Preparation and Properties of Optically Active Poly(α-methyl-α-n-propyl-β-propiolactone)

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ABSTRACT: α-Methyl-α-n-propyl-β-propiolactone monomer was polymerized at room temperature using typical anionic initiators (sparteine, Na, tetrahexylammonium benzoate) and a "stereoelective" initiator made from a 1:1 mixture of diethylzinc and of (R)-(−)3,3-dimethyl-1,2-butanediol. The anionic initiators lead to racemic polymers while the "stereoelective" initiator gave an optically active polymer. X-ray measurements indicated the same crystal structure for both polymers. Thermal measurements lead to an equilibrium melting point of 110 °C for the optically active polymer and to an equilibrium melting point of 97 °C for the racemic polymer. These results suggest the presence of stereoblocks in the racemic polymer, with isotactic sequences, which in average increase their length in the optically active polymer.

The polymerization of racemic α,α-disubstituted β-propiolactones has been studied using anionic initiators such as tertiary amines[1] or quaternary ammonium carboxylates.[2] Solvent and counterion effects on this polymerization were also recently investigated.[3] Several polymers prepared in such a way have been reported to be crystalline.[1] Thermal, mechanical, and crystalline properties of poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL) have been studied and the presence of two crystalline forms, the first one characterized by a planar zig-zag conformation of its chains and the second one by a 2_1 helical conformation, have been found as in the case of polypivalolactone.[4-8] The type of stereoregularity of PMPPL (random or alternate copolymer, stereoblocks or racemic mixture of homopolymers) is not yet established. In order to obtain such information on PMPPL, it seems desirable to compare the crystalline properties of polymers prepared from racemic mixtures and from optically pure monomers.

Recently, one of us has described the preparation of optically active α-phenyl-α-ethyl-β-propiolactone[9] (optical purity 80%) starting from the corresponding amino ester. It appeared that crystalline and thermal properties of racemic and optically active polymers were substantially different.[9,10] It was not possible using the same technique to resolve the methylisopropyl precursor to a reasonable optical purity and to obtain therefore the corresponding optically active monomer and polymers

But the so-called "stereoelective" polymerization is a possible way for obtaining optically active polymers starting from racemic monomers. This method was used successfully in the case of heterocyclic compounds such as oxiranes and thiiranes.[11-13] It was also demonstrated that this reaction can be used as an original resolution method allowing in some cases the preparation of monomers of high optical purity starting from racemic mixtures.[14] Chiral zinc alkoxides and zinc glycolates were found to be the most efficient catalysts for oxirane and thiirane resolution.[14]

In this paper, we describe preliminary results obtained using the same type of chiral catalysts as used for oxiranes and thiiranes for the polymerization of α,α-disubstituted β-lactones. Optically active α-methyl-α-n-propyl-β-lactone monomer and polymers were obtained. Differences in physical properties between racemic and optically active polymers are reported.

Polymerization of Racemic Monomer with Chiral Initiators

The system obtained from the reaction between diethylzinc and (R)-(−)3,3-dimethyl-1,2-butanediol (DMBD) in equal amounts was used as initiator. This system was previously found to be the best "stereoelective" initiator for thiiranes and oxiranes.[12-15]

The polymerization of α-methyl-α-n-propyl-β-propiolactone (MPPL) was carried out in bulk at room temperature. Main experimental results are reported in Table I. MPPL polymerized with a reasonable rate, much slower than methyl thiirane[15] but faster than methyl oxirane.[16] The optical activity of the residual monomer increased with conversion while that of the resulting polymer decreased as expected.

The sign of the residual monomer indicates that the dextrorotatory monomer is preferentially incorporated in the polymer. Although the absolute configuration of optically active PMPPL is not yet known, it has been found previously that in most cases the enantiomer having the same configuration as the chiral ligand used in the catalyst is preferentially chosen in the reaction.[13,14] Such a choice is called "homosteric". In the case of monosubstituted oxiranes and thiiranes, it corresponds to the preferential choice of the (R) enantiomer according to the definition of Cahn, Ingold, and Prelog. In the present case, the sign of the polymer is levorotatory in chloroform which is opposite to the sign of the monomer as in the case of α-phenyl-α-ethyl-β-propiolactone.[8,9]

Usually the whole polymer could be fractionated from chloroform solution with one part immediately insoluble in methanol and a second part which precipitated after staying overnight in the methanol. Both fractions had the same optical rotation. The first fraction only is reported in Table I. Molecular weights increased with conversion as in a living polymerization. However they were relatively low as compared with those obtained in the case of methyloxirane and methylthiirane. The polymerization had an heterogeneous character and only 10^{-2} to 10^{-3} of the catalyst was efficient. The limitation of molecular weights could be due to some transfer or termination reactions.

