*Macromolecules* **1995,** *28,* 5135–5138

# Induction of a Single-Handed Helical Conformation through Radical Polymerization of Optically Active Phenyl-2-pyridyl-*o*-tolylmethyl Methacrylate

**Yoshio Okamoto,*,† Mitsuhiro Nishikawa,‡ Tamaki Nakano,† Eiji Yashima,† and Koichi Hatada‡**

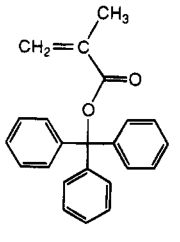
*Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan, and Department of Synthetic Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan*

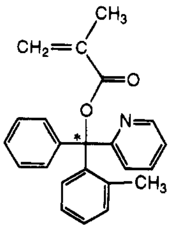
*Received January 23, 1995; Revised Manuscript Received April 25, 1995®*

ABSTRACT: Optically active phenyl-2-pyridyl-*o*-tolylmethyl methacrylate (PPyoTMA) having various enantiomeric excesses was polymerized with diisopropyl peroxydicarbonate in toluene at 40 °C. Isotactic polymers were obtained. The polymers showed large optical rotations which are opposite in sign to the rotation of the starting monomer and the optical activity was higher than expected from the enantiomeric purity of the monomeric units in the polymer, indicating that a right- or left-handed helix was formed in excess from the steric effect of the chiral side group. Copolymerization of PPyoTMA with triphenylmethyl methacrylate (TrMA) also gave optically active, isotactic polymers; the phenyl-2-pyridyl-*o*-tolylmethyl group is also effective in inducing an excess of a single-handed helix consisting of TrMA monomeric sequences. Copolymerization with MMA gave atactic polymers showing much smaller optical activity than that of the copolymers with TrMA.

## Introduction

Triphenylmethyl methacrylate (TrMA) gives a highly isotactic, optically active polymer through asymmetric anionic polymerization using complexes of organolithium and chiral ligands.[1–3] The optical activity of poly(TrMA) is based mainly on a one-handed helical conformation of the main chain which is maintained by steric repulsion between the bulky side groups. The direction of the helix is controlled by the chirality of the ligands of the initiator complexes. Optically active phenyl-2-pyridyl-*o*-tolylmethyl methacrylate (PPyoTMA),[4–6] a TrMA analog with a chiral ester group, also gives an optically active helical polymer by asymmetric anionic polymerization;[5] however, in this polymerization, the helix sense is controlled by the chirality of the ester group rather than by that of the initiator. This is in contrast to the fact that the helicity is controlled by the chiral ligand in the polymerization of phenyl-2-pyridyl-*m*-tolylmethyl methacrylate.[7] A high enantiomer selectivity has been found for the polymerization of racemic PPyoTMA using optically active anionic initiators.[4] In addition, it has also been found that the helical polymer anion consisting of pure enantiomeric monomeric units of PPyoTMA can discriminate enantiomers of the racemic monomer and polymerizes exclusively one antipode when used as a polymeric initiator.[5]


TrMA


PPyoTMA

The present study deals with the radical polymerization of optically active PPyoTMA and copolymerization with TrMA and methyl methacrylate (MMA). We are interested in the helix-forming propensity and asymmetric induction leading to a one-handed helix based on the side chain chirality in the radical polymerization of PPyoTMA. Enantiomer selectivity is also of interest. There are several examples available concerned with stereocontrol in radical polymerization.[8–10] However, as far as we know, there is no clear example of controlling helix direction nor enantiomer selection through a radical process other than the present work.

## Experimental Section

**Materials.** Diisopropyl peroxydicarbonate (($i$PrOCOO)$_2$) was kindly provided by NOF Co. (Taketoyo-cho, Chita-gun, Aichi 470-23, Japan) and used as obtained. PPyoTMA was prepared and chromatographically resolved in the same manner as reported:[5] (+)-PPyoTMA, ee 100%, $[\alpha]^{25}_{365}$ +190.1°, $[\alpha]^{25}_{D}$ +48.6° (*c* 0.8, CHCl$_3$).

**Polymerization and Treatment of the Products.** Polymerization was carried out in a glass ampule under a dry N$_2$ atmosphere. The monomer was dissolved in toluene, and the solution was cooled at 0 °C. A toluene solution of ($i$PrOCOO)$_2$ was then added to the cooled monomer solution, and the mixed solution was heated at 40 °C to initiate reaction. The reaction was terminated by cooling the polymerization solution at 0 °C. The obtained polymer was precipitated in hexane, collected with a centrifuge, and dried under vacuum at 50 °C. The hexane-soluble part of the reaction mixture was saved as unreacted monomer. See also Tables 1 and 2 for more detail.

