

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Asymmetry in the Main Chain of Poly-9-O-methacryloylquinine

Kiyoshi Yamauchi^a; Yasuhiro Mitsuda^a; Masayoshi Kinoshita^a

^a Department of Applied Chemistry Osaka City, University Sumiyoshi, Osaka, Japan

To cite this Article Yamauchi, Kiyoshi , Mitsuda, Yasuhiro and Kinoshita, Masayoshi(1976) 'Asymmetry in the Main Chain of Poly-9-O-methacryloylquinine', Journal of Macromolecular Science, Part A, 10: 6, 981 – 991

To link to this Article: DOI: 10.1080/00222337608061230

URL: <http://dx.doi.org/10.1080/00222337608061230>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Asymmetry in the Main Chain of Poly-9-O-methacryloylquinine

KIYOSHI YAMAUCHI, YASUHIRO MITSUDA, and
MASAYOSHI KINOSHITA

Department of Applied Chemistry
Osaka City University
Sumiyoshi, Osaka, Japan

ABSTRACT

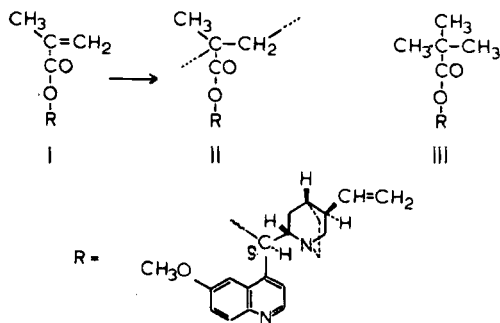
Anionic and radical polymerizations of 9-O-methacryloylquinine were performed by using *n*-butyllithium and azobisisobutyronitrile as initiators. Temperature and solvent effects on optical rotation of the polymers were studied. Based on these effects and ORD and CD spectra of polymers, it was concluded that the polymer, which was prepared by *n*-butyllithium in toluene, has asymmetric conformation in the main chain.

The development of highly stereospecific polymerization has aroused interest in the preparation of polymers having optically active side chains. It was hoped that the study of optical activity under different conditions (temperature, solvent, wavelength, etc.) as well as investigation of the relationship between rotatory power and polymerization conditions (initiator, temperature, etc.) would provide information on the conformation of such macromolecules.

Particularly, optically active poly- α -olefins and poly(vinyl ethers) have been studied extensively, and the differences between the rotatory power of the polymers with respect to the model compounds suggested the presence of an asymmetric main chain conformation or conformational rigidity in poly-(S)- α -olefins, (-)poly(menthyl vinyl ether), (+)poly(neomenthyl vinyl ether), and similar polymers [1-5].

However, polymers of acrylic and methacrylic acid esters of optically active alcohols (menthol, borneol, *sec*-butanol, 1-phenylethanol, etc.) have not shown such asymmetry in main chains [6-9], probably because the alkyl side groups lie apart from the main chains of these polyacid esters and thus have been considered incapable of inducing the conformational asymmetry in the main chains [10].

We, therefore, undertook the polymerization of 9-O-methacryloylquinine (I). The presence of a bulky asymmetric quinine moiety in I is expected to influence both the configuration and conformation of the main chain of the resulting polymer (II). For comparison with the optical behavior of II, 9-O-pivaloylquinine (III) was chosen as a model compound.



RESULTS AND DISCUSSION

Polymerization of I [11] was performed by use of azobisisobutyronitrile (AIBN) and *n*-butyllithium (*n*-BuLi) as initiators. The polymerization conditions and results are summarized in Table 1. All the polymers prepared are soluble in chloroform, benzene, and dimethylformamide, but insoluble in methanol, tetrahydrofuran, and diethyl ether.

