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Syntheses of Monodispersed Methyl Methacrylate Oligomers via Organolanthanide Complexes and Introduction of Hydroxyl Groups into the Oligomer

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Methyl methacrylate (MMA) oligomers ($M_n \simeq 2500$) with a narrow molecular weight distribution ($M_w/M_n < 1.10$) were synthesized by using a $Cp^*_2SmMe(THF)$ initiator ($Co = \eta - C$). The oligomerization proceeds via a samarium enolate as the propagating species and the reaction of the living oligomer with *p*-tolualdehyde produced *p*-tolyl hydroxymethyl-terminated oligoMMA.

Keywords: oligo MMA; $Cp^*_2SmMe(THF)$; *p*-tolualdehyde

INTRODUCTION

It is well known that organolanthanide complexes are efficient catalysts for the polymerization of both polar and nonpolar monomers. Methyl methacrylate (MMA), alkyl acrylate and lactones are typical examples of polar monomers and their polymerizations proceed in a living manner.[1-3] Particularly, we have shown that the organolanthanide-initiated polymerization of MMA affords poly(methyl methacrylate) with high molecular weight, extremely narrow molecular weight distribution and a high yield.[1,2] Furthermore, highly syndiotactic polymers were obtained by the reaction at low temperature. On the other hand, organolanthanide complexes can polymerize nonpolar monomers such as ethylene and α-olefins.[3] Combining catalytic activity towards both types of monomers, we have succeeded in synthesizing a block copolymer of polar monomers with ethylene.[4]

This paper deals with the synthesis of relatively low-molecular-weight PMMA (oligoMMA) with a narrow molecular weight distribution by organolanthanide complexes. The oligomerization should proceed stereoselectively to give syndiotactic oligoMMA. For further application of monodispersive stereoselective oligoMMA, we tried to introduce the functional group HOCHR— into the oligomers' terminal.

RESULTS AND DISCUSSION

We have proved that the organolanthanide-initiated polymerization of MMA proceeds via a lanthanide enolate as propagating species by isolation and characterization of the 1:2 adduct of Cp^*_2SmH with MMA (Scheme 1). The lanthanide enolate can react with various electrophiles. For example, the reaction of the cerium enolate with aldehyde was reported to give aldol adduct in high yield as shown in Scheme 2.[5] We applied this reaction to the propagating species in the oligomerization of MMA to introduce a hydroxyl group into the chain end (Scheme 3). *p*-Tolu-

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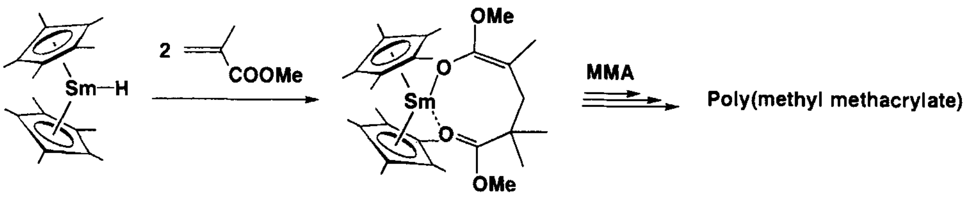

Scheme 1

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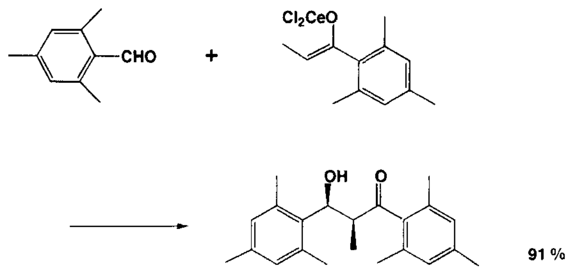


Scheme 2

aldehyde was used as the electrophile in order to calculate the exact molecular weight of the oligoMMA from the peak area ratio of the terminal *p*-tolyl (7.1–7.2 ppm) and the methyl ester (3.60 ppm) group in ^1H NMR (Fig. 1).

Table 1 summarizes the lanthanide-initiated oligomerization of MMA. The lanthanide initiator, $Cp^*_2SmMe(THF)$, and methyl methacrylate were reacted in toluene at −78 °C for 1 h, then *p*-tolualdehyde was added at that temperaure. The oligomers obtained were purified by reprecipitation from chloroform into hexane and complete removal of the aldehyde was confirmed by thin-layer chromatography.

The molecular weight of the oligomers was determined by both GPC (polystyrene standard) and NMR analyses. In every case, the M_n value from GPC is in line with that from NMR. This fact suggests that the introduction of the *p*-tolylhydroxymethyl group is quantitative.

To produce oligomers with different chain length, the ratio of initiator to monomer was varied from 1:20 to 1:5. However, oligoMMA species with $M_n \simeq 2500$ were always obtained. Moreover, at the ratio of 1:5, the yield was quite low. These results indicate that the lanthanide complex cannot initiate the polymerization of MMA effectively when its concentration ratio is high.

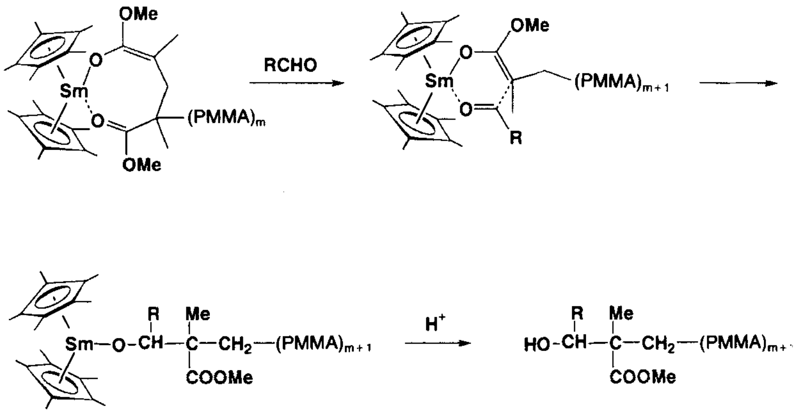
MMA oligomers with narrow molecular weight distribution were obtained in high yield in the cases of 1:10 or 1:20 feed ratios. As for their tacticity, the peak for the rr triad is only clearly seen at 0.82 ppm in the ^1H NMR spectrum (Fig. 1). Peaks for the other triads, mr, mm are lower than 10%. As well as the high-molecular-weight PMMA obtained via the lanthanide complex, a syndiotactic sequence predominates in the oligomers (>90%).

