CHEMISTRY LETTERS, pp. 1879-1882, 1988.

Highly Helix-Sense-Selective Polymerization of Diphenyl-2-pyridylmethyl Methacrylate

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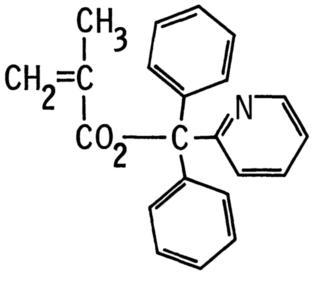
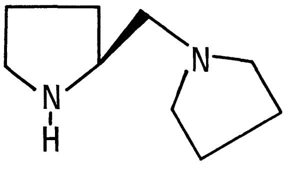
Asymmetric anionic polymerization of diphenyl-2-pyridylmethyl methacrylate by fluorenyllithium or N,N'-diphenylethylenediamine monolithium amide complex of (S)-(+)-2-(1-pyrrolidinylmethyl)-pyrrolidine gave quantitatively an almost purely one-handed helical polymer with narrow molecular weight distribution.

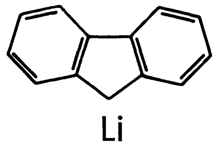
Triphenylmethyl methacrylate (TrMA) and diphenyl-2-pyridylmethyl methacrylate (D2PyMA) are the unique monomers which form only highly isotactic polymers regardless of polymerization conditions such as initiators and solvents.$^{1,2)}$ The polymerization of TrMA and D2PyMA with chiral anionic initiators gives the optically active polymers whose chirality arises from only helicity.$^{3-9)}$ These isotactic polymers have the relatively stable helical conformation even in solution because of the bulkiness of the ester groups. (-)-Sparteine-fluorenyllithium (FlLi) and (S,S)-(+)-1,4-bis(dimethylamino)-2,3-dimethoxybutane-N,N'-diphenylethylenediamine monolithium amide (DPEDA-Li) complexes afford poly(TrMA)s of almost pure one-handedness accompanying with a small amount (∿10%) of oligomers.$^{5,6)}$ On the other hand, these initiators are not effective for the helix-sense-selective polymerization of D2PyMA, and a mixture of (+)- and (-)-poly(D2PyMA)s was always obtained.$^{7)}$ The difference of (+)- and (-)-polymers were 80:20 at most. More recently, we found that (S,S)-(+)-2,3-dimethoxy-1,4-bis(1-perhydroazepinyl)butane was a more effective chiral ligand, giving the polymer consisting of a mixture of 93% (-)- and 7% (+)-fractions.$^{8)}$ Kanoh and Suda have recently reported that the complex of t-butyllithium with an axially chiral biphenyl diamine is an excellent initiator for the asymmetric polymerization of D2PyMA,$^{9)}$ which gave the polymer of $[\alpha]_{365}^{25}$ +1328°.



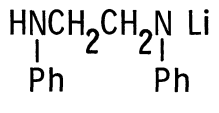
D2PyMA



(+)-PMP



FlLi



$\underset{Ph}{HN}CH_2CH_2\underset{Ph}{N}Li$

DPEDA-Li

Optically active poly(D2PyMA) possesses interesting chiral recognition ability[7)] as well as poly(TrMA)[10-14)] and can resolve many racemates effectively as a chiral stationary phase for high-performance liquid chromatography. The optical resolving power of the chiral stationary phases depends on the one-handedness and degree of polymerization (DP) of the polymers. Therefore, the preparation of poly(D2PyMA) with purely one-handed helicity and controlled molecular weight is highly desirable.

In this communication, we will report the very useful, efficient chiral initiator systems composing of (S)-(+)-2-(1-pyrrolidinylmethyl)pyrrolidine (PMP) and lithium compounds, which gave us the polymer of almost 100% one-handed helicity and controlled molecular weight of narrow molecular weight distribution.