A part of the obtained poly(PPyoTMA) was fractionated to benzene–hexane (1/1)-soluble and -insoluble parts. The benzene–hexane-insoluble and unfractionated polymers were converted to poly(MMA) through hydrolysis with MeOH-HCl followed by methylation with CH$_2$N$_2$ to obtain samples for $^1$H NMR and gel permeation chromatographic (GPC) analyses, respectively.

The ee of the remaining monomer (column 9 in Table 1) was determined by HPLC resolution.[5] The ee of the monomeric units in the polymer (column 7 in Table 1) was calculated according to the following equation:

$$\mathrm{ee}_{(\mathrm{polymer})} = 100\mathrm{ee}_{(\mathrm{f})}/Y - 100\mathrm{ee}_{(\mathrm{r})}/Y + \mathrm{ee}_{(\mathrm{r})}$$

where ee$_{(\mathrm{f})}$, ee$_{(\mathrm{r})}$, and $Y$ are the ee of the monomer in the feed

---

† Nagoya University.
‡ Osaka University.
® Abstract published in *Advance ACS Abstracts,* June 1, 1995.

0024-9297/95/2228-5135$09.00/0

**Table 1. Radical Polymerization of PPyoTMA in Toluene**[a]

| | | polymer | | | | | | remaining monomer |
|---|---|---|---|---|---|---|---|---|
| run | ee (%) of monomer in feed | yield (%) | $[\alpha]^{25}_{365}$[b] (deg) | DP[c] | Mw/Mn[c] | ee (%) of monomeric units[d] | tacticity (%)[e] mm/mr/rr | ee (%)[f] |
| 1 | 0 | 90.4 | 0 | 34 | 1.73 | 0 | 74/19/7 | 0 |
| 2 | −6.9 | 98.6 | +76 | 35 | 1.53 | −7.0 | 73/19/8 | −3.4 |
| 3 | −15.9 | 88.4 | +246 | 35 | 1.55 | −16.8 | 72/19/9 | −9.0 |
| 4 | −26.1 | 84.9 | +313 | 32 | 1.64 | −27.1 | 72/21/7 | −20.6 |
| 5 | −53.4 | 95.5 | +520 | 33 | 1.68 | −53.5 | 75/19/7 | −50.3 |
| 6 | −80.0 | 90.8 | +608 | 32 | 1.69 | −80.6 | 75/19/7 | −74.6 |
| 7 | +100 | 93.7 | −617 | 35 | 1.77 | +100 | 74/16/10 | +100 |
| 8[g] | +100 | | −1280 | | | | 98/1/1 | +100 |

[a] Conditions: monomer 0.7 g, toluene 5 mL, [monomer]/[($i$PrOCOO)$_2$] = 13, temperature 40 °C, time 24 h. [b] In $CHCl_3$−2,2,2-trifluoroethanol (9/1). [c] Determined by GPC of poly(MMA) derived from poly(PPyoTMA). [d] Calculated from ee of monomer in feed, yield, and ee of remaining monomer shown in this table (see Experimental Section). [e] Determined by $^1$H NMR analysis of poly(MMA) derived from benzene−hexane (1/1)-insobluble poly(PPyoTMA). [f] Determined by HPLC resolution.[5] [g] The sample was prepared by anionic polymerization using $n$BuLi as an initiator in tetrahydrofuran at −78 °C and available from our previous work.[6] Rotation at 365 nm has not been reported.

**Table 2. Radical Copolymerization of (+)-PPyoTMA ($M_1$) with MMA and TrMA ($M_2$) with ($i$PrOCOO)$_2$ in Toluene**[a]

| run | $M_2$ | $M_2/(M_1 + M_2)$ in feed (mol/mol) | yield[b] (%) | $M_2/(M_1 + M_2)$[c] in polymer (mol/mol) | $[\alpha]^{25}_{365}$[d] (deg) | DP[e] | $M_w/M_n$[e] | tacticity (%) mm/mr/rr |
|---|---|---|---|---|---|---|---|---|
| 1 | MMA | 0.20 | 86.1 | 0.21 | −132 | 34 | 1.69 | 35/47/18[f] |
| 2 | MMA | 0.50 | 86.3 | 0.48 | +56 | 38 | 1.60 | 21/47/32[f] |
| 3 | MMA | 0.80 | 85.5 | 0.79 | +59 | 41 | 1.43 | 10/46/44[f] |
| 4 | TrMA | 0.20 | 86.4 | 0.20 | −535 | 59 | 2.00 | 74/19/7[g] |
| 5 | TrMA | 0.50 | 90.1 | 0.50 | −408 | 43 | 1.48 | 76/17/7[g] |
| 6 | TrMA | 0.91 | 94.1 | 0.92 | −53 | 39 | 1.51 | 69/22/9[g] |