The epimerization of quinine moiety in the polymers during polymerizations was excluded by controlled experiments; viz., the model compound (III) was recovered quantitatively when III was subjected to reaction conditions similar to those used in polymerization of I. The above results also exclude the formation of nonlinear polymer through

TABLE 1. Polymerization of 9-O-Methacryloylquinine (I)

Initiator	Solvent	I/Initiator mole ratio	Temp (°C)	Time (hr)	Yield (%)	MW
n-BuLi	Toluene	4	-78	24	43	4200
"	"	4	-78	24	55	2800
"	"	10	-78	24	97	10600
AIBN	Benzene	75	70	6	31	2100
AIBN	"	240	70	7	28	13700

the participation of the vinyl group in the quinine moiety of I at the polymerization.

The molar rotatory power $[\phi]$ of polymers was measured at 589 nm in benzene at various temperatures. (The molar rotatory $[\phi]_{\lambda}^t$ is defined as $[\alpha]_{\lambda}^t \text{ MW}/100$, where MW is the molecular weight of the monomeric unit of a polymer, $[\alpha]_{\lambda}^t$ is $\alpha/\ell d$, ℓ being the sample thickness in decimeters, d is the concentration of compound in grams per cubic centimeter, and α is the angle in degrees at temperature t with monochromatic light of wavelength λ .) The results are shown in Fig. 1 along with those for the model compound III.

One of the features of the temperature effects on the optical activity of the polymers is the appearance of peaks (maximum negative $[\phi]$ at specific temperatures, particularly in polymers obtained anionically. Thus, the absolute values of $[\phi]$ of the polymer prepared radically (AIBN-13700) increases gradually, followed by flattening with increasing temperature in a similar fashion as III, while those of polymers obtained by n-BuLi (n-BuLi-2800, -4200, and -10600) increase at first but then decrease, exhibiting a most negative $[\phi]$ at a characteristic temperature for the system.

Another significant feature in Fig. 1 is the increase of the temperature at the maximum negative $[\phi]$ with increasing molecular weight of polymers; e.g., n-BuLi-2800, -4200, and -10600 at about 12, 16, and 21°C, respectively.

This optical behavior may be explained when the polymers prepared anionically have an asymmetric main chain conformation or conformational rigidity which contributes negative rotatory power. Thus, polymers such as n-BuLi-10600 may retain its main chain conformation at low temperature, and, therefore, temperature variation operates only in each monomeric unit to show a trend similar to that of III. Unwinding of the main chain conformation or loss of rigidity occurs

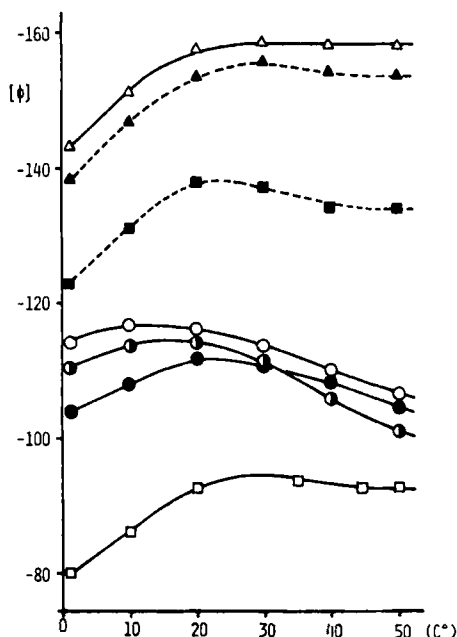


FIG. 1. Effects of temperature on optical rotation (—) in benzene and (---) in benzene-ethanol (3:2): (Δ , \blacktriangle) model compound; (\circ) *n*-BuLi-2800; (\bullet) *n*-BuLi-4200; (\blacksquare , \bullet) *n*-BuLi-10600; (\square) AIBN-13700. Polymer designations indicate first the initiator and next the molecular weight of the polymer.

at high temperature, lowering the optical rotation by the decreased asymmetry in the chain. The difference in $[\phi]$ among polymers produced by AIBN and *n*-BuLi at the same temperature may be originate in differences in the terminal groups and molecular weights of polymers and the degree of asymmetry of the chains.

