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Mechanism of Asymmetric Polymerization of Triphenylmethyl Methacrylate. Separation and Optical Resolution of Oligomers

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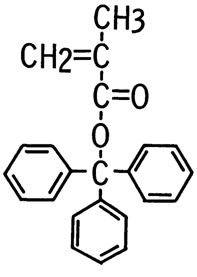
Asymmetric oligomerization of triphenylmethyl methacrylate (TrMA) was carried out with (-)-sparteine-fluorenyllithium complex in toluene at -78 °C and the oligomers of methyl methacrylate (DP=2 and 3) derived therefrom were separated into diastereomers and optical isomers on silica gel and chiral HPLC columns, respectively. On the basis of the obtained data, the mechanism of asymmetric polymerization of TrMA was discussed.

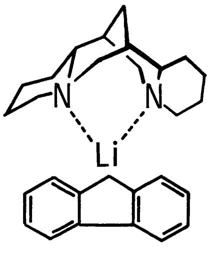
Optically active poly(triphenylmethyl methacrylate) (PTrMA) is the first example of optically active vinyl polymer whose chirality arises only from the stable one-handed helicity and can be directly prepared by asymmetric polymerization of triphenylmethyl methacrylate (TrMA) with chiral anionic initiators such as (-)-sparteine-n-butyllithium (Sp-n-BuLi),1,2) Sp-fluorenyllithium (Sp-FlLi),3) Sp-1,1-diphenylhexyllithium (Sp-DPHLi)3) complexes and (+)-(2S,3S)- or (-)-(2R,3R)-dimethoxy-1,4-bis(dimethylamino)butane (DDB)-lithium amide complexes.4) The last three initiators gave PTrMA having almost pure one-handed helicity. However, in these cases, the obtained polymers were always a mixture of benzene-hexane (1/1)-soluble and -insoluble parts. The soluble part (10-20%) was the oligomers of low optical activities and the insoluble part (80-90%) was the polymer of high optical activities ($[\alpha]_D^{25}$ 350-390°). It has been pointed out that the oligomers with certain specific structures would propagate to the one-handed helical polymer and the others would remain as oligomers until the completion of the polymerization.2)

In the present study, asymmetric oligomerization of TrMA with Sp-FlLi complex was carried out. The resulting oligomers and MMA oligomers derived therefrom were first fractionated in terms of degree of polymerization (DP) with a GPC column. The oligomers of DP=2 and 3 were further separated into diastereomers with a silica gel column and each diastereomer was then optically resolved by HPLC using chiral stationary phases. The results gave us important information on the mechanism of the asymmetric polymerization of TrMA.

When we had almost completed our study,5) Wulff and coworkers reported a similar asymmetric oligomerization of TrMA with Sp-DPHLi.6) They separated the



TrMA



Sp-FlLi

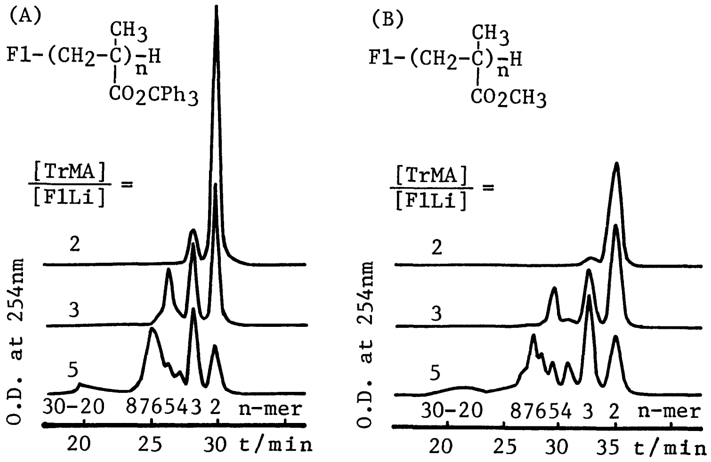


Fig. 1. GPC curves of oligo(TrMA)s (A) and oligo(MMA)s derived therefrom (B).

oligomers and MMA oligomers derived only with a GPC column and analyzed the structures of the separated oligomers (DP=1, 2, 3, and 4) by ^{1}H and ^{13}C NMR spectroscopies as a mixture of diastereomers.