[a] Conditions: monomer ([$M_1$] + [$M_2$]) 1.75 mmol, toluene 4.3 mL, [monomer]/[($i$PrOCOO)$_2$] = 13, temperature 40 °C, time 24 h. [b] Hexane-insoluble part of the product. [c] Determined from $^1$H NMR spectra of the copolymers. [d] In $CHCl_3$−2,2,2-trifluoroethanol (9/1). [e] Determined by GPC of poly(MMA) derived fom the original copolymer. [f] Determined by $^1$H NMR analysis of poly(MMA) derived from the hexane-insoluble copolymer. [g] Determined by $^1$H NMR analysis of poly(MMA) derived from the benzene−hexane (1/1)-insoluble copolymer.

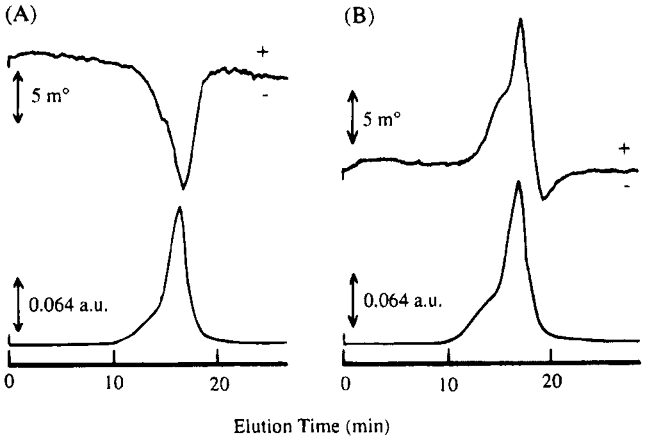


**Figure 1.** HPLC resolution of poly[(±)-PPyoTMA] (run 1 in Table 1) using columns (25 × 0.46 cm (i.d.)) packed with (+)-poly(TrMA) (A) and (−)-poly(TrMA) (B) chemically bonded to silica gel; top curve shows polarimetric (Hg) response and bottom curve UV (254 nm) response. Resolution was done at 23 °C with $CHCl_3$ as an eluent (0.2 mL min$^{-1}$).

(%), that of the remaining monomer (%), and the polymer yield (%), respectively.

**Measurements.** $^1$H NMR spectra were taken on JNM MN-100 (100 MHz) and FX-100 (100 MHz) spectrometers. Optical rotation was measured with a JASCO DIP-181 digital polarimeter. Gel permeation chromatography (GPC) of poly(MMA) was performed using a JASCO FLC-A10 chromatograph equipped with two Shodex A-80M columns connected in series. GPC analysis of poly(PPyoTMA) was carried out with a JASCO Trirotar II chromatographic pump equipped with UVIDEC-100-III UV and DIP-181C polarimetric detectors using TSK KF-802.5 and Shodex AC80M GPC columns connected in series. HPLC resolution of poly[(±)-PPyoTMA] was done using the same apparatuses as those for the latter GPC experiment.

## Results and Discussion

**Homopolymerization.** The results of polymerization of PPyoTMA having various enantiomeric excesses (ee) are shown in Table 1. The obtained polymers had isotactic configurations, suggesting that those polymers have a helical conformation. The isotacticity was higher than that for the radically prepared poly(TrMA) (mm 64%)[8a] and lower than that of poly(1-phenyldibenzosuberyl methacrylate),[8b,11] indicating that the steric effect of the phenyl-2-pyridyl-$o$-tolyl group is intermediate between those of the trityl and 1-phenyldibenzosuberyl groups in stereoregulation. However, the ee of the starting monomer had little effect on the tacticity in the radical polymerization. Anionic polymerization of the optically pure (+)-monomer gave an almost perfectly isotactic polymer (run 8 in Table 1).