On the other hand, the polymer obtained by AIBN at relatively high temperature (70°C) is expected to consist of a large proportion of syndiotactic or atactic structure, and each monomeric unit may contribute to the overall optical behavior of the polymer to give a curve similar to that of III over the range of temperature employed (3–50°C).

When the optical rotatory power of *n*-BuLi-10600 was measured by changing the solvent from benzene to a mixture of benzene and ethanol (3/2 v/v), the effect of temperature on $[\phi]$ became similar to that of III as shown in Fig. 2. Since the polymer consists mostly of hydrophobic parts, this solvent effect may indicate that main chain asymmetric conformation or conformational rigidity becomes stable to an

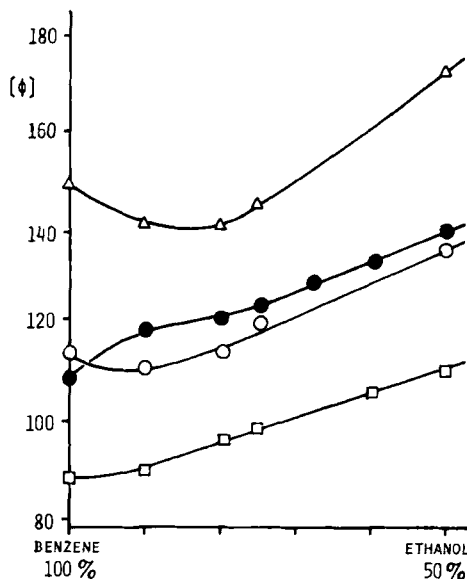


FIG. 2. Effects of solvent composition on optical rotation: (Δ) model compound; (\circ) n-BuLi-2800; (\bullet) n-BuLi-10600; (\square) AIBN 13700.

increase in temperature as a result of intramolecular hydrophobic interaction in a polar solvent (benzene-ethanol).

The observed change of optical rotation of the polymers at the same temperature in different solvents (for instance, n-BuLi-10600 showing -108° and -133° at 10°C with benzene and benzene-ethanol, 3:2 by volume, respectively) is a phenomenon commonly observed [12].

The effect of solvent on optical rotation of polymer was further investigated with various mixtures of benzene and ethanol at 15°C (Fig. 2). While AIBN-13700 and n-BuLi-2800 showed similar behavior as III, the absolute value of $[\phi]$ of n-BuLi-10600 rose with increasing polarity of the solvent, and then behaved similarly as III. These results may be explained as follows. Upon increasing the polarity of the solvent (0-30% ethanol), the degree of asymmetry in the main chain of n-BuLi-10600 increases through winding of the chain or increasing rigidity by a favored hydrophobic interaction to enhance the optical rotation as already mentioned above. At still higher solvent polarities (< 30% ethanol) only the optical behavior of each monomeric unit contributes to $[\phi]$, resulting in a similar trend in optical activity as in III. Short polymers, such as n-BuLi-2800, are incapable of

increasing asymmetry in the main chain sufficiently by an increase of a solvent polarity and therefore cannot show a similar curve as that of III. AIBN-13700, though a long molecule, cannot coil its chain or increase conformational rigidity with increasing solvent polarity because of its syndiotactic or atactic structure. It is well known [1-4, 9, 13, 14] that isotacticity is a necessary condition for achieving conformational selection.

Additional proof for the asymmetric property of polymers prepared by *n*-BuLi was obtained by optical rotatory dispersion (ORD) and circular dichroism (CD) measurements with chloroform as a solvent (Fig. 3). Thus, while *n*-BuLi-10600 exhibited a strong negative Cotton effect, having a trough at 243 nm, AIBN-13700 showed a very weak Cotton effect, even smaller than that of *n*-BuLi-2800. The model compound III shows the least Cotton effect. These results suggest that quinoline rings in the polymers obtained by *n*-BuLi are situated in a strong optically asymmetric environment and are optically active chromophores. A similar Cotton effect induced by an aromatic ring was reported by Verbit et al. [15] and was shown to be conformation-dependent. The much smaller Cotton effects in III and AIBN-13700 indicate that quinoline rings in these substances are almost optically inactive chromophores. These ORD and CD spectra may be explained