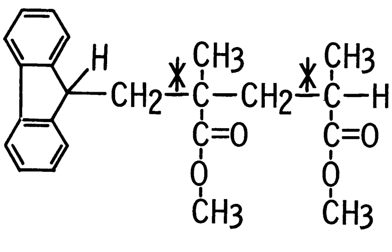
Asymmetric oligomerization was carried out in a glass ampule in toluene at -78 °C. A toluene solution of Sp-FlLi complex was added to a toluene (20 ml) solution of TrMA (1 g) cooled to -78 °C. The reaction was terminated by the addition of a slight excess of methanol. Oligo(TrMA) was converted to oligo(MMA) in the same manner as described previously.[2)] GPC separation of oligomers was carried out on a GPC column (60 cm x 2 (i.d.) cm) packed with polystyrene gel (maximum porosity 3000). Separation of diastereomers was accomplished with an HPLC column (25 cm x 0.46 (i.d.) cm) of silica gel (5 μm) using a butyl chrolide-acetonitrile (97 : 3) mixture as eluent. Optical resolution of enantiomers was done on a chiral HPLC column (25 cm x 0.46 (i.d.) cm) which we developed recently.[7)] UV (254 nm) and polarimetric (Hg) detectors were employed for chromatography.

Figure 1 illustrates the GPC curves of oligo(TrMA)s obtained at [TrMA]/[Sp-FlLi]=2, 3, and 5, and oligo(MMA)s derived from the oligo(TrMA)s. Both chromatograms showed similar distribution patterns.[8)] In all cases, the reaction of TrMA with Sp-FlLi seemed to proceed almost quantitatively to give the oligomers depicted in Fig. 1A because no clear sign of unreacted reagents and side products was observed on the IR spectra of reaction mixtures. GPC analysis also supported this. The existence of unimer (DP=1) was not confirmed even in the equimolar reaction of TrMA and Sp-FlLi, suggesting that unimer anion is much more reactive than Sp-FlLi and dimer anion.

The oligomer distributions at [TrMA]/[Sp-FlLi]=3 and 5 were not simple. In the latter case, although the oligomers of DP<9 in addition to the formation of a polymer (DP= 20-30) were observed, the existence of the intermediate oligomers (DP= 9-20) was not obviously detected. This was also found in the oligomerization with [TrMA]/[Sp-FlLi]=10. Wulff et al.[6)] also reported a similar distributions in the oligomerization with [TrMA]/[Sp-DPHLi]=5. These unusual oligomer distributions indicate that the reactivity of each oligomer anion depends greatly on its degree of polymerization. This is likely correlated with the specific conformation of the oligomers; 3 or 4 monomeric units may form one turn of helix. Analogous possibility has been discussed by Wulff and coworkers.⁶⁾ A stable one-handed helix may start to form at DP≃9. Once an oligomer anion grows to DP≃9, it is likely to add TrMA more readily than other oligomer anions of lower DP probably because of its stable helical conformation suitable to the addition of TrMA. PTrMA (DP=20-30) produced at [TrMA]/[Sp-FlLi]=5 showed a large positive rotation, while oligo(TrMA) showed small negative rotations as in the case of the oligomerization with Sp-DPHLi.6)

In order to obtain deeper information on the stereochemistry of the oligomerization, MMA-dimer and -trimer were separated into diastereomers with a silica gel column. The results are shown in Fig. 2A. Dimer was completely separated into two components which were assigned to meso (m) and racemo (r) isomers by 270 MHz ^{1}H NMR spectroscopy.9) Trimer was fractionated into three components, a mixture of mr and rr, rm, and mm isomers. Trimer assignments were also reasonably accomplished by ^{1}H NMR spectroscopy. The chromatogram shows that in the oligomerization with [TrMA]/[Sp-FlLi]=2 meso addition is preferred in both dimer and trimer formations. Relatively low intensities of m dimer and mm trimer in the chromatogram for [TrMA]/[Sp-FlLi]=3 are ascribed to predominant propagation of m- and mm-anions to higher oligomers. Here, m- and mm-anions mean the anions that give m and mm isomers, respectively, when protonated with methanol. Although the stereochemistry of methanol addition may be different from that of TrMA addition, they seem to be rather similar at least on the dimer anions, because the major isomer of four trimers formed at [TrMA]/[FlLi]=2 is mm isomer which predominantly propagated from m-dimer anion.