In conclusion, organolanthanide-initiated oligomerization of MMA produced hydroxyl-terminated monodispersed MMA oligomers ($M_n \simeq 2500$) with high syndiotacticity. We are now undertaking the reaction of the hydroxyl end group with methacryloyl chloride to produce oligoMMA macromonomers.

EXPERIMENTAL

General Considerations

All the operations were performed under argon using standard Schlenk techniques. $Cp^*_2SmMe(THF)$ was prepared according to the literature.[6] Methyl methacrylate (MMA) was dried over calcium hydride (CaH_2) and distilled twice, then kept with activated molecular sieves 3A. Toluene was dried over Na/K alloy and distilled before use. ^1H NMR spectra were recorded on a JEOL GX-270 spectrometer. Gel permeation chromatographic analyses were run on a Tosoh Model SC-8010 using TSK gel G1000,



Scheme 3

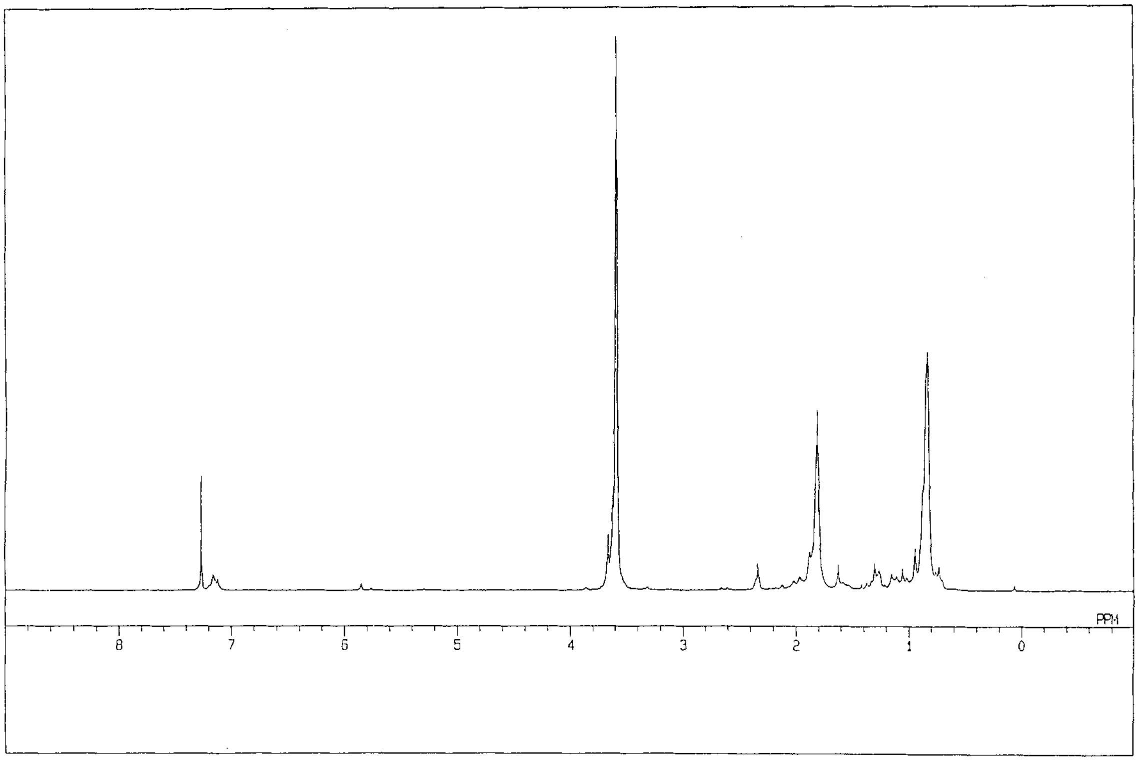


Figure 1 ^{1}H NMR spectrum of *p*-tolylhydroxymethyl-terminated oligoMMA (1 : 10 feed ratio).

G2500, G4000H and G7000H columns in chloroform.

Oligomerization of MMA initiated by Cp*$_2$SmMe(THF) and termination with *p*-tolualdehyde (1 : 20 feed ratio)

A typical example is as follows. To a toluene solution (20 ml) of Cp*$_2$SmMe(THF) (0.254 g, 0.500 mmol) was added at once MMA (1.07 ml, 10.0 mmol) with vigorous magnetic stirring at −78 °C. After the solution had been stirred at −78 °C for 1 h, *p*-tolualdehyde (0.28 ml, 2.4 mmol) was added at −78 °C and the mixture was stirred for 12 h at −78 °C to room temperature (rt). After the solvent had been removed *in vacuo*, the remaining solid was purified by reprecipitation from chloroform to hexane.

Table 1 Syntheses of *p*-tolylhydroxymethyl-terminated MMA oligomer via lanthanide complex

Feed ratio	M_n (GPC)	M_w/M_n	M_n (NMR)	Yield (%)
1:5	2470	1.05	2420	18
1:10	2570	1.06	2500	81
1:20	2710	1.08	2700	94

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