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Highly syndiotactic poly(methyl methacrylate) with narrow molecular weight distribution formed by tert-butyllithium-trialkylaluminium in toluene

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Summary

Polymerization of MMA with t-C_4H_9Li in toluene in the presence of trialkylaluminum(alkyl=methyl, ethyl, butyl, isobutyl, and octyl) was examined at various Al/Li ratios. Triethyl-, tributyl- and trioctylaluminums worked quite effectively in the polymerization to give highly syndiotactic PMMA with narrow molecular weight distribution (MWD) at the Al/Li ratio of 3 and higher than 3. The highest syndiotacticity of 96% was attained with t-$C_4H_9Li/(n\text{-}C_8H_{17})_3Al$ (1/3) at -93°C. The polymerization was initiated by t-C_4H_9- anion and proceeded in a living manner. The structure of the syndiotactic PMMA is chemically identical to that of isotactic PMMA prepared with t-C_4H_9MgBr. Consequently, highly isotactic and syndiotactic PMMAs with narrow MWD and with the same chemical structure from α-end to ω-end were obtained.

Introduction

Preparation of highly syndiotactic poly(methyl methacrylate) (PMMA) of finely controlled structure is one of the most interesting and important subjects in polymer synthesis, since PMMA of high glass transition temperature (T_g) is needed for industrial materials such as optical disks and fibers, and the T_g increases with the syndiotacticity. Anionic and living polymerization is one of the promising ways to the preparation of polymers with desired structure, and syndiotactic PMMA with narrow molecular weight distribution (MWD) can be prepared by the living polymerization with bulky alkyllithiums in polar solvents(1-3). However, the syndiotacticities in triad of the polymers do not exceed 85%(4). On the other hand, preparation of PMMA with higher syndiotacticity has been achieved by using Zieglar type initiators in toluene(5,6), organomagnesium compounds with a piperidine ring in toluene or tetrahydrofuran (THF) (7) and triphenylmethylcalcium chloride in 1,2-dimethoxyethane(8,9), but the MWD's were mostly broad. Recently, certain types of Grignard reagents were found to be effective in polar solvents for the preparation of highly syndiotactic PMMA with fairly narrow MWD(10-12). Polymerization of MMA with m-vinylbenzylmagnesium chloride in THF at -110°C gave methanolsoluble and -insoluble fractions, and the latter PMMA showed very high syndiotacticity (96.6% in triad) and narrow MWD(11).

We reported the preparation of highly isotactic PMMA with narrow MWD by t-C_4H_9MgBr(13). In the course of searching syndiotactic PMMA with the same chemical structure as this isotactic PMMA, we recently found that t-C_4H_9Li gave syndiotactic PMMA of narrow MWD in the polymerization carried out in toluene in the presence of trialkylaluminums(14). In this report, some of the characteristics of the polymerization are described briefly.

Experimental

Methacrylate monomers were purified by distillation, and distilled twice over calcium dihydride under high vacuum just before use. t-C_4H_9Li obtained commercially was used as heptane solution. The concentration was determined from ^1H NMR signal intensities of t-C_4H_9 group and heptane*. Trialkylaluminums were used as heptane solutions.

Polymerization was carried out in a glass ampoule filled with dried nitrogen. t-C_4H_9Li was added to a trialkylaluminum solution in toluene cooled to the reaction temperature. The polymerization reaction was initiated by adding the monomer slowly to this mixture. The reaction was terminated with methanol containing HCl at the polymerization temperature. The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The precipitate was collected by filtration, washed with hexane, dilute HCl and water, successively, and dried under vacuum.

^1H NMR spectra of the polymers in nitrobenzene-d_5 were taken at 110°C on a JNM-FX100, a JNM-MH-100 or a JNM-GX500 spectrometer. The molecular weights of the polymers were measured on a Hitachi 117 vapor pressure osmometer in toluene at 60°C or on a JASCO FLC-A10 GPC chromatograph with a Shodex GPC column A-80M (50cmx2) using tetrahydrofuran as an eluent. The GPC chromatogram was calibrated against standard polystyrene samples.

