practical Approach to Chiral Separations by Liquid Chromatography*; Subramanian, G., Ed.; VCH: New York, 1994; Chapter 1. (d) Caldwell, J. *J. Chromatogr. A* **1995**, *694,* 39−48.

(2) For reviews of chiral recognition in addition to molecular recognition, see: (a) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009−1020. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89−112. (c) Schneider, H.-J.; Dürr, H.; Lehn, J.-M., Eds. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; VCH: Weinheim, 1988. (d) Pirkle, W.; Pochapsky, T. C. *Chem. Rev.* **1989**, *89*, 347−362. (e) Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245−255. (f) Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 528−549. (g) Webb, T. H.; Wilcox, C. S. *Chem. Soc. Rev.* **1993**, 383−395. (h) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713−745. (i) Kirby, A. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 707−724.

(3) For reviews, see: (a) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1977. (b) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170−177. (c) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66−72. (d) Li, S.; Purdy, W. C. *Chem. Rev.* **1992**, *92*, 1457−1470. (e) Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803−822. (f) Rekharsky, M. V.; Goldberg, R. N.; Schwarz, F. P.; Tewari, Y. B.; Ross, P. D.; Yamashoji, Y.; Inoue, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8830−8840 and references cited therein.

(4) For reviews, see: (a) Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 362−386. (b) Murakami, Y.; Kikuchi, J.; Hisaeda, Y.; Ohno, T. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Lehn, J.-M., Eds.; VCH: Weinheim, 1988; pp 144−166. (c) Diederich, F. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Lehn, J.-M., Eds.; VCH: Weinheim, 1988; pp 167−191.

(5) For reviews, see: van Veggel, F. C. J. M.; Reihoudt, D. N. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Lehn, J.-M., Eds.; VCH: Weinheim, 1988; pp 82−108.

(6) For reviews, see: (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, UK, 1989. (b) Gutsche, C. D.; Iqbal, M.; Nam, K. S.; See, K.; Alam, I. *Pure Appl. Chem.* **1989**, *60*, 483−488. (c) Diamond, D.; McKervey, M. A. *Chem. Soc. Rev.* **1996**, 15−24. (d) Ungaro, R.; Pochini, A. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Lehn, J.-M., Eds.; VCH: Weinheim, 1988; pp 57−81. (e) Takeshita, M.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1088−1097.

(7) For reviews, see: (a) Schneider, H.-J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1417−1436. (b) Buckingham, A. D.; Legon, A. C.; Roberts, S. M., Eds. *Principles of Molecular Recognition*; Blackie: London, 1993. (c) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1995**, *95*, 2529−2586. (d) Fujimoto, T.; Yanagihara, R.; Kobayashi, K.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2113−2124.

(8) (a) Kano, K.; Matsumoto, H.; Yoshimura, Y.; Hashimoto, S. *J. Am. Chem. Soc.* **1988**, *110*, 204−209. (b) Ueno, A.; Suzuki, I.; Osa, T. *J. Am. Chem. Soc.* **1989**, *111*, 6391−6397. (c) Kubik, S.; Höller, O.; Steinert, A.; Tolksdorf, M.; Wulff, G. *Macromol. Symp.* **1995**, *99*, 93−102. (d) Nakanishi, K.; Berova, N.; Woody, R. W., Eds. *Circular Dichroism—Principles and Applications*; VCH: New York, 1994. (e) Owen, D. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 259−260.

changes of biopolymers such as DNA and proteins.[9] In these cases, the host molecules are chiral, but if a guest is achiral and chromophoric, the host−guest complex will show an induced CD (ICD) in the UV and/or visible region of the guest molecule, and their binding constants and guest orientations can be determined by using CD titrations or ICD curves.[10]

Recently, a very interesting approach has been performed with achiral, chromophoric hosts, calixarenes,[6e,11] resocinol cyclic tetramers,[12] porphyrin derivatives,[13] and diboronic acid derivatives.[14] They can form complexes with particular guests, such as chiral ammoniums, polyols, amino acid esters, and saccharides, respectively, and the complexes exhibited a characteristic, exciton-type coupled ICD[15] in the absorption region of the hosts, the sign of which reflects the absolute configuration of the guests.[16]

Very recently, we also found a similar phenomenon for the complexes of an optically inactive, chromophoric polymer with chiral amines; a stereoregular poly((4-carboxyphenyl)acetylene) (poly-**1**) can change its structure into the prevailing, dynamic

poly-**1**
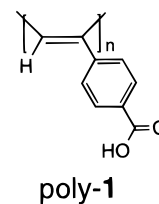
one-handed helix upon complexation with chiral amines and amino alcohols, and the complexes showed a characteristic, exciton-type coupled ICDs in the UV−visible region.[17] The Cotton effect signs corresponding to the helical sense can be used as a novel probe for the chirality assignments of amines.[18,19] This may be the first example of the prevailing helix induction on an optically inactive polymer due to an acid−base interaction.[20,21]

From the previous results of poly-**1**, we expected that related stereoregular poly(phenylacetylenes) bearing other functional groups, for instance, a boronic acid residue or an amino group, would also respond to chiral compounds capable of interacting with these functional groups on the phenyl groups and show a characteristic ICD depending on the stereochemistry of the chiral

(9) For reviews, see: (a) Hatano, M. *Induced Circular Dichroism in Biopolymer-Dye Systems*; SVH: Berlin, 1986. (b) Woody, R. W. In *Circular Dichroism—Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH: New York, 1994; Chapter 17. (c) Johnson, W. C. In *Circular Dichroism—Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH: New York, 1994; Chapter 19.

(10) Forman, J. E.; Barrans, R. E., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9213−9228 and references cited therein.

(11) (a) Arimura, T.; Edamitsu, S.; Shinkai, S.; Manabe, O.; Muramatsu, T.; Tashiro, M. *Chem. Lett.* **1987**, 2269−2272. (b) Arimura, T.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1896−1900. (c) Morozumi, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1219−1220. (d) Morozumi, T.; Shinkai, S. *Chem. Lett.* **1994**, 1515−1518.

(12) (a) Kikuchi, Y.; Kobayashi, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1351−1358. (b) Kikuchi, Y.; Tanaka, Y.; Sutarto, S.; Kobayashi, K.; Toi, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10302−10306. (c) Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1993**, *115*, 2648−2654. (d) Kikuchi, Y.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 217−220.

(13) (a) Mizutani, T.; Ema, T.; Yoshida, T.; Kuroda, Y.; Ogoshi, H. *Inorg. Chem.* **1993**, *32*, 2072−2077. (b) Mizutani, T.; Murakami, T.; Kurahashi, T.; Ogoshi, H. *J. Org. Chem.* **1996**, *61*, 539−548. (c) Mizutani, T.; Yagi, S.; Honmura, A.; Ogoshi, H. *J. Am. Chem. Soc.* **1996**, *118*, 5318−5319.

(14) (a) Tsukagoshi, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4089−4091. (b) Kondo, K.; Shiomi, Y.; Saisho, M.; Harada, T.; Shinkai, S. *Tetrahedron* **1992**, *48*, 8239−8252. (c) Shiomi, Y.; Saisho, M.; Tsukagoshi, K.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2111−2117. (d) Deng, G.; James, T. D.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 4567−4572. (e) Imada, T.; Murakami, H.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1557−1558. (f) Nakashima, K.; Shinkai, S. *Chem. Lett.* **1995**, 443−444. (g) Mikami, M.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1995**, 153−154. (h) Takeuchi, M.; Mizuno, T.; Shinmori, H.; Nakashima, M.; Shinkai, S. *Tetrahedron* **1996**, *52*, 1195−1204. (i) Ohseto, F.; Yamamoto, H.; Matsumoto, H.; Shinkai, S. *Tetrahedron Lett.* **1995**, *36*, 6911−6914. (j) Suenaga, H.; Arimori, S.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1996**, 607−612. (k) James, T. D.; Linnane, P.; Shinkai, S. *Chem. Commun.* **1996**, 281−288. (l) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1911−1922.

(15) The CD exciton chirality method developed by Nakanishi and Harada has been extensively applied for determining the absolute configurations of chiral molecules. For reviews, see: (a) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Book: Mill Valley, CA, 1983. (b) Nakanishi, K.; Berova, N. In *Circular Dichroism—Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH: New York, 1994; Chapter 13. For recent examples, see: (c) Wiesler, W. T.; Nakanishi, K. *J. Am. Chem. Soc.* **1990**, *112*, 5574−5583. (d) Harada, N.; Saito, A.; Ono, H.; Gawronski, J.; Gawronska, K.; Sugioka, T.; Uda, H.; Kuriki, T. *J. Am. Chem. Soc.* **1991**, *113*, 3842−3850. (e) Berova, N.; Gargiulo, D.; Nakanishi, K.; Harada, N. *J. Am. Chem. Soc.* **1993**, *115*, 4769−4775. (f) Gargiulo, D.; Cai, G.; Ikemoto, N.; Bozhkova, N.; Odingo, J.; Berova, N.; Nakanishi, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 888−891. (g) Gargiulo, D.; Ikemoto, N.; Odingo, J.; Bozhkova, N.; Iwashita, T.; Berova, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1994**, *116*, 3760−3767. (h) Matile, S.; Berova, N.; Nakanishi, K.; Novkova, S.; Philipova, I.; Blagoev, B. *J. Am. Chem. Soc.* **1995**, *117*, 7021−7022. (i) Matile, S.; Berova, N.; Nakanishi, K.; Fleischhauer, J.; Woody, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 5198−5206. (j) Rele, D.; Zhao, N.; Nakanishi, K.; Berova, N. *Tetrahedron* **1996**, *52*, 2759−2776.

(16) For recent examples of chirality recognition with chiral hosts, see: (a) Kaneda, T.; Hirose, K.; Misumi, S. *J. Am. Chem. Soc.* **1989**, *111*, 742−743. (b) Shinkai, S.; Nishi, T.; Matsuda, T. *Chem. Lett.* **1991**, 437−440. (c) Ueno, A.; Kuwabara, T.; Nakamura, A.; Toda, F. *Nature* **1992**, *356*, 136−137. (d) James, T. D.; Harada, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1993**, 857−858. (e) James, T. D.; Sandanayake, K. R. A. S.; Iguchi, R.; Shinkai, S. *J. Am. Chem. Soc.* **1995**, *117*, 8982−8987. (f) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Nature* **1995**, *374*, 345−347. (g) James, T. D.; Kawabata, H.; Ludwig, R.; Murata, K.; Shinkai, S. *Tetrahedron* **1995**, *51*, 555−566.

(17) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1995**, *117*, 11596−11597.

(18) For examples of chirality assignments of amines by CD, see refs 15e−g and 19. (a) Smith, H. E. *Chem. Rev.* **1983**, *83*, 359−377. (b) Hoye, T. R.; Renner, M. K. *J. Org. Chem.* **1996**, *61*, 2056−2064. (c) Smith, H. E.; Neergaard, J. R. *J. Am. Chem. Soc.* **1996**, *118*, 7694−7701.

(19) (a) Tokura, N.; Nagai, T.; Takenaka, S.; Oshima, T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 337−342. (b) Takenaka, S.; Kondo, K.; Tokura, N. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1520−1524. (c) Takenaka, S.; Miyauchi, Y.; Tokura, N. *Tetrahedron Lett.* **1976**, 3811−3814. (d) Takenaka, S.; Ako, M.; Kotani, T.; Matsubara, A.; Tokura, N. *J. Chem. Soc., Perkin Trans. 2* **1978**, 95−99. (e) Takenaka, S.; Koden, M. *J. Chem. Soc., Chem. Commun.* **1978**, 830. (f) Schipper, P. E.; O'Brien, J. M.; Ridley, D. D. *J. Phys. Chem.* **1985**, *89*, 5805−5810.

(20) For CD studies of a predominantly one-handed helix induction of polymers, see: (a) Green, M. M.; Andreola, C.; Munoz, B.; Reidy, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 4063−4065. (b) Green, M. M.; Lifson, S.; Teramoto, A. *Chirality* **1991**, *3*, 285−291. (c) Green, M. M.; Khatri, C.; Peterson, N. C. *J. Am. Chem. Soc.* **1993**, *115*, 4941−4942. (d) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11976−11981. (e) Khatri, C. A.; Vaidya, M. M.; Levon, K.; Jha, S. K.; Green, M. M. *Macromolecules* **1995**, *28*, 4719−4728. For examples of CD studies on a one-handed helix formation of polypeptides, see: (f) Libman, J.; Tor, Y.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 5880−5881. (g) Ruan, F.; Chen, Y.; Hopkins, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 9403−9404. (h) Ghadiri, M. R.; Soares, C.; Choi, C. *J. Am. Chem. Soc.* **1992**, *114*, 825−831. (i) Wittung, P.; Nielsen, P. E.; Buchardt, O.; Egholm, M.; Nordén, B. *Nature* **1994**, *368*, 561−563. For CD studies of a chiral helix induction of small molecules, see ref 13. (j) Lightner, D. A.; Gawronski, J. K.; Gawronska, K. *J. Am. Chem. Soc.* **1985**, *107*, 2456−2461. (k) Lightner, D. A.; Gawronski, J. K.; Wijekoon, W. M. D. *J. Am. Chem. Soc.* **1987**, *109*, 6354−6362. (l) Zarges, W.; Hall, J.; Lehn, J.-M.; Bolm, C. *Helv. Chim. Acta* **1991**, *74*, 1843−1852. (m) Krämer, R.; Lehn, J.-M.; Cian, A. D.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703−706. (n) Charbonniére, L. J.; Bernardinelli, G.; Piguet, C.; Sargeson, A. M.; Williams, A. F. *J. Chem. Soc., Chem. Commun.* **1994**, 1419−1420. (o) Charbonniére, L. J.; Gilet, M.-F.; Bernauer, K.; Williams, A. F. *J. Chem. Soc., Chem. Commun.* **1996**, 39−40. (p) Sánchez-Quesada, J.; Seel, C.; Prados, P.; Mendoza, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 277−278. (q) Wood, C. R.; Benaglia, M.; Cozzi, F.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1830−1833. For reviews of helical polymer syntheses, see: (r) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349−372. (s) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, 11−19. (t) Qin, M.; Bartus, J.; Vogl, O. *Macromol. Symp.* **1995**, *98*, 387−402. (u) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 1906−1916.

compounds. Actually, stereoregular poly((4-(dihydroxyboro)-phenyl)acetylene)[22] and poly((4-(diisopropylamino)methyl)-phenyl)acetylene)[23] were found to exhibit similar ICDs during the complexation with optically active diols and sugars and acids, respectively. The Cotton effect signs can be used for the assignment of the absolute configuration of the chiral compounds.

