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Asymmetric Polymerization of Menthyl Methacrylate by Anionic Catalysts

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Abstract: In this paper, (-)menthyl methacrylate((-)MnMA) was polymerized at –78°C in toluene with three types of anionic catalysts, which were complexes of fluorenyllithium with (-)sparteine -((-)-Sp) , (S, S)-(+)-2, 3-dimethoxy-1, 4-bis(dimethylamino)butane((+)DDB) and N,N,N′,N′-tetra-methylethylenediamine(TMEDA), and the chiral optical property of the obtained polymer was studied. The circular dichroism **(**CD) spectrum of the polymer showed negative Cotton effect.

Keywords: Asymmetric polymerization, menthyl methacrylate, specific rotation.

Recently, optically active polymers with bulky side group have attracted many scientis-ts′ concentration because of their wide and useful applications[1]. Some researches about poly(MnMA) were already reported[2]. However the influences of molecular weight and ligands on the optical rotation were not reported. In this communication some new results of above influences were given. (-)MnMA was prepared from methacryloyl chloride and *l*-menthol[2]. The polymerization was carried out in a dry glass ampule, which was evacuated on a vacuum line and flushed with pure dry argon[3].

Y. Okamoto and his coworkers reported that poly(TrMA) can form rigid helix when DP>9[4]. In this paper poly(MnMA) with different molecular weight initiated by FlLi-((+)DDB) were prepared, and their specific rotations were given respectively in **Figure 1**. We can see that the optical rotation values rise slightly with the increase of molecular weight. **Figure 2** showed that the polymer had strong negative Cotton effect.

The yield and specific rotation of poly(MnMA) initiated by different anionic catalysts were listed in **Table 1**. The molecular weight distribution of the polymer initiated by FlLi-(+)DDB complex was narrow, and the conversion of it was the highest. The yield of poly(MnMA) was higher than that reported by K. Matsuzaki (11.2% initiated by *n*-BuLi**,** 8.7% initiated by PhMgBr) (**Table 1)**. The polymer was very easy to form gel without ligands, probably this is the reason why K. Matsuzaki′s polymers have the lower conversion. From the results mentioned above, we can see that (-)MnMA can be stably polymerized in the presence of ligands by asymmetric anionic polymerization.

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Figure 1 The relationship between Mn and specific rotation of polymer initiated by FlLi-(+)DDB

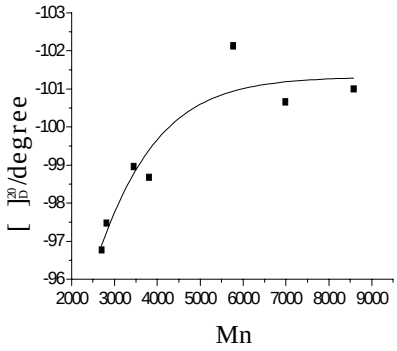

Figure 2 CD spectrum of poly((-)MnMA) initiated by FlLi-(+)DDB

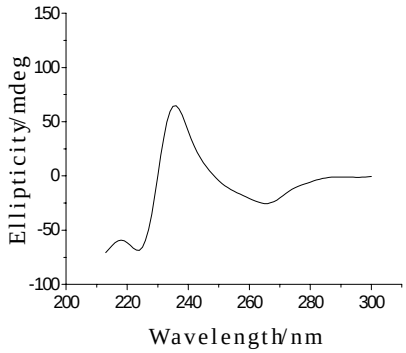

Table 1 The asymmetric polymerization of (-)MnMA initiated by anionic catalysts[a]

No.	ligand	t(hr)	Yield[b](%)	$[\alpha]_D^{20}$ [c]	Mn[d]	Mw/Mn[d]
1	(+)DDB	16	96.2	-102.1	5767	1.09
2	(-)Sp	16	92.0	-94.8	5927	1.11
3	TMEDA	16	51.9	-102.5	15546	1.26

a: Polymerized in toluene at –78°C, [Ligand]/[Li] = 1.2 (mol), [Monomer]/[Li] = 20 (mol), [Toluen-e]/[Monomer]=20 (v/w). b: CH_3OH-insoluble part. c: Measured in THF, concentrated, 0.04. d: Determined by GPC(polystyrene standard).

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