tional motions of the polymer[23] may also play a somewhat unexpected role on k_D as well as D since the translating finite-size particle will exert both a force and a torque on a second particle within its velocity field. Moreover, some kind of inner structure of a particle (or coil), e.g., self-knots,[24] may not be neglected, though this effect on k_D is minor in good solvents compared to the case for Θ solvent.

As described already, $D(q = 0)$ reflects mainly the long-range hydrodynamic interaction. However, the experimental k_D value for the hard spheres[25] has been explained completely by only the theories of Batchelor[4] and Felderhof,[5] who calculated the hydrodynamic interaction by taking into account the short-range potential as well as long-range one without using the Kirkwood–Riseman approximation. The short-range force may play a much more complicated role especially for a very low concentration system of high molecular weight polymers.[4,5,26] These may indicate that in the high molecular weight range $M_w > 4 \times 10^6$, $D(q = 0)$ and k_D have to be calculated by taking into account the short-range hydrodynamic interaction as well as the long-range one between segments of finite size.

The deviation of the k_D value from AB observed for the highest molecular weight ($=1.34 \times 10^7$) is about 40% and exceeds clearly from the data uncertainties (±4%). Experimentally this deviation, however, should be tested further. We are now carrying out similar experiments to those described here using polyisoprene (PIP) with molecular weights as high as 8×10^7, since PIP is more flexible than PS.

Acknowledgment. We thank Professor Michio Kurata for his encouragement.

References and Notes

(1) Kops-Werkhoven, M. M.; Vrij, A.; Lekkerkerker, H. N. W. *J. Chem. Phys.* **1983**, *78*, 2760.
(2) Fijnaut, H. M. *J. Chem. Phys.* **1981**, *74*, 6857.
(3) In a previous paper on the concentration dependence of D of polystyrene in the Θ state,[21] we used the relation $k_D = 2A_2M - k_s - \bar{v}$ instead of eq 4. The omission of the $\bar{v}$ (partial specific volume of polystyrene) term however presses only the theoretical curves of Figure 1 in ref 21 downward in the k_D^Θ region $k_D^\Theta < 15$ cm^3 g^{-1}. This does not affect the conclusions reached in ref 21.
(4) Batchelor, G. R. *J. Fluid Mech.* **1972**, *52*, 245; **1976**, *74*, 1.
(5) Felderhof, B. U. *Physica A (Amsterdam)* **1977**, *89*, 373; *J. Phys. A* **1978**, *11*, 929.
(6) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1964**, *41*, 937.
(7) Yamakawa, H. *J. Chem. Phys.* **1962**, *36*, 2995.
(8) Akcasu, A. Z.; Benmouna, M. *Macromolecules* **1978**, *11*, 1193.
(9) Akcasu, A. Z. *Polymer* **1981**, *22*, 1169.
(10) Nemoto, N.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1984**, *17*, 425.
(11) Mandema, W.; Zeldenrust, H. *Polymer* **1977**, *18*, 835.
(12) Han, C. C.; Akcasu, A. Z. *Polymer* **1981**, *22*, 1165. PS samples of various molecular weights measured in three solvents at various temperatures were discussed.
(13) Yu. T. L.; Reihanian, H.; Jamieson, A. M. *Macromolecules* **1980**, *13*, 1590.
(14) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229. The k_D values were roughly estimated from the graph.
(15) Pusey, P. N.; Vaughan, J. M.; Williams, G. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1696.
(16) Fukuda, M.; Fukumoto, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(17) Van den Berg, J. W. A.; Jamieson, A. M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2311. A poly(2-vinylpyridine) sample of $M_w = 6.6 \times 10^5$ was measured in THF at various temperatures.
(18) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(19) Witten, T. A., Jr.; Shäfer, L. *J. Chem. Phys.* **1981**, *74*, 2582.
(20) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(21) Tsunashima, Y.; Nemoto, N. *Macromolecules* **1983**, *16*, 1941.
(22) Fixman, M. *Macromolecules* **1981**, *14*, 1710.
(23) Montgomery, J. A., Jr.; Berne, B. J. *J. Chem. Phys.* **1977**, *67*, 4589. Montgomery, J. A., Jr.; Berne, B. J.; Wolynes, P. G.; Deutch, J. M. *J. Chem. Phys.* **1977**, *67*, 5971.
(24) Brochard, E.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(25) Kops-Werkhoven, M. M.; Fijnaut, H. M. *J. Chem. Phys.* **1981**, *74*, 1618.
(26) Hess, W. In "Light Scattering in Liquids and Macromolecular Solutions"; Degiorgio, V., Corti, M., Giglio, M., Eds.; Plenum Press: New York, 1980.

