

SHORT COMMUNICATIONS

Preparation of Highly Stereoregular Poly(methacrylic acid) by Stereospecific Anionic Polymerization of Trimethylsilyl Methacrylate

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(Received October 31, 1994)

KEY WORDS Isotactic Poly(methacrylic acid) / Syndiotactic Poly(methacrylic acid) / Aluminium Phenoxide / *t*-Butyllithium / Tacticity / Poly(methyl methacrylate) /

Trimethylsilyl methacrylate (TMSMA) has been used as a protected monomer of methacrylic acid to prepare poly(methacrylic acid) (PMAD) and, in particular, block copolymers comprising PMAD block by anionic polymerization, since trimethylsilyl ester is easily hydrolyzed to form carboxylic function.¹⁻⁴ Some of the block copolymers have drawn attention as amphiphilic polymer materials.⁵⁻⁷ However, little has been known about stereospecific polymerization of TMSMA. Aylward claimed that the polymerization of TMSMA with *n*-C₄H₉Li in toluene at -78°C gave an isotactic polymer (*mm* = 89%) and that in tetrahydrofuran (THF) at -78°C gave a syndiotactic polymer (*rr* + *mr* = 90%).² Highly syndiotactic PMAD was prepared from methacrylic acid itself by γ -ray induced polymerization in propan-2-ol (*rr* = 95%) at -78°C.⁸

We have reported several stereospecific living polymerizations of methacrylate; isotactic-specific one by *t*-C₄H₉MgBr,^{9,10} syndiotactic-specific one with *t*-C₄H₉Li/R₃Al^{11,12} and heterotactic-specific one by *t*-C₄H₉Li/bis(2,6-di-*t*-butylphenoxy)methyl-aluminium[MeAl(ODBP)₂].^{13,14} The present communication

reports anionic polymerization of TMSMA with several anionic initiators including above-mentioned initiators effective for the stereospecific living polymerizations of alkyl methacrylate. Among the polymerizations examined, the polymerization with *t*-C₄H₉Li in toluene at -78°C was found to give a highly isotactic polymer and that with *t*-C₄H₉Li/MeAl(ODBP)₂ in toluene at -78°C to give a highly syndiotactic polymer. The results were discussed in comparison with those for methyl methacrylate (MMA) and *t*-butyl methacrylate (*t*-BuMA).

EXPERIMENTAL

TMSMA was prepared by the reaction of potassium methacrylate and trimethylsilyl chloride in benzene at room temperature for 48 h.¹⁵⁻¹⁷ After the white solid formed during the reaction was removed by filtration, the filtrate was distilled under reduced pressure to recover the resulting TMSMA. The crude product was purified by fractional distillation through a 30 cm column (yield 33%, bp 44.4°C/22.8 mmHg; lit. value¹⁷: bp 45°C/20 mmHg). The purity was checked by gas

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chromatography and ^1H NMR spectroscopy (>99.7%). *t*-BuMA was obtained commercially and purified by fractional distillation. These monomers were dried over calcium dihydride and vacuum-distilled just before use.

Toluene and heptane were purified in the usual manner, mixed with a small amount of $n\text{-C}_4\text{H}_9\text{Li}$ to remove a trace amount of water, and then distilled under high vacuum.

$t\text{-C}_4\text{H}_9\text{MgBr}^{9,10}$ and $\text{MeAl(ODBP)}_2^{18,19}$ were prepared as reported previously.

$t\text{-C}_4\text{H}_9\text{Li}$ was obtained commercially (Aldrich Chemical Company, Inc.) as a pentane solution. To replace the pentane with heptane, most of the solvent was removed under vacuum and heptane was added by vacuum-distillation. The procedure was repeated three times to remove pentane completely.

Trimethyl- and tributylaluminiums obtained commercially (Nippon Aluminium Alkyls, Ltd.) were used as heptane solutions.

Polymerization of TMSMA was carried out in a glass ampoule under dry nitrogen. The polymerization reaction was initiated by adding the monomer with a hypodermic syringe slowly to an initiator solution at the polymerization temperature and terminated by adding methanol containing aqueous HCl (1*N*) at the reaction temperature. By this termination procedure, the polymer formed was quantitatively converted to PMAD. The reaction mixture was poured into a large amount of acetone to precipitate the polymeric product. The precipitate was collected by filtration, washed with acetone several times, and dried under vacuum at 35°C. The polymers obtained were converted to poly(methyl methacrylate) (PMMA) by the reaction with diazomethane²⁰ in chloroform, and the resulting PMMA was subjected to tacticity determination by ^1H NMR and molecular weight determination by GPC.