The original polyacetylenes are not optically active. However, they can show an ICD if the twist of adjacent double bonds around a single bond preferentially occurs in one direction.[24] Ciardelli et al.[24a] and Moore and Grubbs et al.[24b] reported that polyacetylenes with a chiral substituent predominantly exist in a favored helical sense due to the nonplanar conformation of the polyene structure based on the CD analysis of the poly-acetylenes. We also found that stereoregular, optically active poly(phenylacetylenes) prepared from an optically active phen-ylacetylene derivative having a chiral substituent such as a (*R*)-1-phenylethylcarbamoyloxy group at the *para* position with use of a rhodium catalyst exhibited an intense ICD in the UV–visible region[24f] and showed high chiral recognition as a chiral stationary phase (CSP) for HPLC.[24e]

The present work is concerned with the induced helix formation of poly-**1** with chiral amines and amino alcohols. The dynamics during the helix formation of poly-**1** in the presence of chiral amines were investigated by means of CD, optical rotatory dispersion (ORD), and ^{1}H NMR titrations. The Cotton effect signs of the ICDs can be used as a novel probe for chirality and stereochemical assignments of the amines and amino alcohols, including the absolute configuration and bulki-ness of the amines in the acid–base complexation. The results also contribute to the understanding of the acid–base equilibria in aprotic polar solvents.[25] In addition, the positive nonlinear effect[26] between the enantiomeric excess (ee) of the chiral amines and amino alcohols and the observed ellipticity of the Cotton effects is also described.

Results and Discussion

Synthesis and Structural Characteristics of Poly((4-car-boxyphenyl)acetylene). Stereoregular poly((4-carboxyphenyl)-acetylene) (poly-**1**) was prepared by polymerization of (4-((triphenylmethoxy)carbonyl)phenyl)acetylene (TrA) with [Rh(nbd)Cl]$_2$ (nbd = norbornadiene),[27] followed by hydrolysis of the ester group (Scheme 1). This rhodium catalyst has been reported to be effective for the polymerization of mono-substituted acetylenes, especially (substituted-phenyl)acetylenes to afford high molecular weight stereoregular polymers. The resulting yellow-red polymer was soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N,N-dimethylacetamide and insoluble in chloroform, acetone and tetrahydrofuran (THF). The molecular weight (*M*n) of poly-**1** was estimated to be 4.6 × 10^4 as determined by gel permeation chromatography (GPC) as its methyl ester.[28]

The stereoregularity of poly-**1** was investigated by ^{1}H and ^{13}C NMR spectroscopy. As for the structure of polyacetylenes, there exist at least four possible conformers (Chart 1); *cis-transoid, cis-cisoid, trans-transoid,* and *trans-cisoid.* The

(21) For reviews of optical resolution based on an acid–base complex-ation, see: (a) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; John Wiley & Sons: New York, 1981. (b) Kinbara, K.; Hashimoto, Y.; Sukegawa, M.; Nohira, H.; Saigo, K. *J. Am. Chem. Soc.* **1996**, *118*, 3441–3449 and references cited therein. For reviews of chiral discrimination as chiral shift reagents based on an acid–base complexation, see: (c) Rinaldi, P. L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1982**, *15*, 291–352. (d) Weisman, G. R. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Chapter 8. (e) Fraser, R. R. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Chapter 9. (f) Parker, D. *Chem. Rev.* **1991**, *91*, 1441–1457. For examples of chiral recognition based on an acid–base complexation in solution, see: (g) Arnet, E. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1981**, *103*, 1221–1222. (h) Echavarren, A.; Galán, A.; Lehn, J.-M.; Mendoza, J. *J. Am. Chem. Soc.* **1989**, *111*, 4994–4995. (i) Garcia-Tellado, F.; Albert, J.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1991**, 1761–1763. (j) Montero, A. V.; Tomlinson, L.; Houk, K. N.; Diederich, F. *Tetrahedron Lett.* **1991**, *39*, 5309–5312. (k) Alcazar, V.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1521–1523. (l) Owens, L.; Thilgen, C.; Diederich, F.; Knobler, C. B. *Helv. Chim. Acta* **1993**, *76*, 2757–2774. For reviews of an acid–base complexation in solution and/or in solid, see: (m) Wilcox, C. S. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Lehn, J.-M., Eds.; VCH: Weinheim, 1988; pp 123–143. (n) Rebek, J., Jr. *Acc. Chem. Res.* **1990**, *23*, 399–404. (o) Zimmerman, S. C. *Top. Curr. Chem.* **1993**, *165*, 71–101. (p) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383–2420. (q) Kato, T.; Fréchet, J. M. J. *Macromol. Symp.* **1995**, *98*, 311–326. (r) Paleos, C. M.; Tsiouvas, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1696–1711. (s) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311–2327. (t) Seel, C.; Galán, A.; Mendoza, J. *Top. Curr. Chem.* **1995**, *175*, 101–132. (u) Schmidtchen, F. P.; Berger, M.; Metzger, A.; Gloe, K.; Stephan, H. In *Molecular Design and Bioorganic Catalysis*; Wilcox, C. S., Hamilton, A. D., Eds.; Kluwer: Dordrecht, The Netherlands, 1996; pp 191–210. (v) Collet, A.; Ziminski, L.; Garcia, C.; Vigné-Maeder, F. In *Supramolecular Stereochemistry*; Siegel, J. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1995; pp 90–110.

(22) Yashima, E.; Nimura, T.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9800–9801.

(23) Yashima, E.; Maeda, Y.; Okamoto, Y. *Chem. Lett.* **1996**, 955–956.

(24) For references of CD studies on other optically active polyacetylenes, see: (a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *2*, 174–179. (b) Moore, J. S.; Gorman, C. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 1704–1712. (c) Yamaguchi, M.; Omata, K.; Hirama, M. *Chem. Lett.* **1992**, 2261–2262. (d) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009–2012. (e) Yashima, E.; Huang, S.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1811–1812. (f) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184–4193. (g) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662–6666. Chiral butadiene derivatives with restricted rotation were successfully resolved into enanti-omers by liquid chromatography with use of a chiral stationary phase. (h) Becher, G.; Mansschrech, A. *Chem. Ber.* **1981**, *114*, 2365–2368.

(25) (a) Bruckenstein, S.; Saito, A. *J. Am. Chem. Soc.* **1965**, *87*, 698–710. (b) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23–28. (c) DeTar, D. F.; Novak, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 1361–1365. (d) Kolthoff, I. M. *Anal. Chem.* **1974**, *46*, 1992–2003. (e) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875–3891. (f) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 5063–5068. (g) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7465–7470. (h) Hughes, D. L.; Bergan, J. J.; Grabowski, E. J. J. *J. Org. Chem.* **1986**, *51*, 2579–2585. (i) Arnett, E. M.; Ahsan, T.; Amarnath, K. *J. Am. Chem. Soc.* **1991**, *113*, 6858–6861.

(26) For leading references of the nonlinear effect on asymmetric synthesis, see: (a) Puchot, C.; Samuel, O.; Dunach, E.; Zhao, S.; Agami, C.; Kagan, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 2353–2357. (b) Oguni, N.; Matsuda, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877–7878. (c) Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49–69. (d) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994; pp 273–293. (e) Mikami, K.; Motoyama, Y.; Terada, M. *J. Am. Chem. Soc.* **1994**, *116*, 2812. (f) Guillaneux, D.; Zhao, S.-H.; Samuel, O.; Rainford, D.; Kagan, H. B. *J. Am. Chem. Soc.* **1994**, *116*, 9430–9439. (g) Kitamura, M.; Suga, S.; Niwa, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 4832–4842. For recent references of the nonlinear effect on helix-sense selective copolymerization, see: (h) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452–6454. (i) Okamoto, Y.; Nishikawa, M.; Nakano, T.; Yashima, E.; Hatada, K. *Macromolecules* **1995**, *28*, 5135–5138. (j) Green, M. M.; Garetz, B. M.; Munoz, B.; Chang, H.; Hoke, S.; Cooks, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 4181–4182. (k) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866. (l) Fujiki, M. *Polym. Prep.* **1996**, *37*, 454–455.

(27) (a) Furlani, A.; Napoletano, C.; V. Russo, M. V.; Feast, W. J. *Polym. Bull.* **1986**, *16*, 311–317. (b) Furlani, A.; Napoletano, C.; Russo, M.; Camus, A.; Marsich, N. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 75–86. (c) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *12*, 1105–1107. (d) Tabata, M.; Takamura, H.; Yokota, K.; Nozaki, Y.; Hoshino, T.; Minakawa, H.; Kodaira, K. *Macromolecules* **1994**, *27*, 6234–6236. (e) Kishimoto, Y.; Eckerle, P.; Miyake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131–12132. (f) Kishimoto, Y.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1996**, *29*, 5054–5055. (g) Tabata, M.; Sadahiro, Y.; Nozaki, Y.; Inaba, Y.; Yokota, K. *Macromolecules* **1996**, *29*, 6673–6675.

(28) In the previous study,[17] we used a higher molecular weight poly-**1** for ICD experiments. However, no significant changes in ICD spectra in the presence of optically active amines were observed.
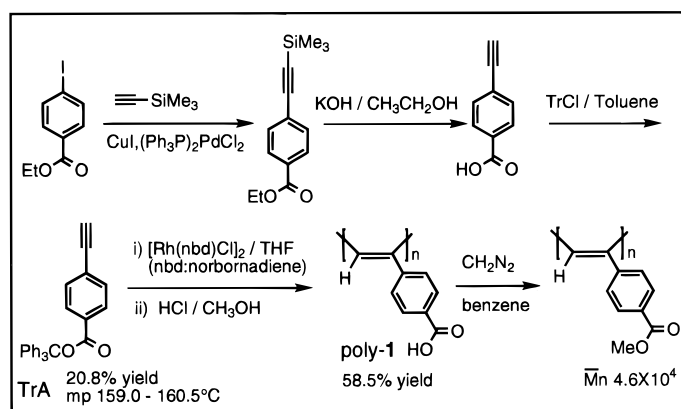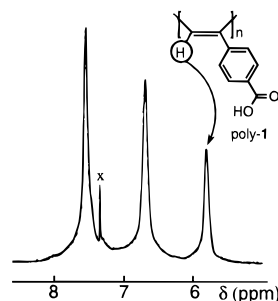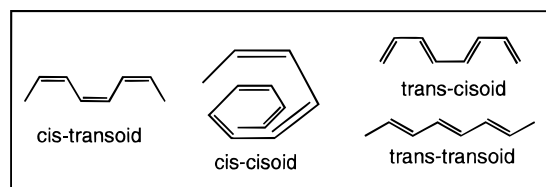
Scheme 1

Chart 1

Figure 1. ^{1}H NMR spectrum of poly-**1** in DMSO-d_6 at 60 °C (500 MHz, TMS). The × denotes protons from CHCl$_3$.

Chart 2

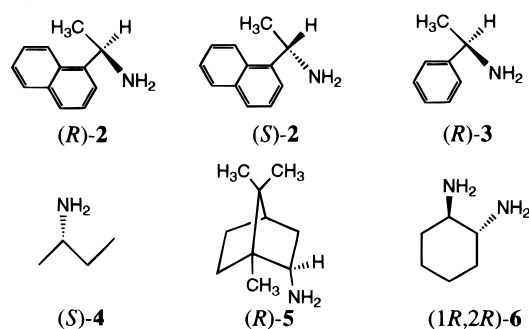Primary Amines

Secondary and/or Tertiary Amines

chemical shift and line shape of the main chain's olefinic protons and aromatic protons are considered to be sensitive to the conformers.[29] The ^{1}H NMR spectrum of poly-**1** in DMSO-d_6 (Figure 1) showed a sharp singlet centered at 5.83 ppm due to the main chain protons, which can be assigned to the *cis-transoidal* main chain's olefinic protons, and the *cis* content is estimated to be approximately 100% by the integral ratio of the olefinic proton resonance and the other aromatic proton resonances based on the literature method for poly(phenylacetylene).[29] Similar sharp resonances were also observed in the ^{13}C NMR spectrum (see Experimental Section). The sample showed the same ^{1}H NMR spectrum even after 1 month, indicating that the poly-**1** is stable in solution.

Other transition metal catalysts such as WCl$_6$-*n*-Bu$_4$Sn and MoCl$_5$-*n*-Bu$_4$Sn complexes are known as excellent catalysts to

polymerize acetylenes.[30] However, these catalysts could not polymerize TrA, and produced stereoirregular poly(phenylacetylenes) in the polymerization of (4-(ethoxycarbonyl)phenyl)-acetylene (EB); their ^{1}H and ^{13}C NMR spectra showed very broad resonances. Poly-**1** compounds derived from these stereoirregular polymers were used to investigate the effect of stereoregularity and conformation of the main chain on the induction of a helix of poly-**1** by the complexation with chiral amines and amino alcohols, which will be discussed later.

CD Studies on the Complexation with Chiral Amines and Amino Alcohols. Poly-**1** forms a complex with various chiral amines (**2**−**17**) (Chart 2) and amino alcohols (**18**−**32**) (Chart 3), including simple primary amines (**2**−**4**), cyclic primary amines (**5**, **6**), secondary and/or tertiary amines (**7**−**16**), and amino alcohols (**18**−**32**), including quinidine (**30**) and quinine (**31**) through an acid−base interaction. The complexes showed a split-type ICD in the UV−visible region in both solution and the film state, the sign of which reflects the stereochemistry, including absolute configuration of the amines. Figure 2 shows typical CD spectra of poly-**1** in the presence of optically active primary amines (Figure 2A) and primary and tertiary amino
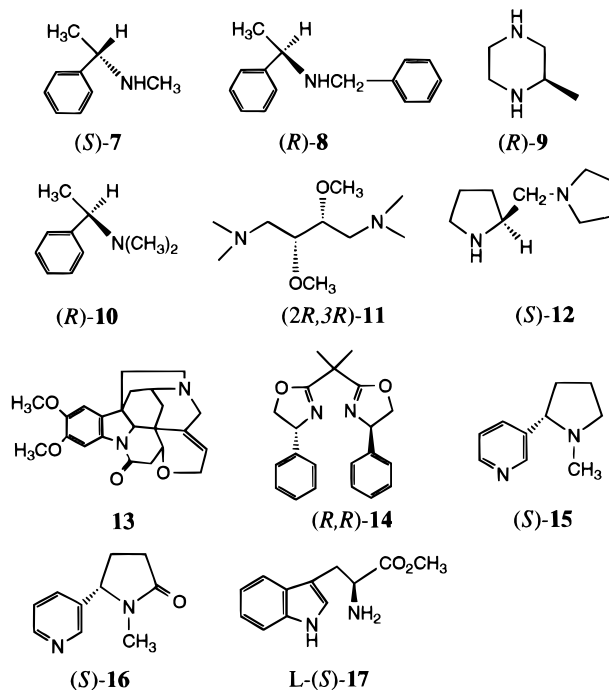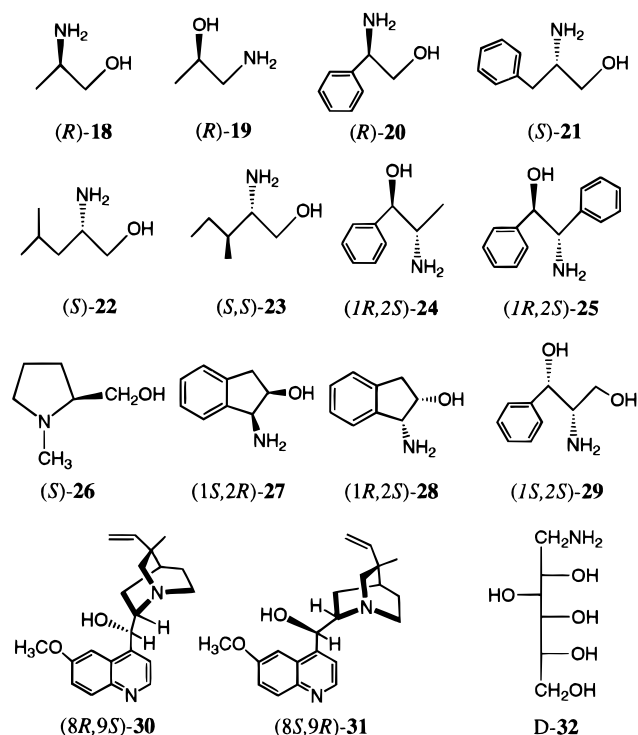
(29) (a) Simionescu, C.; Dumitrescu, S.; Percec, V. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 209−227. (b) Furlani, A.; Napoletano, C.; V. Russo, M. V.; Feast, W. J. *Polym. Bull.* **1986**, *16*, 311−317. (c) Furlani, A.; Licoccia, S.; Russo, M. V. *J. Polym. Sci., Part A, Polym. Chem.* **1986**, *24*, 991−1005. (d) Furlani, A.; Napoletano, C.; V. Russo, M. V.; Marsich, N. *J. Polym. Sci., Part A, Polym. Chem.* **1989**, *27*, 75−86. (e) Lee, D.-H.; Lee, D.-H.; Soga, K. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 559−563. (f) Very recently, Noyori and co-workers have determined the structure of poly(phenylacetylene) prepared with a rhodium catalyst to be exactly *cis-transoidal* in both solution and solid state by means of NMR spectroscopy using the poly(phenylacetylenes) partially labeled with ^{2}H and/or [13]C: Proceeding of the International Symposium on Molecular Catalysis '96: Tokyo, Japan, 1996; pp 21 and 22.