Chiral Novolacs. Enantiocontrolled Synthesis of Alkylidene-Linked Binuclear Phenolic Compounds

GIOVANNI CASIRAGHI,* MARA CORNIA,
GIUSEPPE CASNATI, and LUCIA ZETTA

Istituto di Chimica Organica dell'Università, I-43100 Parma, Italy, and Istituto di Chimica delle Macromolecole del CNR, I-20133 Milano, Italy. *Received May 22, 1984*

Recent studies from this laboratory have emphasized the cardinal role played by the coordinating metal phenolates in providing regio- and diastereoselectivity in the synthesis of alkylidene-bridged oligomers related to novolac resins.[1–3] We now communicate that chirally modified aluminum phenolates[4] permit the asymmetric and regiospecific synthesis of alkylidene-bridged binuclear oligomers to be reached for the first time via chirality transfer from the auxiliary located at the metal to the bridging moiety.

Treatment of (−)-menthoxyphenoxyaluminum chlorides **1**, prepared in situ from (−)-menthoxyethylaluminum chloride and the corresponding phenol, with racemic α-substituted 2-hydroxybenzyl alcohols **2** in anhydrous toluene at room temperature (Scheme I) gave unsymmetrical binuclear novolacs **3** in good chemical yield with varying enantiomeric excess (ee). Yields, optical rotations, and ee's for the prepared dimers are presented in Table I.

Some features about this reaction are worthy of mention. While the steric requirement of the phenolic substrates had little effect on the degree of enantioselection, changes in the steric environment of the reactive site of **2** produced a pronounced effect on the asymmetric induction. Thus, while α-methylcarbinol **2a** (entries 1, 4, and 9) and α-phenylcarbinol **2c** (entries 3 and 6–8) exhibited remarkable differentiating ability (28–41% ee), an enantiomeric excess of only 12–18% was observed by using the quite congested α-isopropyl derivative **2b** (entries 2 and 5).

Strict observance to a precise reaction protocol was required to obtain optimum stereocontrol. In a typical procedure, 1.0 equiv of natural (−)-menthol[5] was added to a stirred solution of 1.0 equiv of Et_2AlCl.[6] After this solution was stirred for at least 1 h at 20 °C, 0.3 equiv of the appropriate phenol was added, and the resulting solution was stirred for an additional hour. Salicyl alcohol (0.3 equiv) was finally added, and the mixture was allowed to react at 20 °C for the indicated period (Table I). All manipulations were done under anhydrous conditions. The final reaction mixture was quenched by stirring with saturated aqueous NH_4Cl. Dimers **3** were then isolated by chromatography while (−)-menthol was recovered unracemized (80% recovery) and recycled if necessary.

If the addition sequence of the reactants was reversed or shorter equilibration times were allowed, the enantiomeric excess of the reaction was greatly diminished. Furthermore, a 10-fold increase in concentration from 0.1

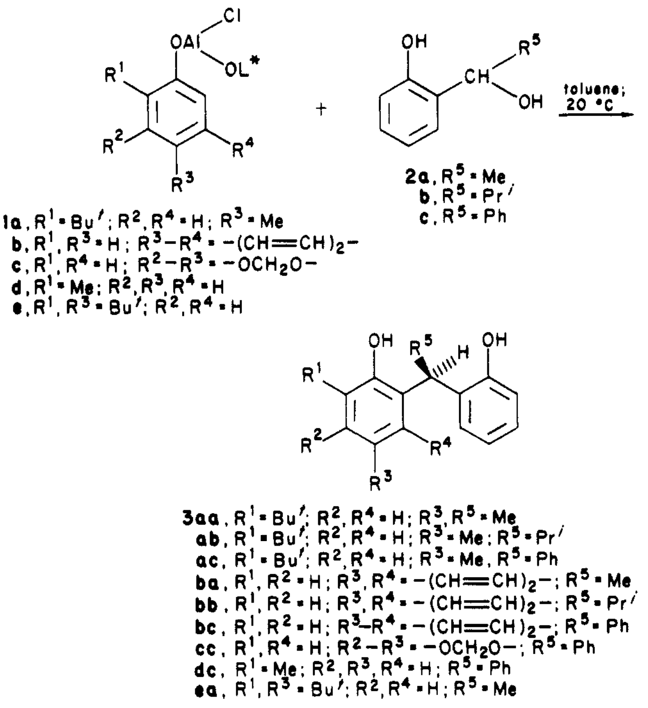
0024-9297/84/2217-2933$01.50/0 © 1984 American Chemical Society