The helical conformation of the polymer obtained by radical polymerization was also indicated by chromatographic resolution of the poly[(±)-PPyoTMA] (run 1 in Table 1) using purely one-handed helical (+)- and (−)-poly(TrMA)-bonded silica gel as the stationary phase[12] (Figure 1). (+)- and (−)-poly(TrMA)s selectively adsorbed the (+)- and (−)-fractions of the sample polymer, respectively, to lead the elution of the (−)- and (+)-fractions. The possible reasons for this chromatographic separation are the recognition of the helix sense and that of the side chain chirality, i.e., the separation of poly[(+)-PPyoTMA] and poly[(−)-PPyoTMA]. However, the production of a mixture of poly[(+)-PPyoTMA] and poly[(−)-PPyoTMA] from (±)-PPyoTMA (stereoselective polymerization) by a radical mechanism is assumed not to be plausible based on the low enantiomer selectivity in the polymerization of the monomers with various ee values (runs 2−6 in Table 1) as described later. Hence, we estimate that the above separation is based on the recognition of the helix direction by poly(TrMA). The

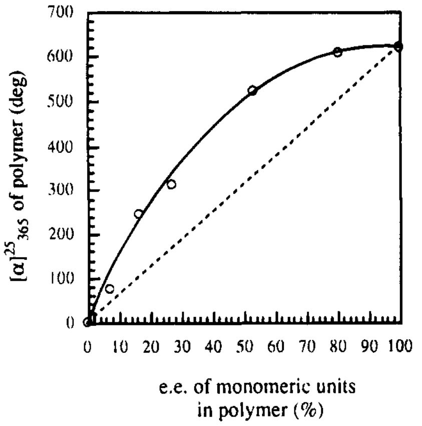


**Figure 2.** Relation between the absolute values of optical activity of the poly[(−)-PPyoTMA]s (runs 2−7) and the enantiomeric excess of monomeric units in the polymers. The dotted line has been drawn between the origin and the point corresponding to an ee of 100%.

present results are consistent with the reported results of the resolution of helical poly(diphenyl-2-pyridylmethyl methacrylate)[13] and poly(TrMA)[12,14] using optically active poly(TrMA) as a stationary phase where the (+)-poly(TrMA) phase selectively adsorbs the (+)-helix of those sample polymers. The discrepancy in the chromatographic patterns in Figure 1A,B seems to be based on the difference of the separation ability of the two HPLC columns.

The polymer obtained from the optically pure (+)-monomer showed a large levorotation (run 7 in Table 1). Anionic polymerization of the (+)-monomer (run 8) also gives a polymer with a higher isotacticity and levorotation, and the rotation has been attributed to the one-handed helical conformation of the main chain.[5] Therefore, the results of run 7 suggest that the optical activity of the polymer, which is opposite in sign to that of the monomer, is mainly based on the main-chain helical conformation induced by the chiral steric effect of the ester group. The smaller rotation compared to the anionically obtained polymer is considered to be based on the lower isotacticity, which leads to a shorter single-handed helical sequence.

The induction of a single-handed helix was further confirmed by the polymerization of (−)-PPyoTMA with various ee values in which the dextrorotatory polymers were obtained (runs 2−6 in Table 1). The absolute values of rotation of the polymers were plotted against the ee values of the monomeric units in the polymers in Figure 2. The optical rotation of the polymer was not proportional to the ee of the monomeric units: it was always larger than the value expected from the ee of the monomeric units (dashed line in the figure). From this nonlinear relation shown in the graph, one can exclude the possibility that the optical activity of the polymer is merely based on the side chain chirality. Furthermore, the chirality of a one-handed helical part induced by a successive sequence of the (−)-monomeric units (monomeric units derived from the (−)-monomer) can overcome the opposite chiral induction by the sporadic (+)-monomeric units. In other words, once a one-handed helical radical comes under the influence of the (−)-monomeric units, an entering (+)-monomer becomes a part of the one-handed helix whose direction may be unfavorable to the chiral nature of the (+)-monomer.[15]

In the polymerization of the (−)-monomers with various ee values, enantiomer selection was observed, though it seems to be low. The ee of the unreacted monomer determined by HPLC resolution was lower and that of the monomeric units in the polymer was slightly higher than that of the starting monomer. This indicates that the antipode of the enantiomers in excess was selectively polymerized to a small extent.