(30) For reviews, see: (a) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1987**, *81*, 121−165. (b) Shirakawa, H.; Masuda, T.; Takeda, K. In *The Chemistry of Triple-Bond Functional Groups*; Patai, S., Ed.; John Wiley & Sons: New York, 1994; Chapter 17.

Chart 3

Figure 2. CD spectra of poly-**1** with (*R*)- or (*S*)-amines (**2**−**6**) (A) and amino alcohols (**18**, **20**, **24**, and **30**) (B) in DMSO. The CD spectra were measured in a 0.05 cm quartz cell at ambient temperature (*ca,* 20−22 °C) with a poly-**1** concentration of 1.0 mg (6.8 μmol monomer units)/mL. [amine]/[poly-**1**] = 50.

Figure 3. Schematical illustrations of the formation of a helical structure with chiral amines.

alcohols (Figure 2B) in dry DMSO.[31] Enantiomers of **2** induced intense split-type ICDs of mirror images (Table 1). There are three Cotton effects with the exciton-type splittings in the ICDs in Figure 2. However, the assignments of the Cotton effects have not yet been done, although conjugated polyenes may be regarded as a suitable chromophore for the exciton-coupled CD.[15] The intensity of the ICD increased with an increase in the concentration of the chiral amine and reached an almost constant value ($[\theta]$ = *ca.* 3 × 10^4 deg cm^2 dmol^{-1} at 375 nm) at [**2**]/[poly-**1**] = 50. The results clearly indicate that the complexation involves an acid−base equilibrium,[33] and the poly-**1** having a rather irregulart twist of the adjacent double bonds around a single bond may be transformed into the helical conformation with a predominant screw-sense by interacting with the chiral amine as schematically illustrated in Figure 3.[34] No ICD signals were observed when the methyl ester of poly-**1** was used with excess (50-fold) (*R*)-**2** in DMSO.

Molecular mechanics and molecular dynamics calculations with the Dreiding force field[35] were carried out for a model polymer (20 repeated monomer units) of poly-**1** in order to gain information regarding the conformation of the poly(phenylacetylene) prepared in this study. A planar extended backbone conformation has been reported for a *trans-transoidal* polyacetylene and substituted polyacetylenes,[36] while a helical conformation has been proposed for a few *cis-transoidal* and

cis-cisoidal substituted polyacetylenes.[37] The rhodium catalyst used in this study may give almost complete *cis-transoidal* poly-(phenylacetylenes).[27,29f] Therefore, we constructed a *cis-transoidal* poly((4-carboxyphenyl)acetylene) (20 mer) as a model polymer for calculations according to the previously reported

(31) Water may affect an acid−base complexation in aprotic organic solvents,[32] and therefore, the effect of water on the ICD magnitude of the complexes of poly-**1** with (*S*)-**2** and (*R*)-**18** was investigated on the basis of CD titrations. As seen in the supporting information, a very small amount of water (less than 2% by volume to DMSO) did not affect the magnitude of ICDs of the complexes, although the ICD signals of poly-**1**−(*R*)-**18** complex decreased with an increase in the amount of water.

(32) (a) Izutsu, K. *Acid−Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackewll: Oxford, 1990. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, Germany, 1990.

(33) The UV−vis spectrum of poly-**1**[17] very slightly changed upon addition of chiral amines. The dilution experiments of the complexes between poly-**1** and (*S*)-**2** or (*R*)-**18** also support the equilibria; dilution of the complexes resulted in a nonlinear decrease in the ICD magnitude (see the Supporting Information).
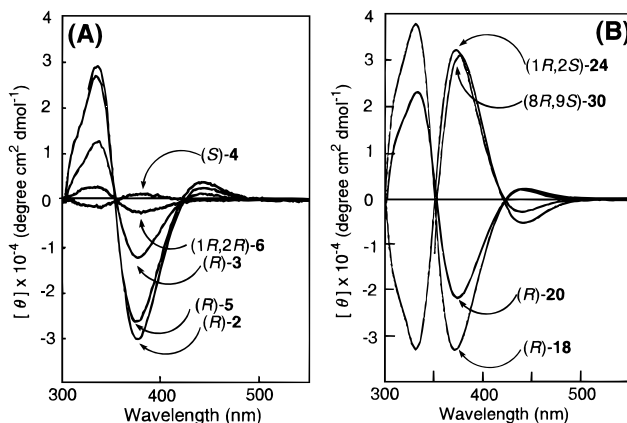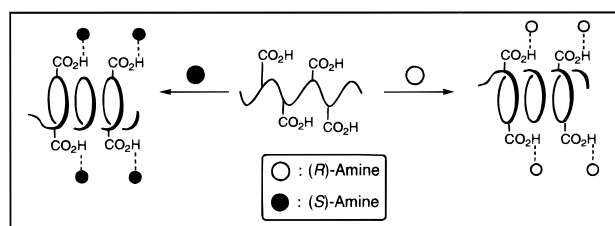
(34) The stereoregular poly-**1** may be regarded as an analog of helical polyisocyanates with very short persistence length. The polyisocyanates have a long, alternate sequence of left- and right-handed helices, in other words, long persistence length (more than 100 monomer units), so as to give a considerable cooperativity.[26k] However, the persistence length of the poly-**1** is very short, and a helix reversal of the poly-**1** would appear on average every 2−4 monomer units on the basis of the copolymerization of optically active phenylacetylenes with achiral phenylacetylenes (see ref 24f). Copolymers of a small amount of optically active phenylacetylene (*ca.* 10 mol %) with achiral phenylacetylene showed much weaker induced CD in the UV−visible region than the homopolymer, and copolymers of the optically active phenylacetylene (30 mol %) with an achiral phenylacetylene derivative bearing a bulky substituent at the *para* position showed an intense induced CD. These results clearly indicate that the chiral monomer units of the poly(phenylacetylenes) affect only neighboring monomer units to take the same helical conformation. The molecular modeling and molecular dynamics simulations also supported the above speculation. Consequently, we think that the poly(phenylacetylenes) are not completely the same as the polyisocyanates. However, as previously described, the poly-**1** can be considered as the limitative analog of the polyisocyanates with a very short persistence length.

(35) (a) Mayo, S. L.; Olafson, B. D.; Goddard, W. A., III *J. Phys. Chem.* **1990**, *94*, 8897−8909. (b) Rappé, A. K.; Goddard, W. A., III *J. Phys. Chem.* **1991**, *95*, 3358−3363. (c) Castonguay, L. A.; Rappé, A. K.; Casewit, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 7177−7183. (d) Wang, Q.; Stidham, H. *Spectrochim. Acta* **1994**, *50A*, 421−433. (e) Smith, T. L.; Masilamani, D.; Bui, L. K.; Khanna, Y. P.; Bray, R. G.; Hammond, W. B.; Curran, S.; Belles, J. J., Jr.; Binder-Castelli, S. *Macromolecules* **1994**, *27*, 3147−3155. (f) Brizzolara, D.; Cantow, H.-J.; Diederichs, K.; Keller, E.; Domb, A. J. *Macromolecules* **1996**, *29*, 191−197.

(36) (a) Cernia, E.; D'ilario, L. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2163−2176. (b) Clough, S. B.; Sun, X.-F.; Subramanyam, S.; Beladakere, N.; Blumstein, A.; Tripathy, S. K. *Macromolecules* **1993**, *26*, 597−600. (c) Gorman, C. B.; Ginsburg, E. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 1397−1409.

(37) (a) Clough, S. B.; Sun, X.-F.; Tripathy, S. K. *Macromolecules* **1991**, *24*, 4264−4269. (b) Nishide, H.; Kaneko, T.; Igarashi, M.; Tsuchida, E.; Yoshioka, N.; Lahti, P. M. *Macromolecules* **1994**, *27*, 3082−3086.
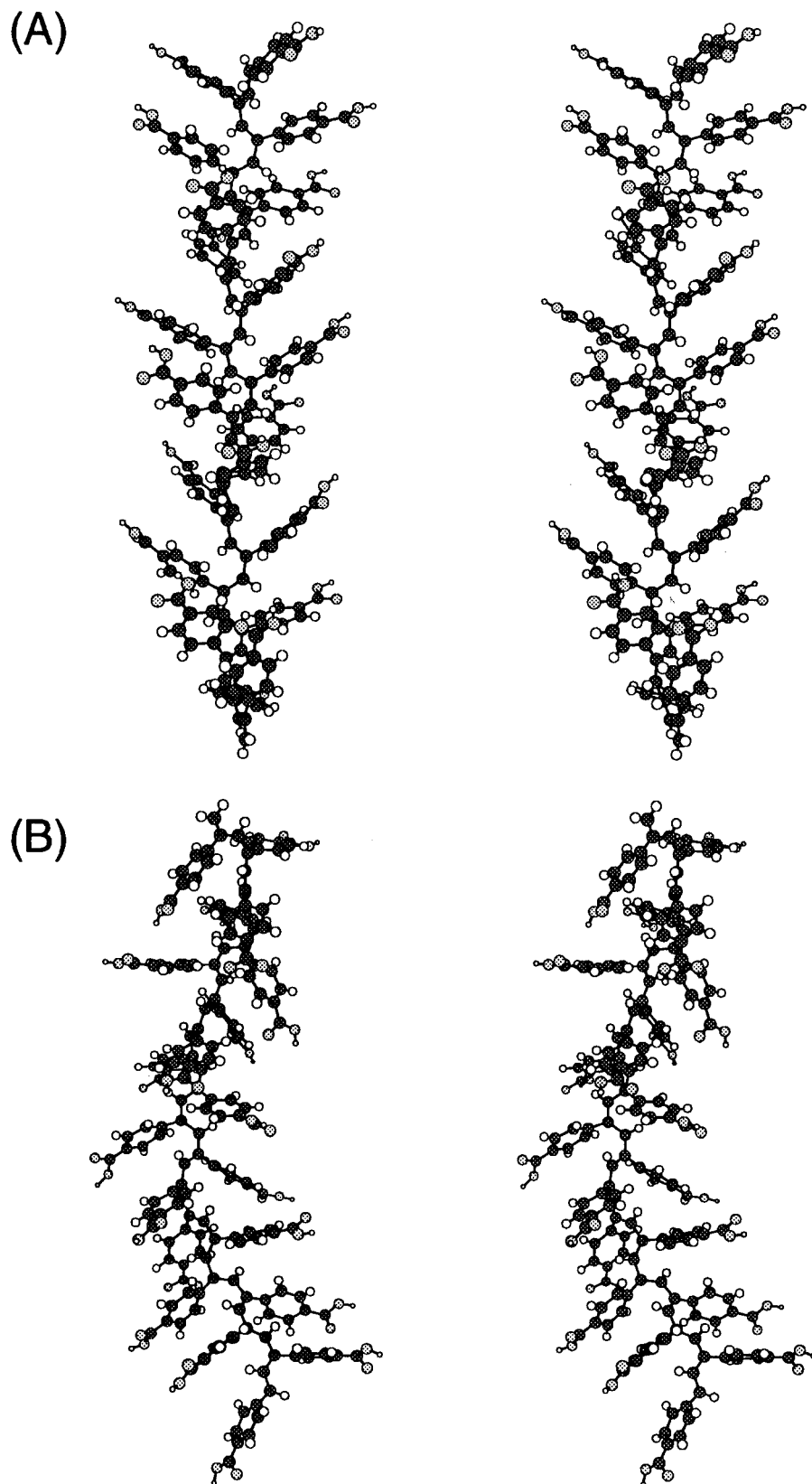
(A)

(B)

Figure 4. Stereoviews of optimized structures of poly-**1** (20 mer) (A) and those after 80 ps of molecular dynamics simulations (B).

method.[24f] The optimized model polymer (Figure 4A) had a left- or right-handed helical structure depending on the initial twist angle about a single bond; the phenyl rings were twisted out of the backbone by 46−68° and the average dihedral angles of the double and single bonds from planarity were 24 ± 7° and 15 ± 3°, respectively. The polymer had a slightly tight helical conformation compared with that of poly(phenyl-

acetylene).[24f] However, the conformation of the helical poly-(phenylacetylene) shown in Figure 4A changed to a rather irregular conformation after 80 ps of molecular dynamics simulations; the dihedral angles of the double bonds from planarity were in the range −156 to 138° (Figure 4B). This indicates that the helical conformation of poly-**1** may not be stable enough in solution and a helix reversal appeared on

average every 2−4 monomer units, but it will take a dynamic, one-handed helical conformation upon complexation with optically active amines and amino alcohols, thus showing ICD.[38]

The split type and magnitude of the Cotton effects appear to reflect the configuration, bulkiness, and type (primary, secondary, or tertiary) of chiral amines and the magnitude of the ICD likely increases with an increase in the bulkiness of the chiral amines; actually, the observed ICD increased in the order **4** < **6** < **3** ≪ **5**, **2**. The bulky groups introduced at the *para* position of poly-**1** appear to contribute more efficiently for the polymer to take a predominant screw sense. This speculation is supported by the previous fact that the magnitude of ICD of copolymers of an optically active phenylacetylene derivative bearing an (*R*)-(1-phenylethyl)carbamoyloxy group at the *para* position and achiral comonomers with the same rhodium catalyst increased with an increase in the bulkiness of the substituents at the *para* position of the comonomers.[24f]

One may think that the basicity of amines in DMSO may also influence the magnitude of the ICDs. However, the above mentioned order of the ICD intensities for the complexes with the primary amines **2**−**6** is not completely correlated with the basicity or binding affinity to poly-**1** of the amines: For instance, an acid−base binding constant (*K*) of (*R*)-**4** with 4-vinylbenzoic acid, a model compound of poly-**1**, obtained by ^{1}H NMR titration experiments in dry DMSO-d_6 was larger than that of (*R*)-**2**. Nevertheless, the poly-**1**−(*R*)-**4** complex exhibited a weaker ICD than that of the poly-**1**−(*R*)-**2** complex. This indicates the importance of the bulkiness of amines for induction of an excess one-handed helical conformation of poly-**1**, accompanied by an intense ICD, which will be discussed later in detail.