Polymerization of *t*-BuMA was also carried

out similarly. The polymer was recovered by freeze-drying from a benzene solution after insoluble materials were removed by centrifugation. The polymer obtained was converted to PMAD by refluxing in methanol containing aqueous HCl for two days, and then to PMMA by methylation with diazomethane, which was subjected to ^1H NMR and GPC analyses.

^1H NMR spectra were recorded on a JEOL JNM-GSX270 spectrometer.

The molecular weights and molecular weight distributions (MWD's) of the polymers were measured on a JASCO 880-PU chromatograph equipped with Shodex GPC columns, KF-802.5 and KF-80M, using THF as an eluent. The GPC chromatograms were calibrated against standard polystyrene samples.

RESULTS AND DISCUSSION

Polymerization of TMSMA with several anionic initiators were carried out in toluene at -78°C . The results are summarized in Table I together with those for the polymerizations of MMA and *t*-BuMA. Polymerization of TMSMA with $t\text{-C}_4\text{H}_9\text{MgBr}$, which is a highly isotactic-specific initiator for the polymerization of MMA,^{9,10} gave a much less stereoregular polymer. Polymerization of TMSMA with $t\text{-C}_4\text{H}_9\text{Li}/(n\text{-C}_4\text{H}_9)_3\text{Al}$ gave a syndiotactic polymer as in the case of the polymerization of MMA, but the syndiotacticity ($rr = 75.6\%$) was much lower than that of the PMMA ($rr = 92\%$).¹¹ Thus these two highly stereospecific initiators effective for polymerization of MMA did not afford highly stereoregular PMAD. Similar results of lower stereospecificity were observed for the polymerization of *t*-BuMA with these initiators, which suggest that the steric bulkiness of these two esters hinders the high stereoregulation.*¹

Polymerization of MMA with $t\text{-C}_4\text{H}_9\text{Li}$ in

* It is worthy to note that both the polymers of TMSMA and *t*-BuMA formed with $t\text{-C}_4\text{H}_9\text{MgBr}$ had equal fractions of *mr* and *rr* triads, suggesting the possibility that regular sequences such as $\cdots mrrrm \cdots$ exist in the chains. Longer-range sequence analysis will be examined by ^{13}C NMR spectroscopy in the near future.

Table I. Polymerization of MMA, TMSMA, and *t*-BuMA with several anionic initiators in toluene at -78°C for 24 h^a

| Initiator | Monomer | Yield | \bar{M}_n^b | \bar{M}_w^b | Tacticity ^b /% | | | Ref |
|---|-----------------------------|-------|---------------|---------------|---------------------------|-----------|-----------|----------|
| | | % | | \bar{M}_n | <i>mm</i> | <i>mr</i> | <i>rr</i> | |
| <i>t</i> -C ₄ H ₉ MgBr | MMA ^c | 73 | 3510 | 1.14 | 96.3 | 3.6 | 0.1 | 10 |
| | TMSMA ^d | 75.4 | 9000 | 1.33 | 20.1 | 39.7 | 40.2 | <i>e</i> |
| | <i>t</i> -BuMA ^f | 19.0 | 1800 | 4.17 | 47.8 | 26.4 | 25.8 | <i>e</i> |
| <i>t</i> -C ₄ H ₉ Li/(<i>n</i> -C ₄ H ₉) ₃ Al (Li/Al=1/3) | MMA | 100 | 5510 | 1.17 | 0 | 8 | 92 | 11 |
| | TMSMA | 100 | 12100 | 1.69 | 2.1 | 22.3 | 75.6 | <i>e</i> |
| | <i>t</i> -BuMA | 87.0 | 7140 | 1.64 | 10 | 33 | 57 | 12 |
| <i>t</i> -C ₄ H ₉ Li | MMA ^g | 92.8 | 10240 | 3.10 | 78 | 16 | 6 | 12 |
| | TMSMA ^h | 100 | 21400 | 1.34 | 94.5 | 4.4 | 1.1 | <i>e</i> |
| | <i>t</i> -BuMA | 100 | 12330 | 3.46 | 100 | 0 | 0 | 21 |
| <i>t</i> -C ₄ H ₉ Li Al/Li=5 | MMA | 100 | 11640 | 1.14 | 11.6 | 67.8 | 20.6 | 13 |
| MeAl(ODBP) ₂ Al/Li=1 | TMSMA | 38.0 | 10300 | 2.10 | 3.1 | 8.3 | 88.6 | <i>e</i> |
| | | 54.1 | 9480 | 1.30 | 2.0 | 4.6 | 93.4 | <i>e</i> |
| | | 100 | 7030 | 1.16 | 0.3 | 3.3 | 96.4 | <i>e</i> |
| Al/Li=5 | <i>t</i> -BuMA | 19.4 | 3050 | 1.19 | 7.4 | 8.5 | 84.1 | 14 |