High molecular weights were obtained when using typical anionic initiators. With sparteine, a chiral amine, no measurable stereoelection was detected. Again the same two types of fractions were isolated in the polymerization initiated with sparteine and sodium.

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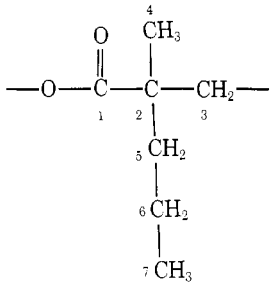
Table I
Polymerization of Racemic MPPL, using Different Initiators (Polymerizations Carried out in Bulk, at Room Temperature)

No.	Initiator	[C]/[M], mol %	Polymerization time, h	Yield,[a] %	Residual monomer α_m (neat, dm)	Polymer [α] ($CHCl_3$, c 0.4)	[η] [b] dL/g	M_{osmo}
1	$ZnEt_2$–(−)DMBD	4.8	24	17	−0.41	−2.4		16 000
2	$ZnEt_2$–(−)DMBD	8.6	14	42	−0.94	−1.2		21 000
3	$ZnEt_2$–(−)DMBD	8.4	24	61	−1.29	−0.6		26 000
4	$ZnEt_2$–(−)DMBD	4.9	16	87	−4.33	−0.33	0.7	40 000
5	Sparteine	10.8	15	50	−0.005	0.0	1.31	340 000
6	Sodium mirror		9	29			2.55	600 000
7	Tetrahexylammonium benzoate	0.128	6	97	0.0	0.0	0.48[c]	88 000

[a] Polymer fraction which precipitates immediately in methanol from a chloroform solution. [b] In benzene, at 25 °C. [c] In THF, at 25 °C. (1, 5 and 6) and (2, 3 and 4): different monomer samples.

^{13}C NMR spectra of polymers were run in $CDCl_3$ solutions. No detectable stereosensitivity was observed for the polymers prepared by stereoelective or anionic methods. Only one single peak was present for each carbon. The following chemical shifts were observed (in ppm from Me_4Si) and assigned by usual partial C–H decoupling: C(1) = 164.1; C(2) =



46.5; (C3) = 69.0; C(4) = 17.7; C(5) = 38.25; C(6) = 20.0; C(7) = 14.6. From this absence of stereosensitivity, one cannot conclude however that all the polymers are perfectly tactic and other evidence is desirable. In fact, the low degree of crystallinity reported for these polymers in the following part of this paper strongly suggests that their degree of stereoregularity [i.e., sequence length] is relatively low. It was not possible, therefore, to obtain information on the optical purity of our products from the tacticity determination as was done before for the polyoxiranes and polythiiranes.

The CD spectrum of an optically active monomer (α^{25}_D −1.29 (neat, dm)) run in trifluoroethanol solution showed a negative Cotton effect located at 207 nm ($\Delta\epsilon_{207}$ = −0.048). Similarly the spectrum of polymer no. 1 (Table I) showed clearly a Cotton effect located at 210 nm ($\Delta\epsilon_{210}$ −0.028 in hexafluoropropanol-2) (Figure 1). These findings are consistent with previously reported Cotton effects in optically active polyesters corresponding to n–π* transition.[17–19] All CD spectra were recorded on a Dichrographe III Jobin Yvon apparatus.