The results of the ICD for the complexes with other chiral amines including secondary and/or tertiary amines are also summarized in Table 1. The complexes with secondary and/or tertiary amines (**7**−**16**) showed a rather weak ICD compared to those with primary amines except for bulky (*S*)-**12** and brucine (**13**). The magnitude of the observed ICDs likely decreases in the following order: primary amine (**3**) > secondary amine (**7**) ≫ tertiary amine (**10**). (*R*)-*N,N*-Dimethyl-1-phenylethylamine (**10**) exhibited almost no ICD at a poly-**1** concentration of 1.0 mg/mL, but it showed a weak ICD with the opposite Cotton effect sign when the concentration of poly-**1** increased five times (5.0 mg/mL). On the contrary to the observed ICDs for the complexes with the primary amines as seen in Figure 2A, this order seems to be correlated with the basicity of amines in DMSO, because they are similar in bulkiness. Therefore, other chiral amines with a weaker basicity such as the (*S*)-nicotine (**15**), (*S*)-cotinine (**16**), and L-tryptophan methyl ester (**17**) showed no ICD. The acid−base binding constants (*K*) for (*R*)-**3**, (*S*)-**7**, and (*R*)-**10** with 4-vinylbenzoic acid obtained by ^{1}H NMR titration experiments support the speculation above; the *K* values decrease in the order **3** > **7** > **10** (see below). An amino group far from the chiral center (**11**) may not work well for inducing a helical conformation to show a clear ICD.

The results of the ICD studies for various chiral amino alcohols (**18**−**32**) are summarized in Table 2, and the typical CD spectra are shown in Figure 2B. In contrast to the ICD results for chiral amines, most chiral amino alcohols exhibited

Table 1. Signs of Split Cotton Effects and Molar Ellipticities ([θ]) for Poly-**1**−Amine Complexes[a]

| amine | first Cotton | | second Cotton | | third Cotton | |
	sign	$[\theta] \times 10^{-3}$ (λ)	sign	$[\theta] \times 10^{-4}$ (λ)	sign	$[\theta] \times 10^{-4}$ (λ)
(*R*)-**2**	+	2.47 (447.0)	−	3.06 (375.0)	+	2.91 (334.0)
(*S*)-**2**	−	2.40 (447.0)	+	2.86 (375.0)	−	2.71 (334.0)
(*R*)-**2**[b]	+	0.36 (447.0)	−	0.44 (375.5)	+	0.40 (334.0)
(*R*)-**2**[b,c]	+	1.40 (447.0)	−	1.33 (375.0)	+	0.88 (316.0)
(*R*)-**3**	+	1.45 (440.0)	−	1.26 (376.0)	+	1.30 (336.0)
(*S*)-**4**	*d*		+	0.14 (377.5)	−	0.14 (330.0)
(*R*)-**5**	+	3.94 (443.0)	−	2.68 (372.5)	+	2.70 (334.0)
(*R,R*)-**6**	*d*		−	0.30 (378.0)	+	0.28 (330.0)
(*S*)-**7**	+	0.89 (438.5)	−	0.85 (376.0)	+	0.89 (333.5)
(*R*)-**8**	*d*		−	0.113 (380.0)	+	0.099 (328.0)
(*R*)-**9**	*d*		−	0.11 (376.0)	+	0.10 (335.0)
(*R*)-**10**	*ca.* 0		*ca.* 0		*ca.* 0	
(*R*)-**10**[e]	*d*		+	0.096 (376.0)	−	0.053 (333.0)
(*R,R*)-**11**	*d*		+	0.06 (386.0)	−	0.12 (334.0)
(*S*)-**12**	+	0.83 (435.0)	−	1.20 (374.0)	+	1.21 (341.0)
13	+	0.97 (441.0)	−	2.04 (374.0)		*f*
(*R,R*)-**14**	*d*		+	0.082 (382.0)	−	0.089 (328.0)
(*S*)-**15**	*ca.* 0		*ca.* 0		*ca.* 0	
(*S*)-**16**	*ca.* 0		*ca.* 0		*ca.* 0	
L-(*S*)-**17**	*ca.* 0		*ca.* 0		*ca.* 0	

[a] All spectra were measured in DMSO at ambient temperature (*ca.* 18−20 °C) with poly-**1** (1.0 mg/mL); the molar ratio of a chiral amine to monomer units of poly-**1** was 50; [θ] (deg cm^2 dmol^{-1}) and λ (nm). [b] The molar ratio of a chiral amine to poly-**1** was 1. [c] In the film. [d] It could not be estimated due to the very weak Cotton effect. [e] The concentration of poly-**1** was 5.0 mg/mL. [f] It could not be measured because of overlap with the guests.

Table 2. Signs of Split Cotton Effects and Molar Ellipticities ([θ]) for Poly-**1**−Amino Alcohol Complexes[a]

| amine | first Cotton | | second Cotton | | third Cotton | |
	sign	$[\theta] \times 10^{-3}$ (λ)	sign	$[\theta] \times 10^{-4}$ (λ)	sign	$[\theta] \times 10^{-4}$ (λ)
(*R*)-**18**[b]	+	2.22 (437.0)	−	3.21 (373.0)	+	3.67 (330.0)
(*R*)-**19**	−	1.84 (442.0)	+	2.44 (374.0)	−	2.91 (331.0)
(*R*)-**20**	+	2.28 (444.0)	−	2.17 (374.0)	+	2.32 (333.0)
(*S*)-**21**	−	1.15 (444.0)	+	1.74 (374.0)	−	1.86 (334.0)
(*S*)-**22**[b]	−	3.06 (443.0)	+	3.30 (371.0)	−	3.65 (331.0)
(*S,S*)-**23**[c]	+	0.33 (422.0)	−	0.24 (352.0)	−	0.49 (317.0)
(1*R*,2*S*)-**24**	−	2.76 (439.0)	+	3.24 (372.0)	−	3.31 (331.0)
(1*R*,2*S*)-**25**	−	3.11 (439.0)	+	2.84 (374.0)	−	2.75 (332.0)
(*S*)-**26**	+	4.96 (429.0)	−	2.12 (374.0)		*d*
(1*S*,2*R*)-**27**	−	1.34 (444.0)	+	3.49 (373.0)	−	4.71 (329.0)
(1*R*,2*S*)-**28**	+	0.76 (444.0)	−	3.41 (374.0)	+	4.65 (328.0)
(1*S*,2*S*)-**29**	−	1.03 (439.0)	+	0.81 (373.0)	−	0.87 (330.0)
(8*R*,9*S*)-**30**	−	5.11 (439.0)	+	3.11 (376.0)		*d*
(8*S*,9*R*)-**31**	+	6.51 (448.0)	−	2.47 (385.0)		*d*
D-**32**[b]	−	2.03 (440.0)	+	2.08 (371.0)	−	2.33 (332.0)

[a] All spectra were measured in DMSO at ambient temperature (*ca.* 18−20 °C) with poly-**1** (1.0 mg/mL); the molar ratio of a chiral amine to poly-**1** was 50; [θ] (deg cm^2 dmol^{-1}) and λ (nm). [b] The molar ratio of a chiral amine to poly-**1** was 10. [c] It gave a different CD pattern compared with other chiral amines and amino alcohols. [d] It could not be measured because of overlap with the guests.

a very intense ICD irrespective of the bulkiness and type of the amino alcohols; two less bulky ethanolamines (**18** and **19**) and tertiary amino alcohols **26**, **30**, and **31** showed a significantly intense ICD. The cooperative hydrogen bond formation of the hydroxy group to a carboxy residue of poly-**1** as well as the acid−base interaction[39] must play an important role in the intense ICD. The importance of both hydroxy and amino groups of amino alcohols for the intense ICD is evidenced by the fact

(38) The calculations of a conformation of poly-**1**−(*S*)-**2** or (*S*)-**18** complex may be particularly interesting, for there are two possible helical conformations with a right- or left-handed helix in the main chain, whose free energies may differ from one another because they are diastereomers. The chiral amines should control a helical sense to one-handedness in excess since the poly-**1**−(*S*)-**2** or (*S*)-**18** complex showed a very intense ICD in the UV−visible region. The calculations are in progress.

(39) (a) Manabe, K.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1992**, *114*, 6940−6941. (b) Manabe, K.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1993**, *115*, 5324−5325. (c) Manabe, K.; Okamura, K.; Date, T.; Koga, K. *J. Org. Chem.* **1993**, *58*, 6692−6700.

Table 3. Polymerization of TrA and EA and ICD Results

monomer[a]	catalyst[b]	solvent	time (h)	temp (°C)	polymer		second Cotton[e]	
					yield (%)[c]	$\bar{M}_n \times 10^{-4 \, d}$	$[\theta] \times 10^{-4}$ (nm)[f]	$[\theta] \times 10^{-4}$ (nm)[g]
TrA	[Rh(nbd)Cl]$_2$	THF	3	30	56.5	4.6[h]	+3.21 (374)	−3.06 (375)
EA	WCl$_6$-n-Bu$_4$Sn	toluene	3	60	93.9	5.1	*ca.* 0	*ca.* 0
	MoCl$_5$-n-Bu$_4$Sn	toluene	24	60	30.1	1.3	−0.04 (375)[i]	+0.04 (332)[l]
	[Rh(nbd)Cl]$_2$	THF	20	30	92.5	21.5	+1.55 (374)[j]	−1.49 (376)[j]
							−2.62 (374)[i,k]	+2.19 (375)[k,l]

[a] TrA: [4-((triphenylmethoxy)carbonyl)phenyl]acetylene. EA: [4-((ethoxy)carbonyl)phenyl]acetylene. [b] [Monomer] = 0.5 M, [monomer]/[Rh or W] = 100, [monomer]/[Mo] = 50, [W or Mo]/[n-Bu$_4$Sn] = 1. [c] Methanol insoluble fraction. [d] Determined by GPC (polystyrene standards using THF as the eluent). [e] CD spectra were measured in DMSO at ambient temperature (ca. 18−20 °C) with poly-**1** derived from polyTrA or polyEA (1.0 mg/mL); the molar ratio of a chiral amine to carboxy residues of poly-**1** was 50. [f] (*S*)-**18** was used. [g] (*R*)-**2** was used. [h] Determined by GPC as its methyl ester. [i] (*R*)-**18** was used. [j] The polymer not completely hydrolyzed (73%) was used. [k] Completely hydrolyzed polymer was used. [l] (*S*)-**2** was used.

that the presence of excess (*S*)-2-aminobutane (**4**) and (*S*)-2-butanol resulted in very weak and no ICD, respectively. Poly-**1** recovered from the poly-**1**−(*S*)-**18** complex in DMSO by reprecipitation into diethyl ether did not show any ICD, but it showed almost the same ICD in the presence of (*S*)-**18** again.

The advantages of the present polyacetylene are not only its long-wavelength absorption, high sensitivity, and response to chiral amines, but also easy preparation into a film in which an excess one-handed helix of poly-**1** may be preferentially fixed in the presence of optically active amines and the two helical conformations may not be in dynamic equilibrium in the film. Actually, the poly-**1**−(*R*)-**2** complex (1:1 mol/mol) exhibited an ICD identical in pattern and sign to that in solution, and the intensity was greater than that observed in DMSO solution for the same molar ratio (see Table 1).

Effect of the Stereoregularity of Poly-1 on ICD. Stereoregularity of poly-**1** seems to be important for induction of a dynamic, helical structure of poly-**1** with chiral amines. To confirm this, stereoirregular poly((4-carboxyphenyl)acetylenes) were prepared with WCl$_6$-n-Bu$_4$Sn and MoCl$_5$-n-Bu$_4$Sn catalysts which are known to give *trans* and *cis* rich poly(phenylacetylenes), respectively.[30] However, these catalysts did not polymerize TrA, and therefore, a less bulky (4-(ethoxycarbonyl)phenyl)acetylene (EB) was used as a monomer and polymerized with these catalysts, followed by alkaline hydrolysis to give poly((4-carboxyphenyl)acetylenes). The polymerization results are summarized in Table 3 together with the ICD results with optically active **2** and **18** in DMSO. The ^{1}H NMR spectra of the polymers showed very broad resonances at 5.0−8.3 ppm, while the poly-**1** derived from polyEB prepared with the rhodium catalyst showed very sharp peaks in its ^{1}H NMR spectrum (see the supporting information), indicating that the polymers prepared with the WCl$_6$-n-Bu$_4$Sn and MoCl$_5$-n-Bu$_4$Sn catalysts may not be stereoregular in the main chain configuration and conformation. Moreover, the stereoirregular poly-**1** compounds showed very weak or almost no ICD in the 300−500-nm range, as shown in Table 3. These results clearly indicate that the regular main chain conformation must be essential for the formation of a helical conformation to exhibit an ICD with chiral amines and amino alcohols.