Results and Discussion

The polymerization of MMA in THF with t-C_4H_9Li at -78°C gave a syndiotactic PMMA as expected, but the syndiotacticity was 61% in triad, and the MWD was broad. An isotactic PMMA

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* The concentration thus determined was lower than that by a procedure of Watson and Eastham (titration with sec-butanol) (15) or by acidimetry; for example, 0.954M by the titration, 0.950M by acidimetry, and 0.786M by ^1H NMR analysis. The NMR signal of t-C_4H_9 anion disappeared when the corresponding amount of sec-butanol to the t-C_4H_9 signal was added. The concentration by ^1H NMR was therefore employed, although the reason for the difference between these concentrations is not clear at present.

was obtained in the polymerization in toluene. Among several additives examined in the polymerization in toluene, triethylaluminum was first found to be an effective additive to give a highly syndiotactic PMMA with narrow MWD. The same initiator system was used very recently by Dimov and Hogen-Esch for the syndiotactic polymerization of 2-vinylpyridine (syndiotacticity in triad=70%) (16).

The polymerization by t-C_4H_9Li in toluene at -78°C was carried out at various ratios of trialkylaluminum(R_3Al) to t-C_4H_9Li. R_3Al's examined were trimethyl, triethyl, tributyl, triisobutyl and trioctylaluminums. The results of polymerization are shown in Table 1. In particular, the effect of the ratio of R_3Al to t-C_4H_9Li on the polymerization was examined in detail for the case of t-C_4H_9Li-trioctylaluminum. As described previously, the polymerization with t-C_4H_9Li in the absence of R_3Al gave an isotactic polymer with broad MWD. The isotacticity of PMMA decreased with an increase in the ratio of Al/Li, and a stereoblend type PMMA with bimodal MWD was formed in low yield at the ratio of 1.5. The high molecular weight fraction was found to be isotactic and the low molecular weight fraction syndiotactic. The lower yield may be partly due to gelation of the reaction mixture through the stereocomplex formation between the isotactic and syndiotactic PMMA chains. Highly syndiotactic PMMA with narrow MWD formed at the ratios of 3 and the higher, and the number average molecular weight of the polymer were near to that calculated from the amount of t-C_4H_9Li used and the monomer consumed. The syndiotacticity

Table 1 Polymerization of MMA with t-C_4H_9Li-R_3Al in toluene at -78°C for 24 hr[a]

R	Al/Li	Yield (%)	Tacticity(%) mm	mr	rr	$\overline{Mn}$[b] (Obsd)	$\overline{Mn}$ (Calcd)	$\overline{Mw}$[c]/$\overline{Mn}$
n-C_8H_{17}	0	93	78	16	6	10240[c]	4700	3.10
	1	93	57	26	17	6170[c]	4730	2.02
	1.5	19	37	19	44	3170[c]	1010	15.8
	3	89	0	7	92	4870	4520	1.13
	5[d]	75	0	4	96	4920	3830	1.18
n-C_4H_9	3	100	0	8	92	5510	5060	1.17
C_2H_5	3	99	0	10	90	5450	5020	1.18
CH_3	3	21	1	9	90	2920	1090	1.38
isoC_4H_9	3	70	60	26	14	5770	3540	1.77
	5	84	1	11	88	4620	4270	1.19

[a] MMA 10mmol, t-C_4H_9Li 0.20mmol, toluene 10ml.

[b] Determined by VPO. [c] Determined by GPC.

[d] Polymerization at -93°C.