Table I
Asymmetric Synthesis of Binuclear Oligomers 3[a]

entry	reactants	product	time, days	% yield[b]	$[\alpha]^{20}_{D}$,[c] deg	ee,[d] %
1	**1a** + **2a**	**3aa**	2	76	-7.2	28
2	**1a** + **2b**	**3ab**	5	57	+2.1	12
3	**1a** + **2c**	**3ac**	2	60	-14.4	41
4	**1b** + **2a**	**3ba**	5	39	-6.0	28
5	**1b** + **2b**	**3bb**	5	45	+3.2	18
6	**1b** + **2c**	**3bc**	5	49	-8.8	36
7	**1c** + **2c**	**3cc**	1	85	-6.0	33
8	**1d** + **2c**	**3dc**	2	74	-4.1	29
9	**1e** + **2a**	**3ea**	2	88	-8.7	37

[a] All these reactions were carried out in 0.1 M toluene solution at 20 ± 0.5 °C. [b] Isolated yield of >98% pure material. All compounds gave appropriate analytical and spectral data. [c] *c* 0.5 (ethanol). [d] Determined by 270 MHz ^1H NMR in $CDCl_3$ using Eu(hfc)$_3$ chiral shift reagent.

Scheme I[a]



[a] L* = (-)-menthyl.

to 1 M did not improve the degree of induction and cooling from +20 to -20 °C resulted in slightly reduced stereoselection.

In summary, we believe that this work, featuring a unique enantiocontrolled alkylation of phenols, may provide useful insight and applicability in the area of asymmetric synthesis of optically active ortho-substituted novolac-type oligomers. Extension of this reaction to the synthesis of higher oligomers is under way, and we are increasing our efforts to obtain higher enantiodifferentiating efficiencies than those reported herein.

References and Notes

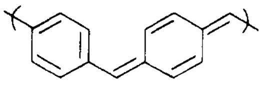
(1) Casiraghi, G.; Cornia, M.; Ricci, G.; Casnati, G.; Andreetti, G. D.; Zetta, L. *Macromolecules* **1984**, *17,* 19-28.
(2) Casiraghi, G.; Casnati, G.; Cornia, M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Sci.* **1983**, *24* (2), 183-184.
(3) Casiraghi, G.; Cornia, M.; Balduzzi, G.; Casnati, G. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23,* 366-369.
(4) The enantioselective ortho-hydroxyalkylation of phenols mediated by chiral alkoxyaluminum chlorides was recently reported: Bigi, F.; Casiraghi, G.; Casnati, G.; Sartori, G.; Zetta, L. *J. Chem. Soc., Chem. Commun.* **1983**, 1210-1211.
(5) $[\alpha]^{20}_{D}$ -49° (*c* 10, ethanol), available from Farmitalia-Carlo Erba, Italy.
(6) 1 M solution in hexane, available from Aldrich Chemical Co.

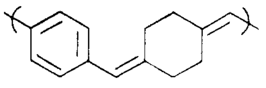
Communications to the Editor

Synthesis of a New Conjugated Hydrocarbon Polymer

The search for electrically conducting organic polymers has expanded enormously since the preparation of polyacetylene film[1] and the subsequent discovery[2] that its electrical conductivity, on doping with various oxidants, can be varied over a range of 11 orders of magnitude to a maximum value of $560\ \Omega^{-1}\ \text{cm}^{-1}$. The few intervening years have seen the synthesis of other conducting organic polymers such as poly(phenylacetylene),[3] poly(methylacetylene),[4] poly(2,5-thiophenediyl),[5] poly(propargyl halides),[6] poly((trifluoromethyl)acetylene),[7] polypyrrole,[8] poly(phenylene sulfide),[9] poly(*p*-phenylene),[10] and poly(phenylenevinylene).[11]

We now report the synthesis of poly(1,4-xylylidene-2′,5′-cyclohexadien-1′,4′-ylidene) (I) by the Wittig reaction. We had previously reported the synthesis of the model compound, 1,4-cyclohexadienylbis(benzylidene) by the same route.[12]


I


II

Polymer I represents a new class of conjugated polymers in which benzenoid rings alternate with quinonoid rings. We believe that this molecular system should be characterized by a high degree of electron delocalization because it can be described in terms of two equivalent resonance forms each of which contains relatively high-energy quinonoid rings:

0024-9297/84/2217-2934$01.50/0