Relation between the Cotton Effect Signs and the Absolute Configuration of Chiral Amines and Amino Alcohols. As shown in Tables 1 and 2, all primary amines (**2**−**6**) and amino alcohols (**18**, **20**−**25**, **27**−**29**, **32**) of the same configuration gave the same Cotton effect signs. The only exception is 2-hydroxy-1-aminopropane (**19**) bearing an amino group on the carbon adjacent to the stereogenic center, which showed the opposite Cotton effect signs compared with the other primary amines and amino alcohols. The relationships between the Cotton effect signs and the absolute configurations of chiral primary amines and amino alcohols can be generalized as follows (Figure 5):
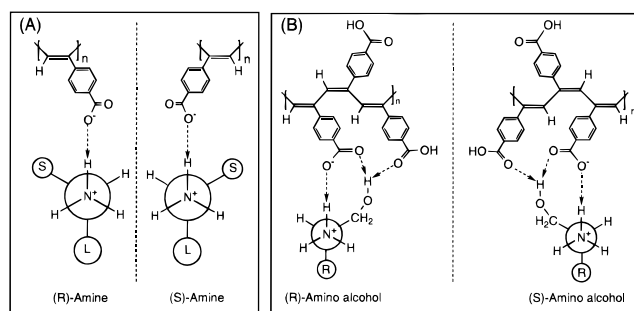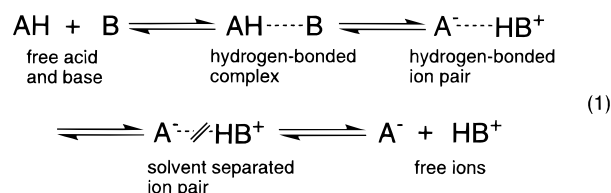

Figure 5. Proposed structures for the poly-**1**−amine (A) or amino alcohol (B) complexes and the relationships between the Cotton effect signs and the absolute configurations of primary amines and amino alcohols.

primary amines may be favorably complexed with poly-**1** to form an ion pair as described in Figure 5A, where the bulkiest substituent (L) is placed remote from the poly-**1** (*anti-staggered*) and the smaller alkyl group (S) and the hydrogen are in a *staggered* position, and therefore, the complexes with (*R*)- and (*S*)-amines may show an ICD with mirror images depending on the configuration. In the complexes, the helical sense (right- or left-handed) or the Cotton effect sign may be governed by the steric difference in the hydrogen (H) and the less-bulky substituent (S), and the bulky substituent (L) may contribute to an extent of a single-handedness, in other words, the ICD magnitude.

In an acid−base complexation, five species, free acid (AH) and base (B), hydrogen bonded complex, contact ion pair (or hydrogen bonded ion-pair), solvent separated ion pair, and free ions, are at equilibrium in solution (eq 1).[19b,32] In DMSO the equilibrium lies between the ion pairs and the free ions, and ion pairing has been shown to be predominant.[40]
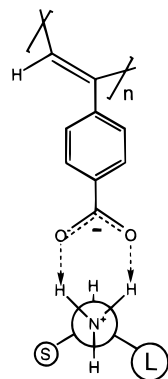
$$AH + B \rightleftharpoons AH\text{-----}B \rightleftharpoons A^-\text{-----}HB^+$$

free acid
and base   hydrogen-bonded   hydrogen-bonded
complex   ion pair

(1)

$$\rightleftharpoons A^-\text{---}/\!/HB^+ \rightleftharpoons A^- + HB^+$$

solvent separated   free ions
ion pair

Although acid−base complexations in solution have been studied extensively,[21m−v,41] a complete structural interpretation of the ion-pairing behavior in solution is still not completely solved,[40] whereas those in crystalline states have clearly been determined by X-ray analysis.[21b,n,o,p,s−v] Takenaka[19c] and Arnett[40] proposed an intermolecular, bidentate-type hydrogen bond

(40) Zingg, S. P.; Arnett, E. M.; McPhail, A. T.; Bothner-By, A. A.; Gilkerson, W. R. *J. Am. Chem. Soc.* **1988**, *110*, 1565−1580.

(41) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; VCH: New York, 1994; Chapter 6, pp 153−295.

Chart 4

Table 4. Structure Effect on Induced CD (Second Cotton; $[\theta] \times 10^{-4}$ deg cm^2 dmol^{-1}) for Poly-**1** (1.0 mg/mL)−Amine Complexes in DMSO and Binding Constants (K) for the Complexation of Amines with 4-Vinylbenzoic Acid

amines	$[\theta] \times 10^{-4}$ [a]	K (M^{-1})[b]
(*R*)-**2**	−3.06	57 ± 2
(*R*)-**3**	−1.26	146 ± 5
(*S*)-**4**	0.14	117 ± 5
(*S*)-**7**	−0.85	37 ± 2
(*R*)-**10**	*ca.* 0 (+0.10)[c]	5 ± 1
(*R*)-**18**	−3.21	509 ± 30

[a] Cited from Tables 1 and 2; the molar ratio of a chiral amine to poly-**1** was 50. [b] Estimated by ^{1}H NMR titrations in DMSO-d_6 with 4-vinylbenzoic acid as the model compound of poly-**1**. [c] Poly-**1** (5.0 mg/mL).

ion pair between 2-benzoylbenzoic acid and optically active primary amines and between (*R*)-mandelic acid and (*R*)-(1-phenylethyl)amine, respectively. A similar bidentate-type ion pair model may be applicable to the present system to explain the relation between the Cotton effect signs and the absolute configuration of chiral amines (Chart 4). The conformation of amine is closer to the *gauche-staggered* rather than to the *anti-staggered* form, and the helical sense appears to be controlled by the difference in the bulkiness of the L and S groups on the stereogenic center.

A similar model can be possible for primary amino alcohols, which may be complexed with the poly-**1** as shown in Figure 5B. The hydroxy group may participate in intermolecular hydrogen bonding with the carboxy group together with the acid−base ion pairing of the amino group.[42] A similar intermolecular hydrogen bonding can be seen in the crystal of the (1*S*,2*R*)-ephedrinium (*R*)-mandelate ion pair.[40] These cooperative interactions might enhance the complexation between poly-**1** and amino alcohols.[39] In the complexes, the direction and affinity of the hydroxy group for the hydrogen bond toward the carboxy group of poly-**1** may be the most important for controlling both the helical sense and an extent of the single-handedness, and therefore, the complexes with amino alcohols showed an intense ICD independent of the bulkiness of the substituent (R) with the same Cotton effect signs as the primary amines.[43]

The above relationship between the absolute configurations and the Cotton effect signs may be extended to secondary and/or tertiary amines and amino alcohols. However, there is not a general relation because of the limited amount of data, but a tendency was observed; **7** and **10**−**14** showed the opposite Cotton effect signs compared with those of the primary amines (**2**−**6**) if their configurations were the same, although the secondary amines **8** and **9** exhibited the same ICD sign as the primary amines. Tertiary amino alcohols (**26**, **30**, and **31**) also showed the opposite ICD signs to the primary amines. More examples and structural studies are needed for proposing a rationale for the chirality assignments of secondary and/or tertiary amines in the complexation with poly-**1**.

Although the CD exciton chirality method developed by Nakanishi and Harada[15] has been extensively applied for determining the absolute configurations of chiral molecules, the method requires the introduction of chromophores suitable for the exciton coupling at hydroxy or amino groups. The present ICD method using poly-**1** requires no derivatization and may have great potential for general use, although the theoretical basis is far less certain of depending on structural interactions than the quantum basis of the exciton chirality method.

^{1}H NMR Studies on the Complexation of Poly-1 with Amines and Amino Alcohols. As described above, the magnitude of ICDs of the poly-**1**−amine complexes depends on the bulkiness and type (primary, secondary, or tertiary) of the amines, while that of the poly-**1**−amino alcohol complexes is almost independent of these factors. It is likely that the complexation power of amines with poly-**1** in nonaqueous, aprotic polar solvents such as DMSO may be closely correlated with "basicity", in other words, binding affinity in the acid−base interaction which is in equilibrium (the proton transfer equilibrium) (see eq 1). The strengths of acids and bases in aprotic polar solvents are known to be influenced by many factors, for instance the electronic properties of the acids and bases, solvent properties, and ion-pair structures,[32,39] and in DMSO the equilibrium appears to be between the hydrogen-bonded ion pair and the free ions as mentioned above.[40] Therefore, it is particularly interesting to investigate the relation between the binding affinity of amines and amino alcohols to poly-**1** in the formation of acid−base complexes and the magnitude of the ICDs of the complexes. The results will contribute to the understanding of acid−base equilibria in aprotic polar solvents.[25,32,39,40]

We first attempted to estimate the binding constants (K) per monomer unit of poly-**1** to chiral amines and amino alcohols using ^{1}H NMR titrations, since the CD titrations[10] could not provide precise K values because of nonlinear changes in the Cotton effect intensity during the complexation of poly-**1** with an increasing amount of chiral amines (see below). However, it was difficult owing to the broadening of the peaks of chiral amines and amino alcohols and the overlapping in the resonances of poly-**1**. 4-Vinylbenzoic acid was then used as a model compound of poly-**1**, and K values for typical chiral amines ((*R*)-**2**, (*R*)-**3**, (*S*)-**4**, (*S*)-**7**, and (*R*)-**10**) and (*R*)-2-amino-1-propanol ((*R*)-**18**) were measured by using the standard ^{1}H NMR titrations in DMSO-d_6.[45]

Table 4 gives the K values of the amines and amino alcohol upon complexation with 4-vinylbenzoic acid together with the $[\theta]$ values for the second Cotton effect in the complexation with poly-**1** at [amine or amino alcohol]/[poly-**1**] = 50 in DMSO. ^{1}H NMR titrations were carried out under the conditions of constant [4-vinylbenzoic acid] with varying [amine or amino alcohol] at 22 °C.

(42) Grunwald, E.; Price, E. *J. Am. Chem. Soc.* **1964**, *86*, 2970−2977.

(43) Takenaka[19c,d] and Arnett[40] reported, however, that in solution five-membered, cyclic intramolecular hydrogen bonding[44] is preferred for β-amino alcohols including ephedrine, pseudoephedrine, alaninol, and leucinol in the presence of acids. Takenaka claimed that the amino alcohols may behave like secondary amines.[19c]

(44) Edund, U.; Holloway, C.; Levy, G. C. *J. Am. Chem. Soc.* **1976**, *98*, 5069−5073.

(45) Yashima, E.; Yamamoto, C.; Okamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 4036−4048.

The titration curves were analyzed by linear ((R)-**10**)[12a,45,46] and nonlinear ((R)-**2**, (R)-**3**, (S)-**4**, (S)-**7**, and (R)-**18**)[45,47] least-square methods by using a binding model with a 1:1 stoichiometry, and are in agreement with the 1:1 complexation. The 1:1 complexation was also confirmed by the continuous variation plot (Job plot)[48] for the 4-vinylbenzoic acid—(R)-**18** complex. The maximal complex formation occurred at around 0.5 mol fraction of (R)-**18**.

Comparison of the K values in DMSO-d_6 indicates a higher affinity of the amino alcohol ((R)-**18**) to 4-vinylbenzoic acid than those of the other amines and the binding constants increased in the order **10** ≪ **7** < **2** < **4** < **3** < **18** (tertiary < secondary < primary amines). The results are very consistent with the basicity order of amines in DMSO (tertiary < secondary < primary amines), for instance, the reported pK_a values of the conjugated acids of alkylamines in DMSO increase in the following order: Me$_3$N (8.4), Et$_3$N (9.0) < Me$_2$NH (10.3), Et$_2$NH (10.5) < MeNH$_2$ (11.0), EtNH$_2$ (11.0).[32a,49] However, the [θ] values for the second Cotton in the complexation with poly-**1** at [amine or amino alcohol]/[poly-**1**] = 50 increased in the order **10** ≪ **4** < **7** < **3** < **2** < **18** (see Tables 1 and 2). More basic, but less bulky amine **4** exhibited a weaker ICD compared with **2**, **3**, and **7**. The results clearly indicate that both basicity and bulkiness of the amines are important factors for the ICD.[50]
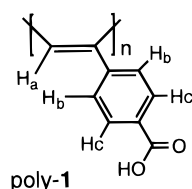
poly-**1**

The binding affinity of amines to poly-**1** can be indirectly evaluated from dynamic ^{1}H NMR experiments of the mixtures at high temperature ranges (30–110 °C) (see the Supporting Information). Spin–spin relaxation time (T_2) is sensitive to molecular motions,[51] and therefore it is informative to know how the mobility of poly-**1** changes upon complexation with chiral amines. The resonances of the methine H$_a$ and aromatic H$_b$ and H$_c$ protons of free poly-**1** exhibited sharp peaks even at 30 °C, while those of the complexes with amines, especially with the amino alcohol (R)-**18**, were much broadened and almost no peak was detected in the 5–8 ppm range even at 70 °C. These results indicate that the mobility of the poly-**1** was

(46) Kelly, T. R.; Kim, M. H. *J. Am. Chem. Soc.* **1994**, *116*, 7072–7080.

(47) (a) Sawada, M.; Okumura, Y.; Shizuma, M.; Takai, Y.; Hidaka, Y.; Yamada, H.; Tanaka, T.; Kaneda, T.; Hirose, K.; Misumi, S.; Takahashi, S. *J. Am. Chem. Soc.* **1993**, *115*, 7381–7388. (b) Albert, J. S.; Goodman, M. S.; Hamilton, A. D. *J. Am. Chem. Soc.* **1995**, *117*, 114–1144. (c) Sawada, M.; Takai, Y.; Yamada, H.; Hirayama, S.; Kaneda, T.; Tanaka, T.; Kamada, K.; Mizooka, T.; Takeuchi, S.; Ueno, K.; Hirose, K.; Tobe, Y.; Naemura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7726–7736.

(48) Job, P. *Ann. Chim. Ser.* **1928**, *9*, 113–134.

(49) The basicity of amines in aprotic polar solvents cannot be deduced from the pK_a values of amines in water; the pK_a values of the conjugated acids of alkylamines in water increase in the following order: MeNH$_2$ < Me$_3$N < Me$_2$NH. (a) Pine, S. F. *Organic Chemistry*, 5th ed.; McGraw-Hill: New York, 1987; Chapter 7. (b) Benoit, R. L.; Mackinnon, M. J.; Bergeron, L. *Can. J. Chem.* **1981**, *59*, 1501–1504.

(50) Takenaka et al. measured binding constants of analogous chiral acid—base complexations of *para*-substituted (S)-1-phenylethylamine derivatives and (R)- or (S)-indane-1-carboxylic acids by means of IR spectroscopy in CCl$_4$.[19e] They observed that the binding constants increased in the order tertiary ≪ primary ≤ secondary amines and claimed that the binding constants were affected by inductive and resonance effects of the substituent at the *para* position rather than by steric hindrance.

(51) Wüthrich, K. *NMR of Proteins and Nucleic Acids*; Wiley: New York, 1986; Chapter 1.

unequivocally restricted due to binding with the amines, especially with (R)-**18**. The half line width may be used as a probe for estimating the interaction occurring in the acid—base complexation, since the half line width ($\Delta\nu_{1/2}$) of an NMR resonance is simply related to T_2 by the following eq 2:[51]

$$\Delta\nu_{1/2} = 1/2\pi T_2 \qquad (2)$$

T_2 is correlated with the dynamic processes in the molecule under study. Comparison of the changes in the half line width of H$_a$–H$_c$ proton resonances of poly-**1** in the presence of (S)-**2** and (R)-**18** suggests that (R)-**18** may bind more strongly with poly-**1** than (S)-**2**. Similar changes in the half line width of poly-**1** were also observed in dynamic ^{1}H NMR experiments of the mixtures of poly-**1** with (R)-**3**, (S)-**7**, or (R)-**10** at temperature ranges of 30–70 °C (see the Supporting Information); the half line width of H$_a$–H$_c$ proton resonances of poly-**1** increased in the order of **10** < **7** < **3** at the temperature ranges, in good agreement with the K values obtained with the ^{1}H NMR titrations (Table 4).