PMP (Aldrich) was dried over CaH_2 and distilled under reduced nitrogen pressure.[15)] The preparation and purification of the other materials were previously reported.[7)] PMP (1.2 equiv.) was mixed with DPEDA-Li or FlLi (1.0 equiv.) in toluene at room temperature to form the complex before use. The polymerization was carried out in a glass ampule or a 1-cm optical cell under dry nitrogen as previously reported.[7)] The polymerization was terminated with a small amount of methanol. The polymer was precipitated in a large amount of methanol and separated by centrifugation as soon as possible. Poly(D2PyMA) was solvolyzed in methanol containing a small amount of hydrochloric acid and the resulting poly(methacrylic acid) was converted to poly(methyl methacrylate) (PMMA) with diazomethane. The tacticity and the degree of polymerization of the PMMA were determined by ^{1}H-NMR and GPC, respectively. The GPC analysis of the optically active polymers was performed with a JASCO TRIROTAR-II chromatograph equipped with UV and polarimetric (JASCO DIP-181C) detectors using $CHCl_3$ (1.0 ml/min) as an eluent. Two Shodex GPC columns, K-802.5 (30 cm) and AC-80M (50 cm), were connected in series.

Figure 1 shows the change of the optical rotation which was directly measured in the polymerization system in a 1-cm optical cell at -78 °C. The optical rotation rapidly increased and reached a constant value in a short time giving the polymers quantitatively. The polymerization rates are much faster than those by other chiral ligands reported previously.[7,8)] The polymerization with (S,S)-(+)-1,4-bis-(dimethylamino)-2,3-dimethoxybutane-DPEDA-Li under the same conditions as (a) in Fig. 1 was completed in about 1.5 h.

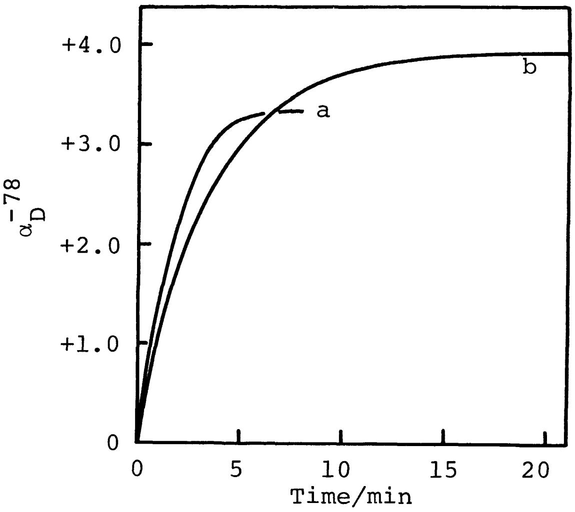


Fig. 1. Observed optical rotation in the polymerization of D2PyMA in a 1-cm cell at -78 °C. (D2PyMA= 0.15 g, toluene= 3.0 ml, [D2PyMA]/[DPEDA-Li]= 20 (a) and 40 (b))

Table 1 shows the results of the polymerization of D2PyMA with the PMP complexes of FlLi, DPEDA-Li, and lithium N-benzylanilide (BzA-Li) in toluene at -78 °C. The polymers of high optical rotation were obtained quantitatively, and DP increased as the amount of the initiator was reduced. The optical rotation of the polymer increased with an increase of the DP of the polymer and seemed to level off at DP= ca. 50. The DP of the polymer obtained with DPEDA-Li was about 1.5 times greater than the value expected from [monomer]/[DPEDA-Li] ratio and that with FlLi about 2 times greater. These discrepancies may be ascribed to the existence of a small amount of the oligomer anions which can not propagate to the polymer.[16)] All the PMMA derived had narrow molecular weight distribution (Mw/Mn=1.04-1.14) regardless of the initiator anions. The polymers (No. 1 and 2 in Table 1) of low DP slowly lost its optical activity in $CHCl_3$ at room temperature.[7)] Some conformational change must proceed. However, higher molecular weight polymer (No. 5) did not show the change of optical activity.