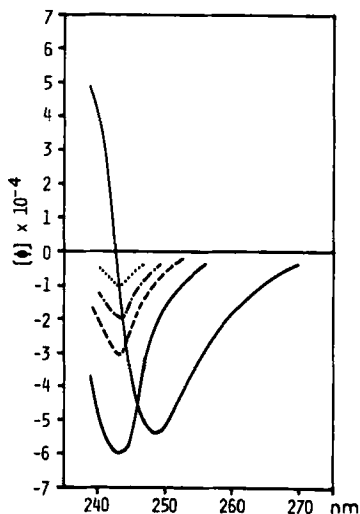


FIG. 3. Optical rotatory dispersion (ORD) and circular dichroism (CD) of III and polymers: (—) ORD, *n*-BuLi-10600; (····) CD, compound III; (-·-·) CD, AIBN-13700; (- -) CD, *n*-BuLi-2800; (—) *n*-BuLi-10600.

on the basis that the polymer prepared by *n*-BuLi has a highly asymmetric main chain conformation or conformational rigidity, whereas the polymer produced by AIBN has a random conformation.

The above differences in optical behavior of the polymers might be due to the differences in tacticity, which in turn have been considered to influence the conformation of a polymer chain. However, the determination of tacticity of polymers (II) by a PMR technique [16] on poly(methyl methacrylate) derived by hydrolysis of II, followed by methylation, was unsuccessful because of resistance of II towards hydrolysis. For instance, II after heating at 100°C in 98% sulfuric acid for 24 hr underwent only 85% cleavage of total ester bonds to give a brown powder.

The tacticity of esters of poly(methacrylic acid) has been studied extensively, however. For example, Goode [17] and Glusker and others [18-20] observed that methyl methacrylate gave predominantly isotactic polymer when the polymerization was performed in toluene with organometallic compounds as initiators. Fox et al. [21, 22], and Tsuruta [23, 24] found that poly(methyl methacrylate) prepared with *n*-BuLi in hydrocarbon solvents has predominantly isotactic linking. Sobue [8] also pointed out that bulky alkyl esters of methacrylic acid tended to polymerize with a greater proportion of isotacticity than methyl methacrylate.

Taking account of these investigations, it would be expected that our polymer (II) produced by *n*-BuLi in toluene at -78°C has predominantly an isotactic structure, whereas the polymer prepared with AIBN contains considerable syndiotactic or atactic structure [16, 24-28].

It should also be mentioned that isotactic linking may cause the main chain of the polymer to assume a helical conformation, whereas in syndiotactic and atactic linkings, various conformations of the chain are possible, as shown by a molecular model [21, 22, 24, 29]. Indeed, Yuki et al. [30] reported recently that polymerization of trityl methacrylate by *n*-BuLi in toluene led to the formation of an isotactic polymer having a helical structure. It was explained that such a conformation was favored by the bulkiness of trityl group.

In these esters poly(methacrylic acid), the ratio of right- to left-handed helices should be one in probability, but in polymer II, which is obtained by *n*-BuLi in toluene, the formation of a helix may lead to a prevalence of one helix, either right-handed or left-handed, by the presence of bulky quinine moiety. The resulting conformational asymmetry of the main chain should contribute to the total optical rotation of polymer II.

The above results would, thus indicate that polymerization of I with the use of *n*-BuLi as initiator and toluene as solvent, might furnish polymer II with asymmetry in the main chain.

EXPERIMENTAL

The infrared (IR) spectra were recorded on a Jasco Model IR-G spectrometer. Molecular weights (MW) were determined with a Knauer Dampdruck osmometer using chloroform as a solvent at 45°C. Benzene, chloroform, and ethanol were purified by the usual methods. A monomer (I, 9-O-methacryloylquinine) was prepared from quinine and methacryloyl chloride by the same procedure described previously [11].