Effect of Solvents on ICD. As mentioned previously, the strengths of acids and bases in aprotic organic solvents are known to be influenced by solvent properties.[19e,32,39,40] In order to investigate the solvent effects on the ICD, CD spectra of poly-**1** in the presence of optically active amines ((R)-**2**, (R)-**3**, (S)-**7**, and (R)-**10**) and amino alcohol ((R)-**18**) were measured in DMF, CH$_3$CN/DMSO (3/1, v/v), and CHCl$_3$/DMSO (3/1, v/v) (Table 5). Because of poor solubility of poly-**1** in CH$_3$CN and CHCl$_3$, DMSO was used as a component for dissolving poly-**1**, and the concentration of poly-**1** in the CHCl$_3$/DMSO mixture was set at 0.125 mg/mL. The complexes in DMF and CH$_3$-CN/DMSO gave much weaker ICDs compared with those in pure DMSO, although the Cotton effect signs agreed with those in DMSO except for the poly-**1**—(R)-**10** complex in DMF, which exhibited smaller ICD with an opposite Cotton effect sign. On the other hand, in the mixture of CHCl$_3$/DMSO, the complexes showed rather intense ICDs by considering the lower concentration of poly-**1** in CHCl$_3$/DMSO (0.125 mg/mL) than in other solvents (1.0 mg/mL) (see also the figure showing the concentration effect on the ICD in DMSO in the Supporting Information). The differences in the magnitude of the ICDs may be ascribed to the difference in binding constants in the acid—base equilibrium or ion-pair structures in these solvents.[32b] In polar DMSO, DMF, and CH$_3$CN (the dielectric constant ϵ_r > 30) ion association is weak and the hydrogen bonded ion pair is predominant,[32,39,40] while in less polar CHCl$_3$ (ϵ_r = 4.8) ion association is strong and a contact-ion pair may be a major specie.[21m,39] Therefore, relatively intense ICDs in CHCl$_3$/DMSO seems to be caused by a strong interaction of the chiral amines with poly-**1** within the contact ion pairs.

Complexation Dynamics. An indication of dynamics of the helix formation of poly-**1** upon complexation with optically active amines and amino alcohols was obtained through CD, ORD, and ^{1}H NMR titration experiments. Figure 6 shows the CD titration curves during the complexation of poly-**1** with (S)-**2**, (S)-**18**, and (8R,9S)-**30** in DMSO. The CD intensity increased with an increase in the concentration of the chiral amines and amino alcohols and reached an almost constant value. Particularly, the magnitude of the ICD of the complex between (S)-**18** and poly-**1** (Figure 6B) dramatically changed with an increase in the amount of (S)-**18**; at around the region where the molar ratio of (S)-**18** to poly-**1** is from 0.5 to 1, the change in the CD signal was abrupt, probably because the polymer may start to form a predominantly one-handed helical structure at around this region.

Table 5. Solvent Effect on Molar Ellipticities ([θ]) for Poly-**1**−Amine Complexes[a]

solvent (v/v)	ϵ_r[b]	amine	first Cotton sign	first Cotton [θ] × 10⁻³ (λ)	second Cotton sign	second Cotton [θ] × 10⁻⁴ (λ)	third Cotton sign	third Cotton [θ] × 10⁻⁴ (λ)
DMSO	46.45	(R)-**2**	+	2.47 (447.0)	−	3.06 (375.0)	+	2.91 (334.0)
		(R)-**3**	+	1.45 (444.0)	−	1.26 (376.0)	+	1.30 (336.0)
		(S)-**7**	+	0.89 (438.5)	−	0.85 (376.0)	+	0.89 (333.5)
		(R)-**10**		*ca.* 0		*ca.* 0		*ca.* 0
		(R)-**10**[c]		d	+	0.10 (376.0)	−	0.05 (333.0)
		(R)-**18**	+	2.22 (437.0)	−	3.21 (373.0)	+	3.67 (330.0)
DMF	36.71	(R)-**2**		d	−	0.11 (375.0)		d
		(R)-**3**		d	−	0.07 (378.0)		d
		(S)-**7**		d	−	0.12 (385.0)	+	0.10 (335.5)
		(R)-**10**		d	−	0.05 (384.0)	+	0.09 (321.5)
		(R)-**18**		d	−	0.15 (381.0)	+	0.24 (328.0)
CH₃CN/DMSO[e] (3/1)	35.94/46.45	(R)-**2**		d	−	0.12 (375.0)	+	0.13 (333.0)
		(R)-**3**		d	−	0.08 (384.5)		d
		(S)-**7**		d	−	0.10 (377.0)	+	0.15 (329.0)
		(R)-**10**		d	+	0.21 (386.0)	−	0.25 (343.0)
		(R)-**18**[f]		d	−	0.11 (378.0)	+	0.14 (327.0)
CHCl₃/DMSO[g] (3/1)	4.81/46.45	(R)-**2**		d	−	0.42 (383.0)	+	0.31 (336.0)
		(R)-**3**		d	−	0.37 (378.0)	+	0.35 (331.0)
		(S)-**7**[h]		d	−	0.27 (377.0)	+	0.28 (337.0)
		(R)-**10**		*ca.* 0		*ca.* 0		*ca.* 0
		(R)-**18**[h]	+	3.33 (442.0)	−	2.72 (380.0)	+	2.59 (333.0)

[a] All spectra were measured at ambient temperature (*ca.* 18−20 °C) with poly-**1** (1.0 mg/mL); the molar ratio of a chiral amine to poly-**1** was 50; [θ] (deg cm² dmol⁻¹) and λ (nm). [b] Relative permittivity (dielectric constant) for the pure liquid at 25 °C. The values are cited from ref 32b. [c] The concentration of poly-**1** was 5 mg/mL. [d] It could not be estimated due to the very weak Cotton effect. [e] Acetonitrile (CH₃CN)/DMSO = 3 (v/v). [f] Because of the low solubility of the poly-**1**−(R)-**18** complex, the molar ratio of a chiral amine to poly-**1** was set at 5. [g] CHCl₃/DMSO = 3 (v/v); because of the low solubility of poly-**1** in the solvent, the concentration of poly-**1** was set at 0.125 mg/mL. [h] Because of the low solubility of the poly-**1**−(S)-**7** or poly-**1**−(R)-**18** complex in the solvent, the molar ratio of a chiral amine to poly-**1** was set at 10.
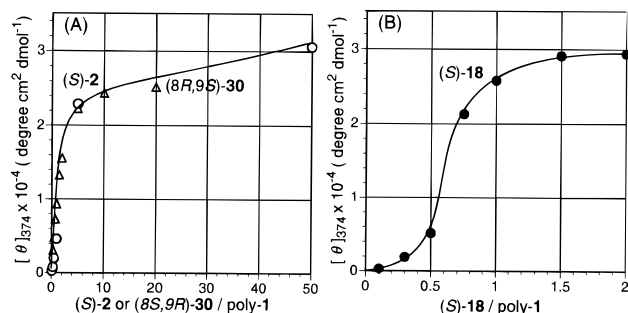

Figure 6. Titration curves of the absolute values of ICD at 374 nm in the complexation of poly-**1** (1.0 mg/mL) with (S)-**2** (○), (8R,9S)-**30** (△) (A), and (S)-**18** (●) (B) in DMSO at ambient temperature (*ca.* 18−20 °C).
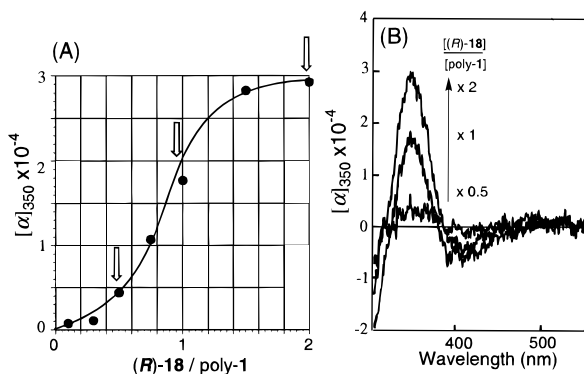

Figure 7. Titration curves of the absolute values of ORD at 350 nm in the complexation of poly-**1** (1.0 mg/mL) with (R)-**18** (●) (A) in DMSO at ambient temperature (*ca.* 18−20 °C). The changes of ORD spectra at [(R)-**18**]/[poly-**1**] = 0.5, 1, and 2 marked by arrows in part A are also shown in B.

Figure 8. Changes of ¹H NMR spectra (A) and $\Delta\nu_{1/2}$ values of proton resonances (H$_a$ (△), H$_b$ (□), H$_c$ (○)) of poly-**1** (15 mg/mL) in complexation with (R)-**18** in DMSO-d_6 at 50 (A and B) and 70 °C (C).

as the CD signal around the same molar ratio and the specific rotation of the complex ([α] at 350 nm) reached up to 30 000°. The value is so high because the Cotton effect is near in the wavelength.

Measurements of changes in ¹H NMR spectra during the complexation of poly-**1** with (R)-**18** also support the above speculation. In the presence of an increasing amount of (R)-**18**, the resonances of the H$_a$−H$_c$ protons of poly-**1** were more broadened (Figure 8A) and the half line width ($\Delta\nu_{1/2}$) for the resonances of poly-**1** significantly increased (Figure 8B). The marked broadening of these proton resonances of poly-**1** indicates that the mobility of the poly-**1** was restricted, probably due to the formation of a one-handed helical conformation upon binding with (R)-**18**.[52]

A similar titration experiment was then carried out between poly-**1** and (R)-**18** with ORD spectroscopy instead of CD (Figure 7). The figure showed a curve similar to the CD titration curve; optical rotation of the complex dramatically increased as well
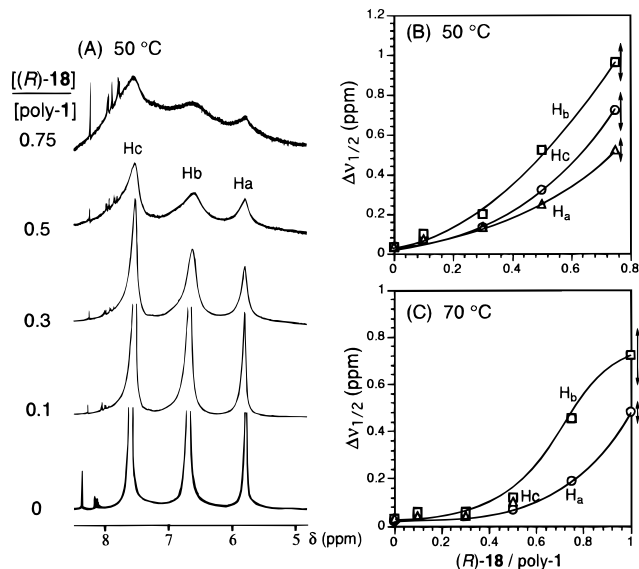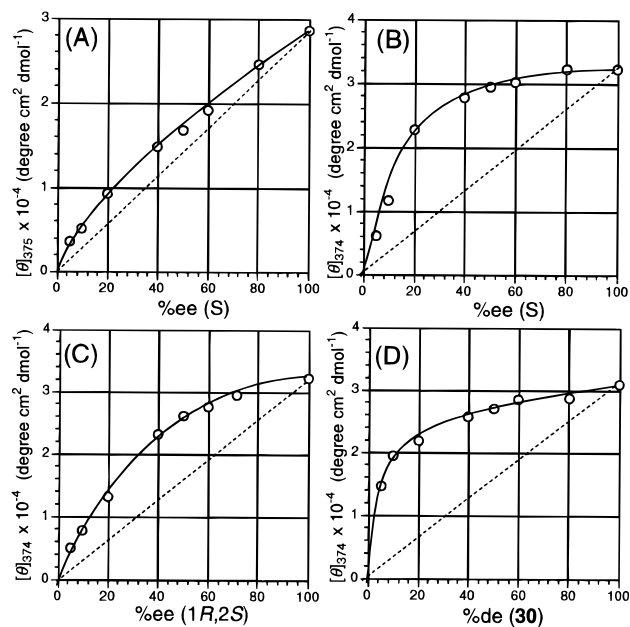
Figure 9. Nonlinear effects between the absolute values of ICD for the second Cotton effect and percent ee of **2** (*S* rich, A), **18** (*S* rich, B), and **24** ((1*R*,2*S*) rich, C) and percent de of **30** and **31** (**30** rich, D) in the complexation with poly-**1** in DMSO; the molar ratio of **2**, **24**, and **30/31** to monomer units of poly-**1** was 50 and the molar ratio of **18** to monomer units of poly-**1** was 5. The dotted line has been drawn between the origin and the point corresponding to an ee or de of 100%.

Positive Nonlinear Effect and Chirality Amplification. In the course of studies described above, optically pure amines and amino alcohols were used for all experiments. However, an interesting phenomenon was found in the complexation of poly-**1** with partially resolved amines or amino alcohols; the complex formation of poly-**1** with partially resolved amines or amino alcohols displays a unique, positive nonlinear relationship, in other words, chirality amplification,[26,54] between the ee of amines and amino alcohols and the observed ellipticity of the Cotton effects as shown in Figure 9. CD intensities of poly-**1**, corresponding to the helical sense excesses, are out of proportion to the ee's of amines and amino alcohols, showing a convex deviation from the linearity through a wide range of ee values of the amine (**2**) and amino alcohols (**18**, **24**, and **30/31**) in DMSO.[55] The extent of the departure from linearity was greater for the amino alcohols (**18**, **24**, and **30/31**) (Figure 9B−D) than the amine (**2**) (Figure 9A). Typically, when poly-**1** was dissolved in DMSO with 50-fold excess 2-amino-1-propanol (**18**) of 50% ee (*S* rich), the complex showed as intense CD as

(52) The changes in the spin−spin relaxation time (*T*₂) or the half line width (Δν₁/₂) are correlated with the dynamic processes of the particular nucleis in the molecule,[51] in other words, the local mobility changes of the molecule, but it may not be directly correlated with the dynamic processes of a global conformational change in the molecule. The change of the viscosity index α in the intrinsic viscosity−molecular weight relationship ([η] = *KM*^α) will be useful for studying a global conformational change[53] of poly-**1** during the complexation with chiral amines or amino alcohols.

(53) (a) Fujiki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7824−7825. (b) DuPré, D. B.; Wang, H. *Macromolecules* **1992**, *25*, 7155−7159. (c) Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C.; Peterson, N. C.; Lifson, S. *Macromolecules* **1995**, *28*, 1016−1024. (d) Okamoto, N.; Mukaida, F.; Gu. H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C.; Peterson, N. C.; Lifson, S. *Macromolecules* **1996**, *29*, 2878−2884.