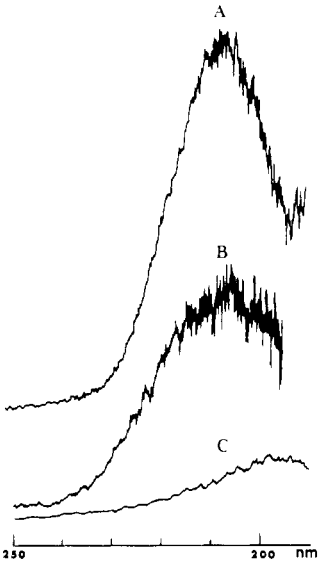


Figure 1. Circular dichroism spectra of an optically active MPPL monomer and of an optically active MPPL polymer: (A) (−)MPPL monomer in 2,2,2-trifluoroethanol solution (c 9 g/L, Δε −0.048); (B) (−)MPPL polymer in 1,1,1,3,3,3-hexafluoropropanol-2 solution (c 7.35 g/L, Δε −0.028); (C) 1,1,1,3,3,3-hexafluoropropanol-2 solvent alone.

Physical Properties

Optically active polymers often have physical properties which are drastically different from those of the corresponding racemic polymers. This behavior has been found for polyoxiranes and polythiiranes where differences in melting point, in crystal structure, in morphology, and in crystallization habits have been reported.[20–22] Similar differences have also been found for several polyesters[9,10,23–26] and a polylactam.[27]

The present part of this paper involves a comparison between the crystalline and thermal properties of a racemic polymer with those of an optically active polymer. The racemic polymer, hereafter called PMPPL-R, is sample no. 7 of Table I, while the optically active polymer, hereafter called PMPPL-OA, is sample no. 3 of Table I.

X-ray diffraction measurements were done on films of both polymers obtained by solvent evaporation. the solvent used was chloroform. The measurements were conducted using a Philips generator and a Cu Kα radiation and the diffracted intensities were recorded on photographic plates enclosed in a Warhus–Statton camera.[28] For the PMPPL-OA sample, crystalline peaks were found at 2θ Bragg angles of 9.5 (s), 14.5 (m), 17.5 (s), 21.3 (m), and 25.7 (w) [s, m, and w stand for strong, medium, and weak values of the diffracted intensity]. For PMPPL-R peak maxima appeared at 2θ equal to 9.4 (s), 14.6 (m), 17.5 (s), 21.3 (m), and 25.7 (w). The small differences in position noted for the first two peaks are due to experimental error and are certainly not significant. These values are in reasonable agreement with those published before in the literature[4] and they indicate that the two samples have the same crystal structure.

Melting experiments were also performed on both samples using a DSC-1B Perkin-Elmer differential scanning calorimeter. It is well known that the melting temperature, T_f, of

a polymer sample depends upon its crystallization temperature, T_c.[29] Consequently a serious comparison of the melting points of two different polymers must involve the determination of their equilibrium melting temperature, T_f^0, which is the melting temperature of a crystal of infinite dimensions. Hoffman and Weeks[30] have shown that T_f^0 can be found by plotting the melting temperature of samples crystallized isothermally as a function of T_c and by extrapolating the results to the point where $T_f = T_c = T_f^0$. We have followed this procedure for the two PMPPL samples (Figure 2); 21 data points, obtained for the PMPPL-OA sample, were treated with the least-squares method and this procedure led to an equilibrium melting point of 110 °C. Note that several of these data are identical and consequently they do not appear in Figure 2; 12 data points were obtained for the PMPPL-R sample and they led to an equilibrium melting point of 97 °C. There is consequently a difference of 13 °C between the equilibrium melting temperatures of the two samples.

The data presented in Figure 2 were obtained at a heating rate of 40 °C/min. Measurements done at a heating rate of 10 °C/min gave similar values within experimental error. It was also observed that at a given crystallization temperature or at a given degree of supercooling, the rate of crystallization of the two polymers was drastically different; the PMPPL-OA sample crystallized much faster than the PMPPL-R sample. It also reached larger values of enthalpy of fusion ($\simeq 12$ J g^{-1} compared to $\simeq 8$ J g^{-1}). The order of magnitude of these values certainly indicates that the degree of crystallinity of these samples is low. This conclusion was also reached by looking at the X-ray diffraction pictures which showed small discrete peaks for both samples on top of a huge amorphous halo.