Preparation of 9-O-Pivaloylquinine (III)

A mixture of quinine monohydrochloride dihydrate (25.0 g, 0.063 mole) and chloroform (200 ml) was treated with 4 N sodium hydroxide to transfer quinine into the chloroform layer. After drying of the organic solution with anhydrous sodium sulfate, it was mixed with triethylamine (7.0 g, 0.07 mole) and pivaloyl chloride (10.0 g, 0.083 mole). The reaction mixture was kept at room temperature overnight. The resulting solution was washed with 10% sodium hydrogen carbonate and dried over anhydrous sodium sulfate. The organic solution was then concentrated and column chromatographed on alumina (300 mesh, neutral, 2 cm × 70 cm). Elution with ethyl acetate gave III as white crystals, 24.1 g (76.2%); mp 148-149°C (ether); IR (KBr) 2990 (s), 1730 (s), 1620 (m), 1590 (m), 1480 (m), 1225 (m), and 1150 (s) cm⁻¹; $[\alpha]_D^{20} = -40.0^\circ$ (c = 5; benzene).

Analysis. Calcd for C₂₅H₃₂N₂O₃: C, 73.48%; H, 7.91%; N, 6.86%. Found: C, 73.82%; H, 7.89%; N, 6.82%.

Polymerization of I

The following polymerization are typical. Other runs were carried out similarly and are summarized in Table 1.

With AIBN

Monomer (I, 1.61 g, 4.11 mmole), AIBN (10.2 mg, 0.08 mmole), and benzene (10 ml) were placed in a glass tube, which was then sealed after several freeze-pump-thaw cycles. The tube was immersed in a water bath thermostatted at 70°C and shaken for 7 hr. The contents were poured into diethyl ether to precipitate a white powdery polymer, which was purified through reprecipitation by adding its benzene solution into ether; yield, 0.45 g (28%); MW, 13700.

With n-BuLi

A mixture of I (1.85 g, 4.73 mmole) and toluene (10 ml) was placed in a glass tube under dry nitrogen, and cooled in a Dry Ice-methanol bath. A solution of n-BuLi (0.5 mmole) in n-hexane (0.32 ml) was then injected through a rubber cap on the tube. The sealed tube was kept at -78°C for 24 hr. Upon pouring the contents into a large amount of ether, polymer II precipitated. Reprecipitation as mentioned above gave 1.80 g (97%) of a white polymer; MW, 10600.

Control Experiments

Compound III (0.1 g, 0.25 mmole) was mixed with AIBN or n-BuLi in the same molar ratio as in the polymerization of I. The mixture was then processed in a manner similar to the reaction of I with these initiators. The solution was concentrated, and the residue in chloroform (20 ml) was washed with water several times. The solvent was evaporated from the solution to give the solid, which was purified by recrystallization from ether to afford crystals of III; the recovered yields were 80-85%. The IR spectra, melting point, and optical rotations of the recovered samples were identical with those of the starting material.

Determination of Optical Rotation

A Yanagimoto photomagnetic polarimeter, OR-10, and a Jasco DIP-4 automatic polarimeter were used for measurement of optical rotatory power at 589 nm. A quartz cell ($l = 1$ cm) containing a benzene solution of a sample ($c = 5$) was placed in a polarimeter. The temperature of the cell was controlled by circulating water. Fig. 2 shows effects of solvent composition on optical rotation. Known amounts of ethanol were added to the benzene solution of the sample in mixed solvents.

ORD and CD spectra in a chloroform solution of the sample (1×10^{-4} mole/liter) at 25°C were measured with a Jasco J-20 spectrometer. Benzene and DMF were not suitable as solvents for measurement at wavelengths less than 245 nm due to their absorptions of light.

Hydrolysis of II

Polymer II (0.27 g) was heated with concentrated sulfuric acid (3 ml) at 100°C for 24 hr. The reaction mixture was then poured

into ice water with stirring. The resulting cloudy solution was filtered after being allowed to stand for a few hours to give a brown powder, 0.05 g (88%). The powder was dissolved in dilute hydrochloric acid and its ultraviolet spectrum was measured. Assuming that the absorption coefficient is equal to 5000 [11], the contents of the quinine moiety remaining in the hydrolyzed polymer was calculated to show a 85% hydrolysis of total ester linkages.