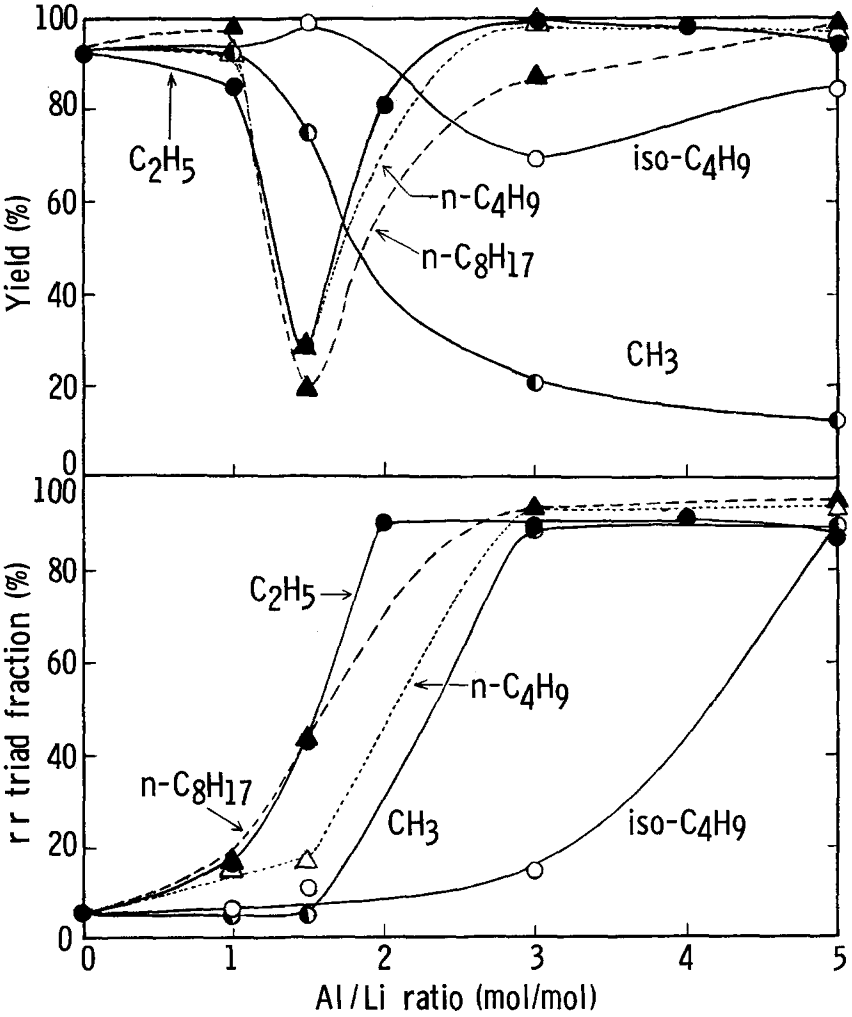


Figure 1 Effect of Al/Li ratio on the yield and rr triad fraction of PMMA prepared with $t\text{-}C_4H_9Li\text{-}R_3Al$ in toluene at -78°C

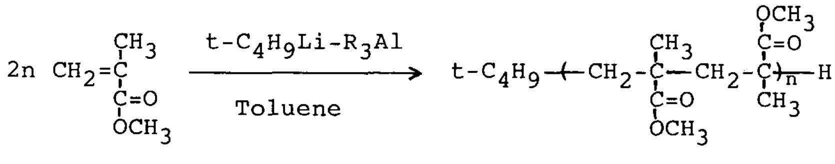
increased with decreasing polymerization temperature and the syndiotacticity in triad of the PMMA formed at -93°C reached to 96%. Initiator efficiency for the polymerization at -93°C was less than unity.

Figure 1 illustrates the effect of several alkylaluminums, including $(n\text{-}C_8H_{17})_3Al$, on the yield and rr triad content of PMMA in the polymerization with $t\text{-}C_4H_9Li$ in toluene at -78°C. The effect of R_3Al in the polymerization by the complex of $t\text{-}C_4H_9Li$ with $(C_2H_5)_3Al$ or $(n\text{-}C_4H_9)_3Al$ was very similar to the case of $(n\text{-}C_8H_{17})_3Al$ and highly syndiotactic PMMAs with narrow MWD were obtained at the Al/Li ratios of 2 ~ 3 and the higher. The syndiotacticity of the polymers decreased slightly in the order of $(n\text{-}C_8H_{17})_3Al$, $(n\text{-}C_4H_9)_3Al$ and $(C_2H_5)_3Al$(see Table 1). The complex of $t\text{-}C_4H_9Li$ with $(CH_3)_3Al$ also gave highly syndiotactic PMMAs at the ratios of $Al/Li\geq 3$ but in low yields. The complex of $t\text{-}C_4H_9Li$ with $(isoC_4H_9)_3Al$ gave highly syndiotactic PMMAs at $Al/Li\geq 5$. These results indicate that slight change in the steric hindrance at aluminum center strongly affects the behavior of the syndiotactic polymerization.