Discussion

The larger crystallization rates, enthalpies, and temperatures of fusion found for the PMPPL-OA sample are easily understood if one considers the PMPPL samples as copolymers made of *d* and *l* sequences. Since the PMPPL-R sample crystallizes despite the asymetric carbon atom of its structure, it probably contains short *d* and *l* sequences. These sequences must be of equal number to create a racemic mixture. This means that the polymerization process is partially stereoselective. But in PMPPL-OA samples, the polymerization is "stereoelective", leading to the optical activity of the polymer. Larger *d* or *l* sequences are thus formed and such sequences will give rise to larger crystal dimensions, higher melting points, and faster crystallization rates. If crystallization would occur as a result of the formation of a random copolymer for the racemic PMPPL, the crystal structure should be able to accommodate both *d* and *l* substituents, the degree of crystallinity of the polymer should be higher than that found experimentally, and the melting point should be independent of optical activity. If crystallization would occur as a result of the formation of an alternate copolymer for the racemic PMPPL, the formation of an optically active polymer should inhibit the alternation of the two repeating units of the polymer, it should provide the formation of shorter crystallizable sequences, and it should give a decrease in melting point with increasing optical activity.[31]

Consequently, the results obtained suggest that the PMPPL samples are made of stereoblocks of *d* and *l* nature. These results could similarly be explained by the formation of a racemic mixture of homopolymers. But in view of the type of initiator used in polymerizing the MPPL-R sample, it seems a very improbable situation.

Similar results have been previously obtained for poly(α-phenyl-α-ethyl-β-propiolactone) (PPEPL) samples.[9] The melting point of the racemic PPEPL was found to be 110 °C,

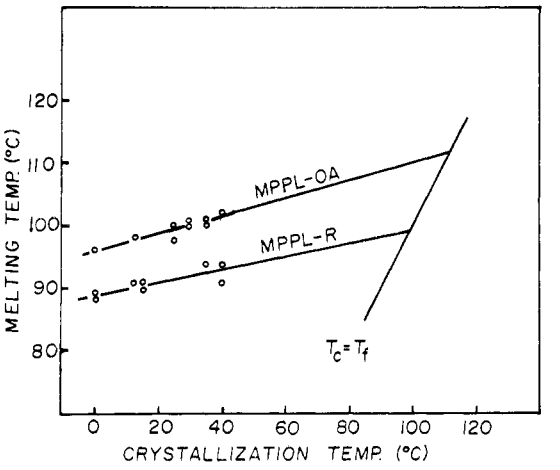


Figure 2. Melting temperatures of an optically active (MPPL-OA) and of a racemic (MPPL-R) poly(α-methyl-α-*n*-propyl-β-propiolactone) as a function of the crystallization temperature.

while the PPEPL prepared from a 26.5–73.5% (+)-(−) monomer enantiomeric mixture gave a melting point of 116 °C. However, it was found that a PPEPL sample with high optical activity (prepared from a monomer mixture whose enantiomeric composition is 90% (+) and 10% (−)) gave a polymer with a different crystal structure than the racemic one and a drastically different melting point, 260 °C. It is thus possible to have short isotactic sequences in the racemic PPEPL sample, sequences which increase their length with increasing optical activity and which crystallize under a different crystal structure when the isotactic content of the polymer becomes large. It will be interesting in a future study to see if the PMPPL also changes its crystal structure under similar conditions.

Conclusions

It is now possible to prepare optically active poly(α-methyl-α-*n*-propyl-β-propiolactones) using the 1:1 diethylzinc–DMBD catalyst used previously for preparing optically active polythiiranes and polyoxiranes. The specific rotation values of the polymers formed are low but we do not know yet the specific rotation of the pure enantiomer of this polymer. The optically active PMPPL has a higher equilibrium melting point than the racemic one, suggesting the formation of short stereoblocks in the racemic polymer and of longer stereoblocks in the optically active polymer.