MMA-dimer was completely resolved into four isomers10) which consist of two enantiomeric pairs of r and m dimers by chiral HPLC on a cellulose tris(3,5-dichlorophenylcarbamate) column7) as shown in Fig. 2B. A remarkable difference can be seen between the chromatograms for [TrMA]/[Sp-FlLi]=2 and 3. Intensity of SS peak is particularly low in the chromatogram for [TrMA]/[FlLi]=3, which is ascribed to



MMA-dimer

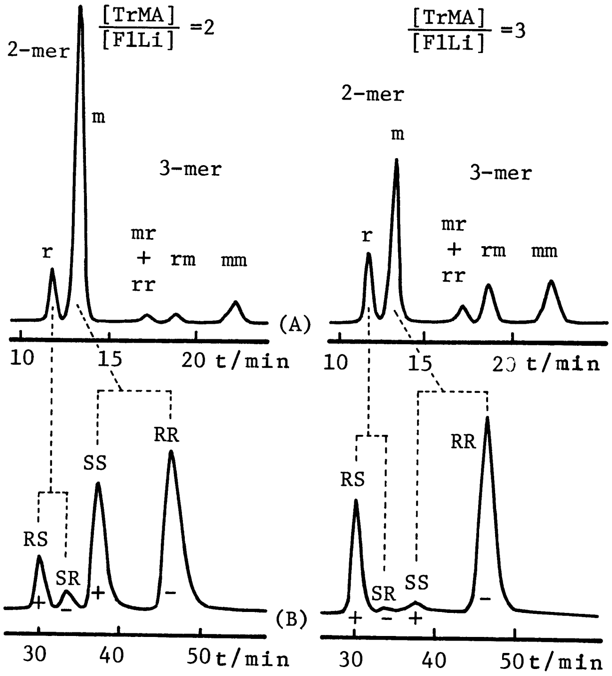


Fig. 2. Separation of diastereomers of MMA--dimer and -trimer (A) and optical resolution of MMA-dimer (B).

predominant propagation of meso anions, particularly SS^- anion to higher oligomers[11]. The chromatogram for [TrMA]/[FlLi]=2 indicates that meso dimers predominated over racemo dimers and the first asymmetric center was slightly rich in R configuration. The RS^- and RR^- dimer anions must be less reactive, and remain unreacted in the oligomerization with [TrMA]/[Sp-FlLi]=3. We also succeeded in complete optical resolution of eight isomers of MMA trimer, and the results indicate that SSS^- and SSR^- anions are much more reactive than other anions, and RRR^- and RRS^- anions are least reactive.[9,12]

From the results mentioned above, the following conclusion may be drawn for the mechanism of the asymmetric polymerization of TrMA by Sp-FlLi complex leading to one-handed helical PTrMA:

1) Sp-FlLi complex adds TrMA very fast and the resulting anion also adds TrMA very fast to give nearly equal amounts of meso dimer anions, RR^- and SS^-.

2) In the third addition, SS^- anion is much more reactive than RR^- and gives mainly SSS^- and SSR^- anions which are the most reactive trimer anion, and RR^- anion slowly affords RRR^- and RRS^- anions which are least reactive.

3) The oligomers start to take a stable helical conformation at DP$\simeq$9. The oligomers which can exceed this DP probably possess continuous ---SSS--- configuration and grow up to a polymer repeating the same isotactic addition.

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8) The field desorption mass spectrum of oligo(MMA) at [TrMA]/[FlLi]=5 showed peaks of M/e=366, 466, 566, 666, 766, 866, and 967 corresponding to the molecular weight of the oligomers (DP=2-8), and the intensity ratio of these peaks was rather similar to that of GPC curve.
9) Detailed data will be reported in a separate paper.
10) Four peaks of the dimers in Fig. 2B were assigned on the basis of the optical rotation, referring to the optical rotation of model compounds ($RCH_2\overset{*}{C}H(CH_3)COOCH_3$) which have very similar structures to the unit of ω-end of the MMA dimer. All (S)-model compounds show positive optical activity regardless of substituent R (H. B. Kagan and J. Jaques, "Stereochemistry", George Thieme Publishers, Stuttgart, Vol. 4, pp. 79-83 (1977)). From the analysis of MMA-dimer derived from TrMA-dimer ended with methyl group, the sign of optical rotation of four MMA-dimers is estimated to depend on the configuration of the asymmetric carbon of the ω-end.[3] However, there exists some possibility that the present assignment could be interchangeable.
11) Here, we assume that SS and RR dimers were produced from configurationally stable SS^- and RR^- anions, because RR/RS ratio in Fig. 2 were not the same at [TrMA]/[FlLi]=2 and 3. However, they might be produced from a single species such as an enolate anion (D. Seebach, R. Amstutz, T. Laube, W. B. Schweizer, and J. D. Dunitz, J. Am. Chem. Soc., 107, 5403 (1985)). In this case, the content of the dimers will be determined by protonation step.
12) In the notation of trimer, R and S for middle asymmetric carbon do not represent absolute configuration. Here, meso addition is represented as RR and SS. Therefore, isotactic sequence is represented as ---RRR--- or ---SSS---.

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