

HELIX SENSE-SELECTIVE COPOLYMERIZATION OF TRIPHENYLMETHYL METHACRYLATE WITH CHIRAL ANIONIC INITIATORS*

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ABSTRACT

Optically active copolymers of pairs of three monomers, triphenyl (methyl methacrylate) and one or two pyridyl substituted methyl methacrylate homologues, were obtained by helix-sense-selective copolymerization using complexes of organolithium with chiral ligand as anionic initiators in toluene at low temperature. The copolymers obtained with (–)-sparteine (Sp) and (S,S)-(+) and (R,R)-(–)-2,3-dimethoxy-1,4-bis(dimethylamino)butanes ((+)- and (–)-DDB) complexes of organolithium showed low optical activity, but PMP complex with N,N-diphenylethylenamine monolithium amide (PMP-DPEDA-Li) was effective in synthesizing copolymers of high optical rotation ($[\alpha]_D^{25}$ about $+320 \sim +370^\circ$) which were comparable to those of relative homopolymers with one-handed helical structure.

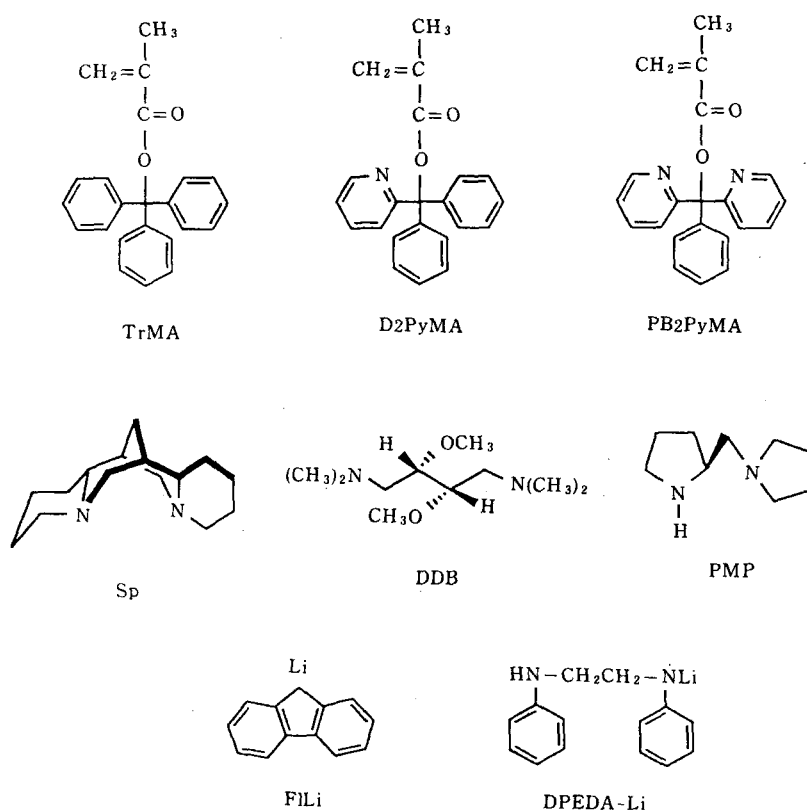
INTRODUCTION

Chiral polymers with optical activity mainly due to helicity have been attracting great interest^[1-7]. In poly(triphenylmethyl methacrylate) (PTrMA) case, it was demonstrated that the polymers showed almost purely one handed helicity and high isotacticity when using initiator systems of organolithium complexes with Sp, DDB and PMP (Scheme 1). The same results were also found by the polymerizations^[5,9] of diphenyl-1-2-pyridylmethyl methacrylate (D2PyMA) and phenyl[bis(2-pyridyl)]methyl methacrylate (PB2PyMA) with PMP complex. These polymers showed excellent chiral recognition ability^[4,8] for many racemic compounds when used as a chiral stationary phase for high performance liquid chromatography. Study on the helix-sense-selective asymmetric copolymerization has not been reported in the literature. It is estimated that the chemical modification of this type of optically active polymers might be

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practised by copolymerization of different monomers. In the present paper, the copolymerizations of TrMA-PB2PyMA, D2PyMA-PB2PyMA and TrMA-D2PyMA with chiral anionic initiators are investigated.



Scheme 1

EXPERIMENTAL

Materials

TrMA was prepared from silver methacrylate and triphenylmethyl chloride in diethyl ether and recrystallized from diethyl ether and hexane. m. p. 103—103.5°C (Lit.^[10] 101—103°C).