Reaction at room temperature gave only partial hydrolysis (less than 20%) after treatment of the reaction mixture in a manner similar to that mentioned above.

REFERENCES

- [1] P. Pino, G. P. Lorenzi, and L. Lardicci, Chim. Ind. (Milan), **42**, 712 (1960).
- [2] P. Pino and G. P. Lorenzi, J. Amer. Chem. Soc., **82**, 4745 (1960).
- [3] P. Pino, G. P. Lorenzi, and L. Lardicci, J. Polym. Sci., **53**, 340 (1961).
- [4] P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, Makromol. Chem., **61**, 207 (1963).
- [5] A. M. Liquori and B. Pispisa, J. Polym. Sci. B, **5**, 375 (1967).
- [6] R. C. Schulz, Z. Naturforsch., **19b**, 387 (1964).
- [7] R. C. Schulz and H. Hilpert, Makromol. Chem., **55**, 132 (1962).
- [8] H. Sobue, K. Matsuzaki, and S. Nakano, J. Polym. Sci. A, **2**, 3339 (1964).
- [9] M. Goodman and Y.-L. Fan, Dissertation Abstr., **26**, 2470 (1965).
- [10] P. Pino, Adv. Polym. Sci., **4**, 393 (1965).
- [11] K. Yamauchi, M. Kinoshita, and M. Imoto, Bull. Chem. Soc. Japan, **44**, 3186 (1971).
- [12] T. M. Lowry, Optical Rotatory Power, Longmans, Green and Co. Ltd., London, 1935, p. 28.
- [13] G. Allegra, P. Corradini, and P. Ganis, Makromol. Chem., **90**, 60 (1966).
- [14] P. Pino and G. P. Lorenzi, Makromol. Chem., **47**, 242 (1961).
- [15] L. Verbit, S. Mitsui, and Y. Senda, Tetrahedron, **1966**, 753.
- [16] F. A. Bovey, and G. V. D. Tiers, J. Polym. Sci., **44**, 173 (1960).
- [17] W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, J. Polym. Sci., **46**, 317 (1960).
- [18] D. E. Glusker, R. A. Gallucio, and R. A. Evans, Polym. Preprints, **3**(2), 336 (1962).
- [19] A. A. Korotkov, S. P. Mitsengendler, and V. N. Krasulina, J. Polym. Sci., **53**, 217 (1961).

- [20] K. Liu, J. S. Lignowski, and P. Ullman, Polymer Preprints, 6(2), 904 (1965).
- [21] T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. E. Kincaid, A. Spell, and J. D. Stroupe, J. Amer. Chem. Soc., 80, 1768 (1958).
- [22] T. G. Fox, W. E. Goode, S. Gratch, C. M. Huggett, J. F. Kincaid, A. Spell, and J. D. Stroupe, J. Polym. Sci., 31, 173 (1958).
- [23] T. Tsuruta and T. Makimoto, paper presented at 19th IUPAC Congress, London, 1963.
- [24] T. Tsuruta, T. Makimoto, and H. Kanai, J. Macromol. Sci.-Chem., 1, 31 (1966).
- [25] F. A. Bovey, J. Polym. Sci., 46, 59 (1960).
- [26] T. G. Fox and H. W. Schnecko, Polymer, 3, 575 (1962).
- [27] C. Walling and D. P. Tanner, J. Polym. Sci., A, 1, 2271 (1963).
- [28] T. Otsu, B. Yamada, and M. Imoto, J. Macromol. Sci.-Chem., 1, 61 (1966).
- [29] A. M. Liquori, G. Anzuino, V. M. D'Alagni, and P. De Saintis, Nature, 206, 358 (1965).
- [30] I. Yuki, K. Hatada, T. Niinomi, and Y. Kikuchi, Polym. J., 1, 36 (1970).

Accepted by editor October 22, 1975

Received for publication October 27, 1975