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References and Notes

(1) R. Thiebaut, N. Fischer, Y. Etienne, and J. Coste, *Ind. Plast. Mod.*, **14 (2)**, 1 (1962).
(2) H. K. Hall, Jr., *Macromolecules*, **2 (5)**, 488 (1969).
(3) C. D. Eisenbach and R. W. Lenz, *Makromol. Chem.*, **177**, 2539 (1976).
(4) J. Cornibert, R. H. Marchessault, A. E. Allegrezza, Jr., and R. W. Lenz, *Macromolecules*, **6 (5)**, 676, (1973).
(5) U.S. Patent No. 3 299 171 (Jan. 17, 1967).
(6) R. E. Prud'homme and R. H. Marchessault, *Macromolecules*, **7**, 541 (1974).
(7) R. E. Prud'homme and R. H. Marchessault, *Makromol. Chem.*, **175**, 2705 (1974).
(8) R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2455 (1974).
(9) C. G. d'Hondt and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 261 (1978).
(10) R. W. Lenz, C. G. d'Hondt, and E. Bigdeli, ACS Meeting, New Orleans, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18 (1)**, 81 (1977).
(11) T. Tsuruta, *J. Polym. Sci. D*, 179 (1972).
(12) P. Sigwalt, *Pure Appl. Chem.*, **48**, 257 (1976).
(13) N. Spassky, *ACS Symp. Ser.*, in press.
(14) N. Sepulchre, N. Spassky, and P. Sigwalt, *Isr. J. Chem.*, **15**, 33, (1976/1977).

(15) A. Deffieux, M. Sepulchre, N. Spassky, and P. Sigwalt, *Makromol. Chem.*, **175**, 339 (1974).
(16) C. Coulon, N. Spassky, and P. Sigwalt, *Polymer*, **17**, 821 (1976).
(17) R. C. Schulz, *Kinet. Mech. Polyreactions, Int. Symp. Macromol. Chem., Prepr.*, 185 (1969).
(18) C. G. Overberger, G. Montaudo, I. Furuyama, and M. Goodman, *J. Polym. Sci., C*, **31**, 33, (1970).
(19) J. Delsarte and G. Weil, *Macromolecules*, **7 (4)**, 450, (1974).
(20) N. Spassky, P. Dumas, M. Sepulchre, and P. Sigwalt, *J. Polym. Sci., Polym. Symp.*, **No. 52**, 327 (1975).
(21) J. H. Magill, *Makromol. Chem.*, **86**, 283 (1965).
(22) H. Matsubayashi, Y. Chatani, H. Tadokoro, P. Dumas, N. Spassky, and P. Sigwalt, *Macromolecules*, **10**, 996 (1977).
(23) C. G. Overberger, S. Osaki, and D. M. Braunstein, *Makromol. Chem.*, **93**, 13 (1966).
(24) C. G. Overberger and J. K. Weise, *J. Am. Chem. Soc.*, **90**, 3538 (1968).
(25) C. G. Overberger and H. Kaye, *J. Am. Chem. Soc.*, **89**, 5649 (1967).
(26) M. Yokouchi, Y. Chatani, H. Tadokoro, K. Teranishi, and H. Tani, *Polymer*, **14**, 267 (1973).
(27) C. G. Overberger and C. Jabloner, *J. Am. Chem. Soc.*, **85**, 3431 (1963).
(28) L. E. Alexander, "X-ray Diffraction Methods in Polymer Science", Wiley-Interscience, New York, N.Y., 1969.
(29) P. Meares, "Polymers: Structure and Bulk Properties", Van Nostrand-Reinhold, New York, N.Y., 1971.
(30) J. D. Hoffman and J. J. Weeks, *J. Res. Natl. Bur. Stand., Sect. A*, **66**, 13 (1962).
(31) L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York, N.Y., 1964.

Asymmetric-Selective Polymerization of (*RS*)-α-Methylbenzyl Methacrylate

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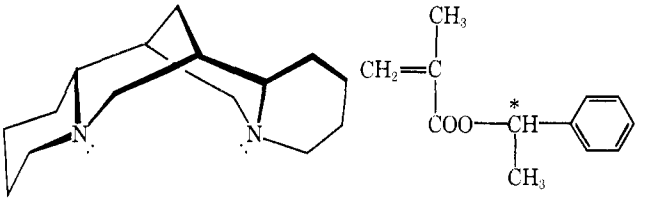
ABSTRACT: The polymerization of (*RS*)-α-methylbenzyl methacrylate [(*RS*)-MBMA] was studied by using diethylmagnesium (Et_2Mg)–chiral alcohol (R*OH) systems and Grignard reagent–(−)-sparteine systems in toluene. Asymmetric selection was observed in the polymerization with Et_2Mg–R*OH systems in which the R* group has heteroatoms like quinine and cinchonine. However, the asymmetric-selective polymerization did not proceed with Et_2Mg–R*OH systems where the R* group was hydrocarbon. Grignard reagent–(−)-sparteine systems polymerized preferentially (*S*)-MBMA over (*R*)-MBMA. In the early stage of the polymerization at −78 °C the optical purity of the polymer was about 90%. The asymmetric selectivity was correlated with the tacticity of the resultant polymer; the triad isotacticity of the polymer increased with an increase of the selectivity. The polymerization process could be used as a method of optical resolution.