PB2PyMA^[9] and D2PyMA^[4] were synthesized from methacryloyl chloride and sodium phenyl [bis (2-pyridyl)] methoxide and sodium diphenyl-2-pyridylmethoxide respectively in THF at 0°C and purified by recrystallization twice from benzene-hexane. m. p. 119.5—120°C and

128—129°C respectively.

n-BuLi used for polymerization was prepared from butyl chloride and lithium metal in heptane according to Ziegler's method^[11].

(-)-Sp (Sigma Chemical co.) and (+)- and (-)-DDB, (+)-PMP (Aldrich Chemical Co.) were commercially obtained. The chiral ligands were dried over CaH₂ and distilled under reduced nitrogen pressure.

Organolithium compounds such as DPEDA-Li and FLLi were prepared by a hydrogen-lithium exchange reaction between the corresponding hydrocarbon or amine and *n*-BuLi in toluene. Chiral initiators were obtained by mixing the toluene solution of lithium compounds and the chiral ligands at room temperature just before use.

Polymerization procedure

The copolymerization was carried out in a dry glass ampule under dry nitrogen. BP2PyMA and TrMA were placed in the ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. The evacuation and flush procedure was repeated three times. Toluene was added with a hypodermic syringe. After cooling the monomer solution to a low temperature then the initiator solution prepared at room temperature was added. The reaction was terminated with a few drops of methanol. The copolymer was precipitated in a large amount of methanol and separated by centrifugation, and was washed with methanol and dried in vacuum at 60°C.

Copolymerizations of BP2PyMA and D2PyMA, or TrMA and D2PyMA were carried out as the same polymerization procedure of BP2PyMA and TrMA.

Poly [PB2PyMA-co-TrMA] and poly [PB2PyMA-co-D2PyMA] were converted into poly(MMA) by refluxing in methanol containing sulfuric acid followed by methylation with diazomethane^[9].

Poly [TrMA-co-D2PyMA] was converted into poly (MMA) by refluxing in methanol containing a small amount of hydrochloric acid^[4].

Measurements

Optical rotation was measured in CHCl₃ and 2, 2, 2-trifluoroethanol (TFE) (10:1, v/v) solution with a Perkin-Elmer 141 MC polarimeter using wavelength 589 nm standard sodium lamp at 25°C.

¹H NMR spectra was measured in CDCl₃ solution with a Varian UNITY-200 (200 MHz) Spectrometer.

RESULTS AND DISCUSSION

Obviously, relative low yields are obtained in most of copolymerizations and these polymers showed low specific rotation and relative low isotacticity. (Tables 1 and 2). It is reasonable because only TrMA can form high rotation and high isotactic homopolymer in toluene with sp-FILi and DDB-DPEDA-Li initiators^[6] at -78°C . In contrast to TrMA, homopolymers of PB2PyMA and D2PyMA showed low optical rotation and low isotacticity at the same polymerization condition^[2,9].

Table 1 Anionic copolymerization of TrMA and PB2PyMA and D2PyMA with S_P complex of FILi in toluene at -78°C for 24 hr. ^{a)}

Composition of Monomers	No.	$\text{M}_1/\text{M}_1+\text{M}_2$ (mole/mole)	Yield (wt %)	$[\alpha]_D^{25\text{b}}$ (deg cm ² /g)	Tacticity ^{c)}		
					I	H	S
PB2PyMA (M_1)	1	0.2	36	+146			
and	2	0.3	28	+128	82	14	4
TrMA (M_2)	3	0.4	14	+61			
	4	0.5	8				
PB2PyMA (M_1)	5	0.3	73	-25			
and	6	0.5	58	-56	89	9	2
D2PyMA (M_2)	7	0.7	76	-39			
TrMA (M_1) and	8	0.3	70	-18			
D2PyMA (M_2)	9	0.5	68	10	90	2	8
	10	0.7	68	+110			

a) Conditions: $\text{M}_1+\text{M}_2=1.52\text{mmol}$; toluene, 10ml; $[\text{M}_1+\text{M}_2]/[\text{Li}]=20$; $[\text{S}_\text{P}]/[\text{Li}]=1.2$

b) Measured in $\text{CHCl}_3\text{-TFE}(10:1 \text{ v/v})$.

c) Determined by ^1H NMR of poly (MMA) derived from poly (PB2PyMA-co-TrMA), poly (PB2PyMA-co-D2PyMA) and poly (TrMA-co-D2PyMA).