Initiator efficiencies were nearly unity but slightly less than unity in most cases. When the polymerization was initiated by adding $t\text{-}C_4H_9Li$ to the mixture of MMA and the aluminum compound in toluene, the initiator efficiency became apparently less than unity and the MWD broadened. Therefore control of the reaction conditions, in particular at the initiation, is substantially important in this polymerization reaction, and detailed investigations are now under way.

The polymerization mixture formed with $t\text{-}C_4H_9Li/(C_2H_5)_3Al$ became heterogeneous in the course of polymerization depending on the reaction conditions. In particular, the lower ratio of monomer to initiator tended to cause heterogeneity in the system. However, the polymerization proceeded in a living manner as described below. Polymerization by $t\text{-}C_4H_9Li/(n\text{-}C_4H_9)_3Al$ or $t\text{-}C_4H_9Li/(n\text{-}C_8H_{17})_3Al$ usually proceeded homogeneously. The difference in the appearance of the polymerization medium might be the reflection of the difference in the extent of association of the active chains with the aluminum compounds.

^1H NMR analysis of the poly(MMA-d_8) prepared with the complex of $t\text{-}C_4H_9Li$ with $(C_2H_5)_3Al$ (Al/Li=3) revealed that the polymer molecule contained one $t\text{-}C_4H_9\text{-}$ group at the α-end (0.82 ppm) and one methine proton attached to the MMA units at the ω-end (2.49 ppm) and no ethyl group in the chain. The ^1H NMR signal of the methine proton disappeared when the polymerization was terminated with CD_3OD instead of CH_3OH. The results indicate that the polymerization is initiated by $t\text{-}C_4H_9\text{-}$ anion and has the living character. The structure of the PMMA prepared by this initiator system is chemically identical to that of the isotactic PMMA prepared with $t\text{-}C_4H_9MgBr$ in toluene(13), and thus the isotactic and syndiotactic PMMAs of narrow MWD with the same chemical structure from α-end to ω-end are now in our hands. Tacticity dependences of some properties of PMMA are now under investigation by using these highly stereoregular PMMA samples (17).



$$2n\ CH_2=\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}} \xrightarrow[\text{Toluene}]{t\text{-}C_4H_9Li\text{-}R_3Al} t\text{-}C_4H_9\left(CH_2-\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{\overset{OCH_3}{C=O}}{C}}\right)_n H$$

Several alkyl methacrylates were polymerized in toluene by $t\text{-}C_4H_9Li\text{-}(n\text{-}C_4H_9)_3Al$ at -78°C (Table 2). In all the cases except for t-butyl methacrylate, highly syndiotactic polymers

Table 2 Polymerization of alkyl methacrylates with $t\text{-}C_4H_9Li\text{-}(C_4H_9)_3Al$ in toluene at -78°C for 24 hr[a]

Ester group	Yield (%)	Tacticity(%) mm	mr	rr	Mn^b (Obsd)	Mn (Calcd)	Mw^c/Mn
C_2H_5	100	2	8	90	6050	5760	1.07
$isoC_3H_7$	92	3	5	92	7200	5940	1.14
$n\text{-}C_4H_9$	76	1	7	92	7020	5450	1.07
$isoC_4H_9$	91	2	5	93	8690	6530	1.06
$t\text{-}C_4H_9$	87	10	33	57	7140	6260	1.64

[a] Monomer 10mmol, $t\text{-}C_4H_9Li$ 0.20mmol, $(C_2H_5)_3Al$ 0.6mmol, toluene 10ml. [b] Determined by VPO. [c] Determined by GPC.

with narrow MWD's were obtained in good yields.

Utilization of the living PMMA formed with $t\text{-}C_4H_9Li\text{-}R_3Al$ for the preparations of highly syndiotactic block and random copolymers of methacrylates and PMMA macromer was succeeded and the details will be published in near future.

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