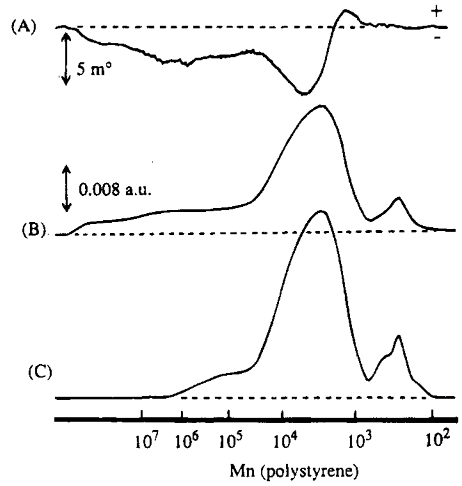


**Figure 3.** GPC curves of poly[(+)-PPyoTMA] (run 1 in Table 1) obtained immediately after being dissolved in $CHCl_3$ with polarimetric (A) and UV (254 nm) (B) detection and the curve of the fractionated polymer (see text) (C) (UV detection). The peaks of the lowest molecular weight (ca. 2.5K) seem to be based on optically inactive impurities; assignment of these peaks has not been done.

In order to obtain information about the chiral structure of the polymer, GPC separation of the poly[(+)-PPyoTMA] of run 7 in Table 1 was performed using UV and polarimetric detectors with $CHCl_3$ as an eluent (Figure 3). *It must be noted that a part of the polymer (higher molecular-weight fraction) was not soluble in $CHCl_3$ and the amount of insoluble part in the sample solution (suspension) increased on standing.* The sample solution was injected immediately after the addition of chloroform to obtain the polarimetric (A) and UV (B) chromatograms. In the chromatogram (B), in addition to the peak corresponding to $M_n$(polystyrene) of ca. 3.5 × $10^3$, a broad peak of a polymer with a higher molecular weight is observed. The highest molecular weight reaches the exclusion limit of the GPC columns we used. This extraordinarily high molecular weight fraction appears to be based on aggregates of the helical polymer[16] because such a high polymer was not seen in the analysis of poly(MMA) derived from the poly(PPyoTMA).

The polarimetric chromatogram (A) has a different pattern from (B) corresponding to the UV chromatogram (B): this means that the fractions in the polymer sample have different optical activities depending on their molecular weights. Two characteristic features about the relation of (A) with (B) can be pointed out. First, the polymer of lower molecular weight fraction at $M_n$ of ca. 3.5 × $10^3$ shows mainly negative rotation with its lower molecular weight fractions showing positive rotation. The dextrorotatory fraction seems to be based on oligomers with random conformations since the positive response in (A) was not seen for a sample washed with a benzene−hexane mixture, which has been found to be a good solvent for removing oligomers from helical polymethacrylates.[2] The positive rotation is likely to be based on side chain chirality. Second, the ratio of the polarimetric response to the UV response is higher for the higher molecular weight fraction with a broad distribution. To make this point clear, the polymer was fractionated using $CHCl_3$ in a 24-h period; in this period the amount of insoluble polymer increased as mentioned earlier. The UV chromatogram of the $CHCl_3$-soluble polymer is shown as curve C in Figure 3. This polymer with a lower amount of the aggregated polymer showed $[\alpha]^{25}_{265}$ −509° and the $CHCl_3$-insoluble part $[\alpha]^{25}_{365}$ −817° in a $CHCl_3$−2,2,2-trifluoroethanol (9/1) mixture. One can propose two possible reasons for these observations. One is that the individual polymer molecules in both the lower and higher molecular weight fractions have the same chiral conformation and aggregation causes a characteristic chiral supramolecular structure which contributes to the levorotation. The other is that the aggregate-forming polymer has some conformationally or configurationally different stereostructure compared to the counterpart. If this is the case, there may be several kinds of propagating species in the reaction system, leading to different stereostructures.

**Copolymerization.** Copolymerizations of (+)-PPyoTMA (ee 100%) with MMA and TrMA were carried out to gain a deeper insight into the chiral-inducing power of the optically active monomer. The results are shown in Table 2. The components of the monomeric units in the copolymers were very close to the corresponding feed components of two monomers for both copolymerizations with MMA and TrMA. On the basis of this result along with the fact that the polymer yields were not quantitative, we assume that the copolymerizations occurred mostly in a random manner.

In the copolymerizations with MMA, the isotacticity of the obtained polymers increased with increasing (+)-PPyoTMA content in the feed monomer mixture. At the ratios of MMA in the feed of 50 and 80%, the obtained polymers were atactic and showed positive rotation. This is ascribed to the side chain chirality. However, at the MMA ratio of 20% in feed, the polymer showed a negative rotation, suggesting that this polymer has single-handed helical portions which presumably are isolated in the flexible MMA monomeric sequences.