I: Isotacticity; H: Heterotacticity; S: Syndiotacticity.

Therefore, in the copolymerization case, it seems that the value of specific rotation depends on mainly the content of monomer TrMA in copolymer. In copolymerization of PB2PyMA-D2PyMA, only low specific rotation copolymers are formed ($[\alpha]_D^{25}=-5\sim-56^{\circ}\text{C}$). Again, suggestion was demonstrated that the existence of polar 2-pyridyl groups in PB2PyMA and D2PyMA caused the difficulty of stereocontrol which also were found in homopolymerization of PB2PyMA and D2PyMA with these anionic initiators^[9].

Table 2 Asymmetric anionic copolymerization of TrMA, PB2PyMA, and D2PyMA with DDB Complex of DPEDA-Li in toluene at -78°C for 24hr^a.

Composition of Monomers	No.	M_1/M_1+M_2 (mole/mole)	Yield (wt %)	$[\alpha]_D^{25b)}$ (deg cm ² /g)	Tacticity ^{c)}		
					I	H	S
PB2PyMA (M_1)	11	0.3	34	-43			
and	12	0.5	30	-12	78	16	6
TrMA (M_2)	13	0.7	14	-6			
DB2PyMA (M_1)	14	0.3	30	-5			
and	15	0.5	31	-7			
D2PyMA (M_2)	16	0.7	32	-5			
TrMA (M_1)	17	0.3	97	-182			
and	18	0.5	96	-295			
D2PyMA (M_2)	19	0.7	97	-334			

a) and b) are as the same as in Table 1. $[\text{DDB}]/[\text{Li}]=1.2$ c) Determined by ^1H NMR of poly (MMA) derived from poly (PB2PyMA-co-TrMA).

Fortunately, PMP was found to be an effective chiral ligand for the helix - sense - selective copolymerization of all these pairs of monomers. The detailed results of the copolymerization with the PMP complex of DPEDA-Li are summarized in Table 3.

Table 3 Asymmetric anionic copolymerization of TrMA, PB2PyMA and D2PyMA with PMP-DPEDA-Li Complex in toluene at -78°C for 24 hr^a)

Composition of Monomers	No.	M_1/M_1+M_2 (mole/mole)	Yield (wt %)	$[\alpha]_D^{25b)}$ (deg cm ² /g)	Tacticity ^{c)}		
					I	H	S
PB2PyMA (M_1)	21	0.3	100	+343	97	1	2
and	22	0.5	100	+367	97	1	2
TrMA (M_2)	23	0.7	98	+367			
PB2PyMA (M_1)	24	0.3	100	+370			
and	25	0.5	99	+363	98	1	1
D2PyMA (M_2)	26	0.7	99	+343			
TrMA (M_1)	27	0.3	100	+371			
and	28	0.5	99	+333	98	0	2
D2PyMA (M_2)	29	0.7	99	+322			

a), b) and c) see Table 1. $[\text{PMP}]/[\text{Li}]=1.2$

The high optical rotations ($[\alpha]_D^{25} + 320 \sim +370^{\circ}$) were observed for all the copolymers. The values of rotation are comparable to that of poly (TrMA)

having almost pure one-handed helicity.

The copolymerizations with PMP anionic initiator give almost quantitative yields and these copolymers show high isotacticity (97–98%). It means that the asymmetric anionic copolymerization of TrMA, PB2PyMA and D2PyMA can be proceeded by the helix-sense-selective mechanism giving stable one-handed helical chain structure at PMP initiator system. These results presented here obviously indicated that chiral ligand PMP may play an important role. The anionic initiator complex with PMP is more suitable for the methacrylate monomers in which the phenyl groups are substituted by polar 2-pyridyl groups.

CONCLUSION

It is obvious that PMP is an effective chiral ligand for the helix-sense-selective copolymerization of all pairs of monomers studied. The values of the rotation are almost not relative to the composition of monomers in copolymers. In Table 3, the optical rotation of poly (PB2PyMA-co-TrMA) changes from $+343^\circ$ to $+367^\circ$ when the ratio of two monomers in feed increased from 0.3, 0.5 to 0.7 respectively. the same situations also have been found in other two copolymer systems.

Keywords:

Phenyl [bis (2-pyridyl) methyl methacrylate; (s)-(+) -1-(2pyrrolidinyl-methyl) pyrrolidine (PMP); Anionic asymmetric copolymerization; Optically active copolymer

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