(54) The nonlinear effects are now frequently observed in asymmetric synthesis, and the origin of the nonlinear effects has been elucidated at a molecular level; see ref 26g. However, a very few examples have been reported on the nonlinear effect in polymer synthesis. See ref 26h−l for examples.

(55) Exactly, **30** and **31** are not enantiomers, but diastereomers, and therefore, de was used in Figure 9D.
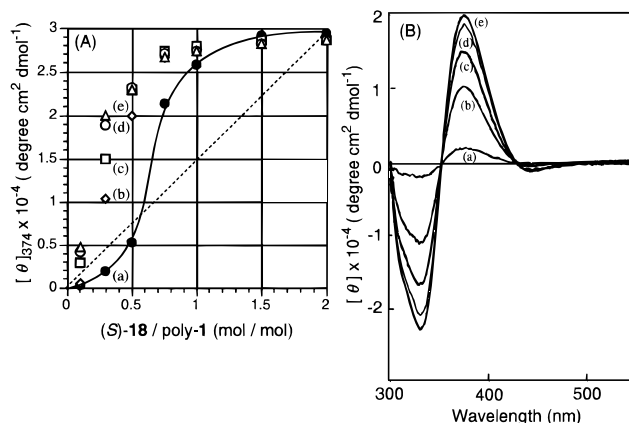

Figure 10. Amplification of ICD by the addition of achiral 2-amino-ethanol (**33**) in the complexation with poly-**1** (A). The solid line (●) represents a titration curve of [θ]₃₇₄ in the complexation between poly-**1** and (*S*)-**18** (see Figure 6B). **33** was added into the solution of poly-**1**−(*S*)-**18** complex; the molar ratio of **33** to (*S*)-**18** was 1 (◇, b), 2 (□, c), 3 (○, d), and 5 (△, e). The dotted line has been drawn to the origin and the point corresponding to [θ]₃₇₄ at [(*S*)-**18**]/[poly-**1**] = 2. The changes of ICD spectra (a−e in A) are also shown in B.

that of 100% ee (Figure 9B). The excess enantiomer bound to the polymer may induce an excess of a single-handed helix (right- or left-handed helix) in spite of its proportion, which will result in a more intense induced CD than that expected from the ee of **18**.[56] Green et al. recently reported a parallel effect in a polyisocyanate with the chiral pendants covalently bound.[26k] This was termed "majority rule" by excess enantiomers.[57]

A more interesting phenomenon of the chirality amplification was observed in the CD titrations during the complexation of poly-**1** in the presence of a small amount of (*S*)-**18** with achiral, optically inactive amines such as 2-aminoethanol (**33**) in DMSO. The CD titrations were carried out as follows (Figure 10A): an increasing amount of achiral **33** was added to the samples containing a constant amount of poly-**1** (*ca.* 1 mg/mL) in the presence of increasing concentrations of (*S*)-**18** ([(*S*)-**18**]/[poly-**1**] = 0.1, 0.3, 0.5, 0.75, 1.0, 1.5, and 2) which had been prepared for the CD titration experiments as shown in Figure 6B. The degree of chirality amplification is significant at [(*S*)-**18**]/[poly-**1**] = 0.3 and 0.5. For instance, addition of **33** to the solution of poly-**1**−(*S*)-**18** (molar ratio, 0.3:1) (which showed, in the absence of **33**, a very weak ICD (a in Figure 10, parts A and B) because of a lack of a helical conformation of the poly-**1**) caused a dramatic increase of the magnitude of the Cotton effect (b−e in Figure 10, parts A and B). A mixture of poly-**1**, (*S*)-**18**, and **33** (e in Figure 10B, molar ratio, 1:0.3:5) showed *ca.* ten times larger ellipticity of the second Cotton effect than that of the original poly-**1**−(*S*)-**18** mixture (a in Figure 10B, molar ratio 0.3:1). The increase of the Cotton effect intensity suggests the formation of a predominantly one-handed helix upon complexation with the achiral **33**. This may be the first example of the chirality amplification by an achiral molecule through

(56) The departure from linearity was found to be sensitive on the mixing manner of (*R*)- and (*S*)-amines with poly-**1**, and the curve in Figure 9A was somewhat different from the previously reported one.[17] See Experimental Section in detail.

(57) There may be another way to explain the positive nonlinear effect—that is the possible exclusion of one enantiomer by the helical sense formed by the excess enantiomer. This is not possible in Green's covalent system and requires further experiments. If this is the case, the polymer could act as a chiral filter for nonracemic amines or amino alcohols of less than 100% ee.
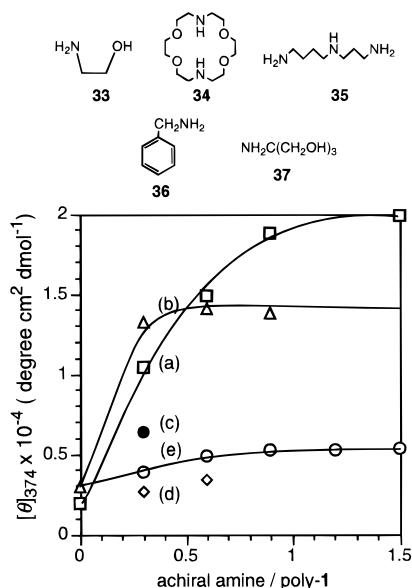
Figure 11. Amplification of ICD by the addition of achiral amines **33** (a, □), **34** (b, △), **35** (c, ●), **36** (d, ◇), and **37** (e, ○) in the complexation with poly-**1** (1.0 mg/mL) in DMSO at ambient temperature (*ca.* 18–20 °C). Achiral amines were added into the solution of poly-**1**−(*S*)-**18** complex ([(*S*)-**18**]/[poly-**1**] = 0.3 (mol/mol)).

the prevailing helix formation due to an acid−base interaction.[58] The existence of **33** on poly-**1** due to its strong chelation (binding) must facilitate the induction of the one-handed helical structure on poly-**1**. This phenomenon is similar to that observed for the copolymers of an optically active phenylacetylene with achiral phenylacetylene derivatives bearing a bulky substituent at the *para* position.[24f]

The coexistence of other achiral amines (**34**−**36**) or an amino alcohol (**37**) with (*S*)-**18** also induced an increased excess of one helical sense of poly-**1** as evidenced by the increase in optical activity. The formation of a predominantly one-handed helix upon addition of achiral compounds into the solution of poly-**1**−(*S*)-**18** (molar ratio 0.3:1) in DMSO was followed by measuring the changes in the ICD intensity at 374 nm (Figure 11). Because of the solubility limit of **35** in the presence of poly-**1** in DMSO, a larger amount of **35** could not be used. Although all achiral compounds enhanced the ICD values depending on the structures of the molecules, the extent of an excess of one helical sense of poly-**1** is significant for **33** and the Crown ether derivative **34**. It seems to be of great interest that the achiral **34** existing along the helical poly-**1** through an acid−base complexation with the poly-**1** may be in a chiral situation and may show chiral recognition ability, for instance to amino acids. Further investigation along this line is now in progress.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled onto LiAlH$_4$ under nitrogen. Toluene was distilled from sodium benzophenone ketyl under nitrogen. These solvents were distilled under high vacuum just before use. DMF and

---

(58) Green et al. reported a similar phenomenon. They found a dramatic effect of a small amount of chiral comonomer during the formation of an excess of one helical sense of a copolymer in the copolymerization of optically active isocyanate with achiral hexyl isocyanate. The obtained copolymer showed optical activity larger than that expected from the content of the feed chiral monomer. This can be considered as a typical example of the chirality amplification in a polymer.[26j,k] For other examples, see ref 24f: (a) Carlini, C.; Ciardelli, F.; Pino, P. *Makromol. Chem.* **1968**, *119*, 244−248. (b) Farina, M. *Top. Stereochem.* **1987**, *17*, 84−87. (c) Ciardelli, F.; Salvadori, P. *Pure Appl. Chem.* **1985**, *57*, 931−940.

DMSO were dried over calcium hydride and distilled under reduced pressure. Acetonitrile and chloroform were dried over calcium hydride and distilled. These solvents were stored under nitrogen over molecular sieves 4 Å (Nacalai Tesque). CDCl$_3$ (99.8 atom % D, Nacalai Tesque), CD$_3$CN (99.8 atom % D, Nippon Sanso), and DMSO-d_6 (99 atom % D, Aldrich) were dried over molecular sieves 4 Å and stored under nitrogen. All solvents used for measurements of CD and NMR spectra were purged with argon prior to use.

Bis(triphenylphosphine)palladium dichloride and [(norbornadiene)-rhodium(I) chloride]$_2$ [Rh(nbd)Cl]$_2$ were purchased from Aldrich and used as received, and MoCl$_5$ and WCl$_6$ were purchased from Mitsuwa Chemical (Osaka, Japan) and used as received. Ethyl 4-iodobenzoate, tetrabutylammonium fluoride (1.0 M in THF), and triphenylmethyl chloride were obtained from Tokyo Kasei (Japan). Triphenylphosphine and copper(I) iodide were from Kishida (Osaka, Japan). (Trimethylsilyl)acetylene was supplied from Shinetsu Chemical (Tokyo, Japan). (*R*)- and (*S*)-**2** were purchased from Yamakawa Chemical (Tokyo, Japan). Other optically active amines and amino alcohols were available from Aldrich.

[4-((Triphenylmethoxy)carbonyl)phenyl]acetylene (TrA). To a mixture of ethyl 4-iodobenzoate (25 g, 0.091 mol), bis(triphenylphosphine)palladium dichloride (0.25 g, 0.36 mmol), triphenylphosphine (0.38 g, 1.45 mmol), and copper(I) iodide (0.41 g, 2.2 mmol) in triethylamine (300 mL) was added (trimethylsilyl)acetylene (19.2 mL, 0.14 mol). The reaction mixture was stirred under nitrogen at room temperature for 15 h. After filtration, the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane−ethyl acetate (1/2, v/v). After the solvent was removed under reduced pressure, the resulting ethyl [4-(trimethylsilyl)ethynyl]benzoate was dissolved in ethanol (60 mL), and 1 N NaOH (90 mL) was added to the solution at 0 °C. The solution was stirred at 0 °C for 2 h and at room temperature overnight, then washed with ether (2 × 150 mL), and the aqueous layer was acidified with 1 N HCl. The precipitated solid was extracted with ether (500 mL), and the ether layer was washed with water (2 × 50 mL) and dried over MgSO$_4$. After filtration, the solvent was removed by evaporation. The resulting (4-carboxyphenyl)-acetylene was dissolved in the mixture of toluene (52 mL) and triethylamine (25 mL), and to this solution was added triphenylmethyl chloride (16.7 g, 0.060 mol). The solution was stirred at room temperature for 2 h and then heated at 50 °C for 5 h (the solution should not be heated under reflux because of the formation of byproducts). After filtration, the solvent was removed by evaporation and the crude residue was purified by recrystallization from hexane−benzene (9/1, v/v) to give 5.7 g of TrA as colorless crystals in 30% yield based on ethyl 4-iodobenzoate (mp 159.0−160.5 °C). TrA thus obtained was used for polymerization immediately after purification. IR (KBr): 1721 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$): δ 3.24 (s, ≡CH, 1H), 7.26−7.45 (m, aromatic, 15H), 7.56 (d, aromatic, 2H), 8.06 (d, aromatic, 2H). Anal. Calcd for C$_{28}$H$_{20}$O$_2$: C, 86.57; H, 5.19. Found: C, 86.58; H, 5.28.

[4-(Ethoxycarbonyl)phenyl]acetylene (EA). To a solution of ethyl [4-(trimethylsilyl)ethynyl]benzoate (12.5 g, 0.051 mol) prepared above in THF (10 mL) was added tetrabutylammonium fluoride (150 mL) in THF (1.0 M). The solution was stirred under nitrogen at room temperature for 20 min before evaporating the solvent. The crude product was diluted with ether, and the solution was washed with 1% aqueous HCl and water, and then dried over MgSO$_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel with hexane−ethyl acetate (2/1, v/v). After the solvent was evaporated, the residue was distilled under reduced pressure (bp 56−59 °C/(0.15 mmHg)) to give EA (3.8 g, 43%). IR (neat): 1721 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$): δ 1.31 (t, CH$_3$, 3H), 3.23 (s, ≡CH, 1H), 4.38 (q, CH$_2$, 2H), 7.56 (d, aromatic, 2H), 8.00 (d, aromatic, 2H).

Polymerization. Polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere with [Rh(nbd)Cl]$_2$, WCl$_6$-n-Bu$_4$Sn, or MoCl$_5$-n-Bu$_4$Sn as catalysts. A typical polymerization procedure is described below.

Monomer TrA (3.5 g, 9.0 mmol) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation−flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and THF was added with a syringe. To this was added a solution of [Rh(nbd)Cl]$_2$ in THF at 30

°C. The concentrations of the monomer and the rhodium catalyst were 0.5 and 0.005 M, respectively. The color of the mixture changed to dark red within 1 h. After 3 h, the resulting polymer was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuo at 50 °C for 2 h. The poly(TrA) was solvolyzed in methanol (270 mL) containing a small amount of HCl, and the solution was stirred for 3 h at room temperature. After filtration, the mixture was concentrated to *ca.* one-fifth of its original volume and the resulting poly((4-carboxylphenyl)acetylene) (poly-**1**) was poured into a large amount of ether, collected by centrifugation, and dried in vacuo at 50 °C for 3 h (0.77 g, 59% yield). Poly-**1** was soluble in DMSO, DMF, and dimethylacetamide (DMA), but insoluble in chloroform, acetonitrile, THF, and acetone. Conversion of poly-**1** into the methyl ester was carried out with CH_2N_2 in ether solution according to the method reported previously.[59] The molecular weight (M_n) of the methyl ester of poly-**1** was estimated to be 46 000 as determined by gel permeation chromatography (GPC) (polystyrene standards with THF as the eluent). The elemental analysis of the polymer agreed satisfactorily with the calculation.

Spectroscopic data of poly-**1**: IR (KBr) 1686 ($\nu_{C=O}$); ^{1}H NMR (DMSO-d_6, 60 °C) δ 5.82 (s, =CH, 1H), 6.70 (singlet-like, aromatic, 2H), 7.56 (singlet-like, aromatic, 2H); ^{13}C NMR (DMSO-d_6, 60 °C) δ 126.8, 129.0, 129.7, 145.5 (aromatic), 132.0, 138.5 (C=C), 166.5 (C=O). Anal. Calcd for $(C_9H_6O_2 \cdot \frac{1}{2}H_2O)_n$: C, 69.67; H, 4.50. Found: C, 69.22; H, 4.09.