Table 1. Polymerization of D2PyMA by organolithium complexes of PMP in toluene at -78 °C for 3 h[a)]

Run No.	Organo-lithium	[D2PyMA]/[Li]	Yield %	$[\alpha]^{25}_{365}$ [b)]	DP[c)]	Mw/Mn[c)]
1	DPEDA-Li	15	100	+1325	27	1.04
2	DPEDA-Li	20	100	+1406	30	1.08
3	DPEDA-Li	30	100	+1651	45	1.13
4	DPEDA-Li	40	100	+1666	58	1.11
5	DPEDA-Li	50	100	+1675[d)]	81	1.12
6	FlLi	15	99	+1530	30	1.14
7	FlLi	20	99	+1582	40	1.11
8	FlLi	30	100	+1641	60	1.10
9	BzA-Li	20	100	+1370	27	1.06

a) D2PyMA= 1.0 g, toluene= 20 ml, [PMP]/[Li]=1.2.

b) In $CHCl_3$-2,2,2-trifluoroethanol (9/1).

c) Determined from GPC curves of the PMMA using an RI detector.

d) $[\alpha]^{25}_{D}$ +414°.

When butyllithium was used in place of DPEDA-Li and FlLi, the polymer yield was low (17% for 5 h) and the obtained polymer was insoluble in THF and $CHCl_3$-2,2,2-trifluoroethanol. In the case of DPEDA-Li and FlLi, PMP must act as a chiral ligand, while in the case of butyllithium, lithium amide is formed by the exchange reaction of lithium and hydrogen.[15)] The amide may be ineffective for the polymerization. The existence of NH proton of PMP may be essential to attain high helix-sense selectivity because an N-methylated ligand (-)-(S)-1-methyl-2-(piperidinomethyl)pyrrolidine was not as effective as PMP.[7)]

Figure 2 shows the GPC curves of poly(D2PyMA) obtained by PMP-DPEDA-Li (No. 1-5 in Table 1). The GPC was monitored with UV and polarimetric detectors. The polarimetric detector always showed almost identical curve to the UV curve as exemplified for No. 5. This indicates that the polymers obtained are uniform and likely consist of only (+)-polymer. The polymers obtained with FlLi and BzA-Li also gave analogous GPC data. The GPC curves of the optically active poly(D2PyMA) was very complicated, although the PMMAs derived therefrom showed narrow molecular weight distribution. When the ratio of monomer to initiator was 15 (No. 1) and 20 (No. 2), unimodal distribution was observed; two or more peaks were observed at the higher ratio. These complicated GPC curves of poly(D2PyMA) may be ascribed to the association of poly(D2PyMA) molecules. Further investigation on this problem is currently under way.

The present chiral initiator systems seem to be very useful from the view points of easy availability, high activity, and high helix-sense-selectivity. The formation of the polymer with narrow molecular weight distribution is also valuable for studying the conformational stability and association of the polymer mentioned above.

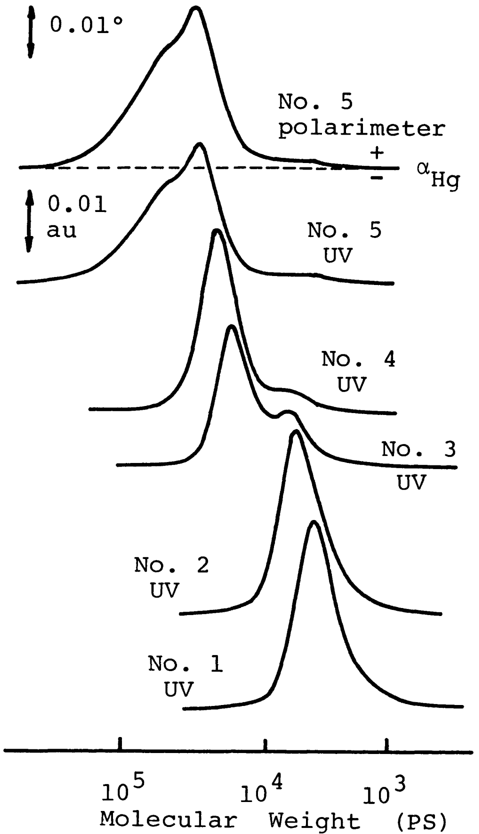


Fig. 2. GPC curves of poly(D2PyMA) (No. 1-5 in Table 1) obtained with PMP-DPEDA-Li.

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(Received August 25, 1988)