Asymmetric-selective (or stereoelective)[1] polymerization is of interest and important from many points of view, e.g., preparation of an optically active polymer, optical resolution of a racemic compound, elucidation of the mechanism of stereospecific polymerization, etc. Stereoelective polymerization of cyclic monomers such as epoxide, episulfide, and α-amino acid *N*-carboxylic acid anhydride has been investigated to a considerable extent.[1] On the other hand, the stereoelective polymerization of racemic α-olefins with asymmetric Ziegler–Natta catalysts has been studied by Pino, Ciardelli, and their co-workers who showed that the asymmetric selectivity decreases as the distance between the carbon–carbon double bond and the asymmetric carbon increases.[2–5] The asymmetric selection was not observed in the polymerization of 5-methyl-1-heptene which has an asymmetric carbon at the γ position from the double bond.[5] Recently, Higashimura and Hirokawa have reported the stereoelective cationic polymerization of racemic vinyl ethers by asymmetric catalysts,[6] but the degree of stereoelection in the polymerization seems to be low. From the above results highly asymmetric-selective polymerization of a racemic methacrylic ester would not be expected because the monomer has an asymmetric carbon at the remote γ position with respect to the carbon–carbon double bond. Matsuzaki et al.[7] polymerized (±)-menthyl methacrylate with (−)-amylmagnesium bromide, Solomatina et al.[8] carried out the polymerization of (*RS*)-MBMA with (+)-2-methylbutyllithium and butyllithium–lithium (−)-menthoxide complex, and Ikeda et al.[9] polymerized (*RS*)-MBMA and (*RS*)-*sec*-butyl methacrylate with the triethylaluminum–(−)-sparteine system. However, almost no asymmetric selectivity has been observed in these polymerizations.

Fortunately, we have recently found that the highly asymmetric-selective polymerization of (RS)–MBMA is possible with Grignard reagent–(−)-sparteine systems in toluene at −78 °C.[10] Furthermore, the catalyst systems



(−)-sparteine MBMA

polymerized stereoelectively (*RS*)-*sec*-butyl methacrylate[10] and 2,3-epoxypropyl methacrylate[11] the later of which has an asymmetric center at the further remote δ position from the carbon–carbon double bond.

In the present paper, we describe the detailed investigation on the polymerization of (*RS*)-MBMA by using diethylmagnesium (Et_2Mg)–chiral alcohol systems and Grignard reagent–(−)-sparteine systems.

Experimental Section

Materials. (*RS*)-MBMA was prepared by the reaction of methacryloyl chloride with (*RS*)-α-methylbenzyl alcohol in the presence of triethylamine. The crude monomer was purified by repeated distillation under reduced pressure. Et_2Mg was prepared from ethylmagnesium bromide as diethyl ether solution according to the method of Schlenk.[12] Optically active menthylmagnesium chloride (MentMgCl, 1.0 M) was prepared from (−)-menthyl chloride and magnesium turnings in ether.[13] Other Grignard reagents, cyclohexylmagnesium chloride (c-HexMgCl, 1.40 M) and bromide (c-HexMgBr, 1.32 M), butylmagnesium chloride (*n*-BuMgCl, 1.02 M), and phenylmagnesium bromide (PhMgBr, 1.58 M) were also prepared from corresponding halides in ether. Commercial optically active alcohols, (−)-*cis*-myrtanol ($[\alpha]^{20}_D$ −19.5°, neat), (−)-borneol ($[\alpha]^{20}_D$ −35°, ethanol), (−)-menthol ($[\alpha]^{20}_D$ −50°, ethanol), (−)-2-methylbutanol ($[\alpha]^{23}_D$ −5.8°, neat), (+)-1-*p*-menthen-9-ol ($[\alpha]^{22}_D$ +94°, benzene), strychinine, nicotine, quinine, cinchonine, and cinchonidine were used without further purification after identification by ^1H NMR

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