Poly((4-carboxyphenyl)acetylenes) with a different stereostructure were prepared by a different route; [4-(ethoxycarbonyl)phenyl]acetylene (EA) (0.88 g in toluene, 1.1 M) was polymerized with WCl_6-*n*-Bu_4Sn (1/1 mol/mol, [EA]/[WCl_6] = 100) or $MoCl_5$-*n*-Bu_4Sn (1/1 mol/mol, [EA]/[$MoCl_5$] = 50) in dry toluene at 60 °C. The resulting polymers were poured into a large amount of methanol, collected by filtration, and dried in vacuo at 50 °C for 2 h. The polymers were converted to poly((4-carboxyphenyl)acetylenes) by hydrolysis of the ester groups in THF−aqueous NaOH (10 N) (4/1, v/v). The hydrolyzed polymer was collected by centrifugation and dissolved in a small amount of distilled water. The aqueous solution was acidified with 1 N aqueous HCl, and the precipitated poly((4-carboxyphenyl)acetylene) was collected by centrifugation and dried in vacuo at 50 °C for 3 h. Conversion of poly-EA obtained with [Rh(nbd)Cl]₂ in THF at 30 °C into poly((4-carboxyphenyl)acetylene) was done in the same way as described above, but the ^{1}H NMR spectrum of the hydrolyzed polymer showed that it contained *ca.* 30% of the ethyl group. Complete hydrolyzed polymer was obtained by further treatment of the polymer in an alkaline−THF solution. The detailed polymerization results are shown in Table 3.

Spectroscopic data of poly-EA obtained with WCl_6-*n*-Bu_4Sn: IR (KBr) 1727 ($\nu_{C=O}$); ^{1}H NMR (CDCl₃, 60 °C) δ 1.25 (broad singlet, CH₃, 3H), 4.30 (broad singlet, CH₂, 2H), 5.6−8.2 (br, =CH and aromatic, 5H); ^{13}C NMR (CDCl₃, 50 °C) δ 14.4 (broad singlet, CH₃), 61.5 (broad singlet, CH₂), 124−150.5 (br, C=C and aromatic), 166.0 (br, C=O). Anal. Calcd for $(C_{11}H_{10}O_2)_n$: C, 75.84; H, 5.79. Found: C, 75.05; H, 5.77.

Spectroscopic data of poly-EA obtained with $MoCl_5$-*n*-Bu_4Sn: IR (KBr) 1727 ($\nu_{C=O}$); ^{1}H NMR (CDCl₃, 60 °C) δ 1.35 (broad singlet, CH₃, 3H), 4.30 (broad singlet, CH₂, 2H), 5.5−8.2 (br, =CH and aromatic, 5H). Anal. Calcd for $(C_{11}H_{10}O_2)_n$: C, 75.84; H, 5.79. Found: C, 74.01; H, 5.98.

Spectroscopic data of poly-EA obtained with [Rh(nbd)Cl]₂: IR (KBr) 1727 ($\nu_{C=O}$); ^{1}H NMR (CDCl₃, 60 °C) δ 1.32 (s, CH₃, 3H), 4.30 (s, CH₂, 2H), 5.76 (s, =CH, 1H), 6.68 (s, aromatic, 2H), 7.62 (s, aromatic, 2H). ^{13}C NMR (CDCl₃, 50 °C) δ 14.2 (s, CH₃), 61.0 (s, CH₂), 127.2, 129.4, 129.7, 146.1 (s, aromatic), 132.3, 139.3 (s, C=C), 165.8 (s, C=O). Anal. Calcd for $(C_{11}H_{10}O_2)_n$: C, 75.84; H, 5.79. Found: C, 75.84; H, 5.76.

Instruments. Melting points were measured on a Büchi melting point apparatus and are uncorrected. NMR spectra were measured on a Varian VXR-500S spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C with TMS as the internal standard. IR spectra were recorded with a Jasco Fourier Transform IR-7000 spectrophotometer with a Jasco PTL-396 data processor. Absorption spectra were taken on a Jasco Ubest-55 spectrophotometer. CD spectra were measured

in a 0.05-cm quartz cell unless otherwise noted with a Jasco J-720 L spectropolarimeter. The concentration of poly-**1** was calculated on the basis of monomer units. The film was prepared by casting a DMSO solution of poly-**1** (1.0 mg) and (*R*)-**2** (6.8 μmol) on a cylindrical quartz cell (0.5 cm thick and 2 cm in diameter) followed by evaporation of the solvent under reduced pressure. The absorption and CD spectra of films cast on the quartz cell were measured four times by rotating the sample quartz plate by 90, 180, and 270° from the first position around the axis of the incident light beam with the same apparatus. The spectral pattern and intensity were scarcely changed by rotating the sample. The CD spectra were calibrated to the same molar concentration on the basis of the data of the absorption measurement.[60] Gel permeation chromatography (GPC) was performed with a Jasco Trirotar-II liquid chromatograph equipped with a UV−visible (254 nm; Jasco 875-UV) detector. GPC columns, Shodex KM-802.5 (30 cm) and A-80M (50 cm), were connected in series and THF was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh).

Effect of H_2O on ICD. A solution of poly-**1** (5 mg/*ca.* 4 mL) in DMSO was prepared in two 5-mL flasks. To this was added (*S*)-**2** or (*R*)-**18** (277 and 27 μL, respectively), the resulting solutions were diluted with DMSO to keep the poly-**1** concentration at 1.0 mg/mL ([(*S*)-**2**]/ [poly-**1**] = 50, [(*R*)-**18**]/[poly-**1**] = 10 mol/mol), and the initial CD spectra were taken. The solutions were diluted with increasing volumes of H_2O (50, 200, 250, 250, 500, and 750 μL for (*S*)-**2** and 50, 200, 250, 500, 500, and 3500 μL for (*R*)-**18**) and CD spectra were recorded for each addition of H_2O. The concentration of poly-**1** was corrected by using the ϵ value of poly-**1** (ϵ_{400} = 2520 cm⁻¹ M⁻¹) which had been previously determined.

CD Measurements: Concentration Effect of Poly-1 on ICD. A typical experimental procedure was described below. A stock solution of (*R*)-**18** (100 μL/1 mL) in DMSO was prepared. A 5 mg/*ca.* 1.5 mL solution of poly-**1** in DMSO was prepared in a 2-mL flask equipped with a stopcock. To this was added 135 μL of the stock solution of (*R*)-**18** with a Hamilton microsyringe, the resulting solution was diluted with DMSO to keep the poly-**1** concentration at 2.5 mg/mL ([(*R*)-**18**]/ [poly-**1**] = 5 mol/mol), and the initial CD spectrum was recorded with a 0.01-cm quartz cell. A 1-mL aliquot of the poly-**1**−(*R*)-**18** solution was transferred to a 5-mL flask with a transfer pipet and diluted with DMSO, giving a 0.5 mg/mL solution of poly-**1**−(*R*)-**18** complex. The CD spectrum of this solution was taken with use of a 0.05-cm quartz cell, and the above similar dilution procedure was repeated (concentrations of poly-**1**−(*R*)-**18** complex were 0.25, 0.05, 0.025, and 0.005 mg/ mL: see the Supporting Information)). In a similar manner, concentration effect on ICD of poly-**1**−(*S*)-**2** complex ([(*S*)-**2**]/[poly-**1**] = 50 mol/mol) was also investigated (concentrations of poly-**1** were 2.5, 1.0, 0.5, and 0.05 mg/mL).

CD Titration. Stock solutions of (*S*)-**2** (100 μL/mL) and (8*R*,9*S*)-**30** (200 mg/2 mL) in DMSO were prepared. In the complexation of poly-**1** with (*S*)-**2**, a 10 mg/10 mL solution of poly-**1** in DMSO was prepared in a 10-mL flask equipped with a stopcock, to this was added 11 μL of the stock solution of (*S*)-**2**, and the initial CD spectrum was recorded. This gave a poly-**1**−(*S*)-**2** complex (1/0.1 mol/mol). Aliquots 3, 2, 2, and 2 mL of the poly-**1**−(*S*)-**2** solution were transferred to four flasks equipped with a stopcock, and 6.6 (poly-**1**/(*S*)-**2**, 1/0.3 mol/mol), 8.9 (1/0.5), 20 (1/1), and 94 (1/5) μL of the stock solution of (*S*)-**2** were added to the flasks, respectively. Then, absorption and CD spectra were taken for each flask to give the titration curve in Figure 6A. The concentration of poly-**1** was corrected by using the ϵ value of poly-**1** (ϵ_{400} = 2520 cm⁻¹ M⁻¹) when the concentration change of poly-**1**− (*S*)-**2** solutions was not negligible. The same procedure was done in the titration of poly-**1** with the stock solution of (8*R*,9*S*)-**30** or with neat (*S*)-**18**.

In the titration experiments of poly-**1**−(*S*)-**18** complexes with achiral amines (Figures 10 and 11), samples containing an almost constant amount of poly-**1** (*ca.* 1 mg/mL) in the presence of increasing concentrations of (*S*)-**18**, which had been prepared for the titration experiments described above, were used. To the samples were added an increasing amount of 2-amino-1-ethanol (**33**) to afford Figure 10.

(59) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318−1329.

(60) Yashima, E.; Noguchi, J.; Okamoto, Y. *Macromolecules* **1995**, *28*, 8368−8374.

In the titration with other achiral amines (**34**−**37**) (Figure 11), stock solutions of poly-**1** (10 mg/10 mL) and (*S*)-**18** (200 μL/2 mL) in DMSO were prepared. To the poly-**1** solution was added 16 μL of the stock solution of (*S*)-**18** to afford a poly-**1**−(*S*)-**18** mixture (1/0.3 mol/mol). Aliquots of 3, 2, 2, and 2 mL of this solution were transferred to four flasks and the initial CD spectra were measured. Increasing amounts of achiral amines (**34**−**37**) were directly added to the flasks, and CD spectra were taken for each flask to give the titration curves in Figure 11.

The nonlinear effects between intensities of ICD and percent ee of **2**, **18**, and **24** and percent de of **30** and **31** in the complexation with poly-**1** were investigated in DMSO. A typical experimental procedure is described below. Stock solutions of poly-**1** (2 mg/mL, 10 mL), (*S*)-**18** (200 μL/2 mL), and (*R*)-**18** (200 μL/2 mL) were prepared. Aliquots of the stock solutions of (*S*)- and (*R*)-**18** were placed into seven 1- or 2-mL flasks so that the percent ee of the mixtures (*S* rich) was 5, 10, 20, 40, 50, 60, and 80, respectively. The solutions were then diluted with DMSO until the total volume of the solutions was less than half of the column of the flasks. To the flasks was added a 0.5- or 1-mL aliquot of the stock solution of poly-**1**, and the resulting solutions were immediately mixed with a vibrator (Iuchi, Japan) and finally diluted with DMSO. The poly-**1** concentration was held constant at 1 mg/mL in all runs ([**18**]/[poly-**1**] = 5 mol/mol).

The separate addition of neat or stock solutions of (*S*)- and (*R*)-**18** to the poly-**1** solution should be avoided, because the complex gave more intense ICD rather than those shown in Figure 9B, or exhibited an opposite Cotton effect depending on the addition order of (*S*)- and (*R*)-**18** to the poly-**1** solution. The same procedure was performed in the experiments with (*S*)-**2** and (*R*)-**2**, (1*R*,2*S*)-**24** and (1*S*,2*R*)-**24**, and (8*R*,9*S*)-**30** and (8*S*,9*R*)-**31** ([**2**, **24**, or **30** and **31**]/[poly-**1**] = 50 mol/mol).

^{1}H NMR Titration. The ^{1}H NMR titration experiments of amines with a model compound of poly-**1**, 4-vinylbenzoic acid, were performed as below. Typically, stock solutions of 4-vinylbenzoic acid (34 mM) and (*R*)-**2** (3.1 M) in DMSO-d_6 were prepared. A 0.8-mL aliquot of the stock solution of 4-vinylbenzoic acid was transferred with a hypodermic syringe to a 5-mm NMR tube, and the initial ^{1}H NMR spectrum was recorded at 22 °C. To this was added 14 aliquots of the stock solution of (*R*)-**2** (11.8−117 mM), and NMR spectra were taken for each addition of (*R*)-**2**. The chemical shifts of aromatic and vinyl proton resonances of 4-vinylbenzoic acid were followed, and the binding constant (*K*) was calculated by a nonlinear least-squares method.[45,47] A similar procedure was done for other amines, while a linear-least-squares method[12a,45,46] was used for estimating the binding constant between 4-vinylbenzoic acid and (*R*)-**10**; the concentrations of 4-vinylbenzoic acid (6.8 mM) and (*R*)-**10** (100−474 mM) were chosen so as to meet the Benesi−Hildebrand conditions ([(*R*)-**10**]$_t$/[4-vinylbenzoic acid]$_t$ ≥ 10) (t = total). Satisfactory fits were observed in all cases for a 1:1 complexation.

Job Plot. The stoichiometry of the complex between 4-vinylbenzoic acid and (*R*)-**18** was determined by the continuous variation plot (Job plot).[48] Stock solutions of 4-vinylbenzoic acid and (*R*)-**18** in DMSO-d_6 were prepared (34 mM). In five NMR tubes, portions of the two solutions were added in such a way that their ratio changed from 0 to 1, keeping the total volume at 0.8 mL. The ^{1}H NMR spectrum for each tube was taken at 22 °C, and the change in chemical shift of the aromatic proton resonances of 4-vinylbenzoic acid was used to calculate the complex concentration. The complex concentration was plotted against the mole fraction of (*R*)-**18**.

Molecular Modeling and Calculations. Molecular modeling and molecular mechanics calculation were performed with the Dreiding force field (version 2.11)[35] as implemented in Cerius^2 software (version 1.5, Molecular Simulations Inc., Burlington, MA, USA) running on an Indigo^2-Extreme graphics workstation (Silicon Graphics). Charges on atoms of poly-**1** were calculated with use of QEq[35a,b] in Cerius^2; total charge of the molecule was zero. The polymer model of 20-mer (20 repeating monomer units) was built by Polymer Builder in Cerius^2. The starting main chain conformation of a polymer model was defined as the double bond geometry (*cis* or *trans*) and a conformation of a rotational single bond. The double bond geometry was fixed to *cis* and the initial dihedral angle of a single bond from planarity was set to 30° (transoid).[24f] The energy minimization was accomplished first by Conjugate Gradient 200 (CG 200) and then by Fletcher Powell (FP) until the root-mean-square (rms) value became less than 0.01 kcal mol^{-1} Å^{-1}, respectively. Molecular dynamics calculations were run for 60 ps at 300 K and 20 ps at 500 K with a step size of 1 fs.

Supporting Information Available: Figures exhibiting the effects of H$_2$O and poly-**1** concentration on ICDs, ^{1}H NMR spectra of poly-**1** prepared with WCl$_6$−*n*-Bu$_4$Sn and MoCl$_5$−*n*-Bu$_4$Sn complexes, and the changes in ^{1}H NMR spectra of poly-**1** during the complexation with **2**, **3**, **7**, **10**, and **18** at various temperatures (5 pages). See any current masthead page for ordering and Internet access instructions.

JA964470Y