The copolymerization with TrMA, a helix-forming monomer, resulted in levorotatory polymers with isotactic configuration in all cases. This indicates that the rotation of the polymer is based on the helical conformation of the main chain. The rotation values for the polymers obtained at the TrMA ratios of 20 and 50% in feed were larger than expected from the feed monomer ratio.[17] Also, the isotacticity of the polymer obtained at the TrMA ratio of 50% was comparable to that of the homopolymer of (+)-PPyoTMA. These results suggest that the chiral induction based on helical sequences consisting of successive (+)-PPyoTMA monomeric units can induce a single-handed helical conformation also for the TrMA monomeric sequence. Nevertheless, sporadically existing (+)-PPyoTMA monomeric units seem to have much lower induction power as can be seen from the results of the copolymerization at a TrMA ratio of 90% in feed.

## Conclusion

We have presented the first example of a helix-sense-selective polymerization via a radical mechanism. The optically active PPyoTMA monomeric units can induce a single-handed helical conformation not only via homopolymerization but also in copolymerization with TrMA. In both the homo- and copolymerization, successions of (+)- or (−)-PPyoTMA monomeric units appear to be important in inducing a right- or left-handed helix in excess, which has not been known so far. In the polymerization of PPyoTMA with various enantiomeric excesses, enantiomer selection was observed though it was low. We are currently attempting to optimize the structure of the chiral side group to achieve higher chiral inductions.

## References and Notes

(1) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763.
(2) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc.* **1992**, *114*, 1318.
(3) For a review of helical polymers in addition to other chiral polymers, see: Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349.
(4) Yashima, E.; Okamoto, Y.; Hatada, K. *Polym. J.* **1987**, *7*, 897.
(5) Yashima, E.; Okamoto, Y.; Hatada, K. *Macromolecules* **1988**, *21*, 854.
(6) Okamoto, Y.; Yashima, E.; Hatada, K. *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 297.
(7) Okamoto, Y.; Nakano, T.; Asakura, T.; Mohri, H.; Hatada, K. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 287.
(8) For isotactic control by helix formation, see: (a) Yuki, H.; Hatada, K.; Niinomi, T.; Kikuchi, Y. *Polym. J.* **1970**, *1*, 36. (b) Nakano, T.; Mori, M.; Okamoto, Y. *Macromolecules* **1993**, *26*, 867 and references cited therein.
(9) For polymerization of optically active acrylamides giving isotactic configuration, see: Porter, N. A.; Allen, T. R.; Breyer, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 7676.
(10) For cyclopolymerization of chiral monomers, see: (a) Porter, N. A.; Miracle, G. S.; Cannizzaro, S. M.; Carter, R. L.; McPhail, A. T.; Liu, L. *J. Am. Chem. Soc.* **1994**, *116*, 10255. (b) Wulff, G.; Dhal, P. K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 196. (c) Kakuchi, T.; Kawai, H.; Katoh, S.; Haba, O.; Yokota, K. *Macromolecules* **1992**, *25*, 5545. (d) Nakano, T.; Sogah, D. Y. *J. Am. Chem. Soc.* **1995**, *117*, 534.
(11) An alternative trivial name of this polymer is poly(5-phenyldibenzosuberan-5-yl methacrylate). The IUPAC systematic name is poly(10,11-dihydro-5-phenyl-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-yl methacrylate).
(12) Okamoto, Y.; Mohri, H.; Nakamura, M.; Hatada, K. *Nippon Kagaku Kaishi* **1987**, 435 (*Chem. Abstr.* **1987**, *106*, 14808a).
(13) Okamoto, Y.; Mohri, H.; Nakano, T.; Hatada, K. *J. Am. Chem. Soc.* **1989**, *111*, 5952.
(14) Okamoto, Y.; Okamoto, I.; Yuki, H. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 451.
(15) The effect of conformational transition discussed in our previous work[6] was not considered here. As the polymerization is carried out at 40 °C, the obtained polymers may have a thermodynamically stable conformation.
(16) Okamoto, Y.; Mohri, H.; Nakano, T.; Hatada, K. *Chirality* **1991**, *3*, 277.
(17) Examples are known of polyisocyanates concerned with the helix induction by a small amount of optically active monomeric units sporadically incorporated into the polymer chain: (a) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452. (b) Green, M. M.; Garetz, B. M.; Munoz, B.; Chang, H.; Hoke, S.; Cooks, R. G. *J. Am. Chem. Soc.*, in press.

MA950073G