^a Initiator, 0.2 mmol; monomer, 10 mmol; toluene, 10 ml. ^b Values for poly(TMSMA) and poly(*t*-BuMA) were determined for PMMA derived therefrom. ^c Toluene 5 ml, [Mg]/[*t*-C₄H₉] ratio of the initiator used was 2.81.^{9,10} ^d Polymerization time 48 h, [Mg]/[*t*-C₄H₉] ratio of the initiator used was 1.88. ^e This work. ^f Polymerization time 48 h, [Mg]/[*t*-C₄H₉] ratio of the initiator used was 1.49. ^g Polymerization time 12 h. ^h Initiator, 0.2 mmol; monomer, 6 mmol; polymerization time, 2 h.

toluene is known to give an isotactic-rich PMMA with insufficient control of MWD.^{11,12} On the other hand, TMSMA gave highly isotactic polymers with much narrower MWD under the same conditions (Table I). *t*-BuMA also gave a highly isotactic polymer but the MWD of the polymer was broad. The formation of highly isotactic poly(*t*-BuMA) with narrow MWD has also been reported for the polymerization in toluene with α -lithioisobutyrate ester.²²

A combination of *t*-C₄H₉Li/MeAl(ODBP)₂ (Al/Li \geq 2) was recently found to be a highly heterotactic-specific initiator for the polymerization of alkyl methacrylate in toluene at low temperature; in particular ethyl and butyl methacrylates gave high *mr* content of 87%.^{13,14} The polymerization of *t*-BuMA with this initiator, however, gives a syndiotac-

tic polymer (*rr* = 84%) instead of a heterotactic one in low yield.¹⁴ The polymerization of TMSMA with *t*-C₄H₉Li/MeAl(ODBP)₂ was carried out at various ratios of Al/Li. The results are shown in Table I. Polymerization with *t*-C₄H₉Li alone gave the highly isotactic polymer as described above. Even at the Al/Li ratio of 1, a syndiotactic polymer was formed but the MWD of the polymer was broad. As the Al/Li ratio increased from 1, the polymer yield increased, the *rr* content of the polymer increased slightly, and the MWD became narrower. At the Al/Li ratio of 5, a highly syndiotactic polymer (*rr* = 96.4%) with narrow MWD was obtained. The syndiotacticity is one of the highest values so far reported for polymethacrylates: PMMA: *rr* = 96.6% (*m*-vinylbenzylmagnesium chloride, THF, -110°C),²³ *rr* = 96% [*t*-C₄H₉Li/(*n*-C₈H₁₇)₃Al,

toluene, -93°C],¹¹ $rr = 95.3\%$ [$\text{SmH}(\text{C}_5\text{Me}_5)_2$, toluene, -95°C],²⁴ $rr = 95\%$ [$(\text{C}_6\text{H}_5)_3\text{P}/(\text{C}_2\text{H}_5)_3\text{Al}$, toluene, -93°C]²⁵; PMAD; $rr = 95\%$ (γ -ray irradiation, propan-2-ol, -78°C).⁸

TMSMA and *t*-BuMA showed a similar tendency of stereoregularity in the anionic polymerizations examined in this work; (1) lower stereospecificity in the polymerizations with *t*-C₄H₉MgBr and *t*-C₄H₉Li/(*n*-C₄H₉)₃Al, (2) high isotactic-specificity with *t*-C₄H₉Li, and (3) high syndiotactic-specificity with *t*-C₄H₉Li/MeAl(ODBP)₂. These features are quite contrasting to other alkyl methacrylates such as MMA, which may arise from the steric bulkiness of the tertiary ester group.

The difference in tacticity between poly(TMSMA) and poly(*t*-BuMA) may come from the slight difference in the steric hindrance owing to the different bond lengths of O–Si (1.60 Å) and O–C (1.43 Å). The polymer yields in the polymerizations of TMSMA were higher than those for *t*-BuMA, except for that of the polymerization by *t*-C₄H₉Li, in which the yields for both monomers reached 100%. The difference in the steric hindrance between the two monomers might be one of the reasons of their different reactivity. Another possible cause of the different reactivity is the difference in electronic effects of alkyl ester and silyl ester. ¹³C NMR chemical shift of β -methylene carbon of vinyl monomer has been proved to be a good measure of the reactivity of the monomer.²⁶ The values for TMSMA and *t*-BuMA in chloroform-*d* at 35°C were 125.83 and 124.06 ppm, respectively. The larger shift value for TMSMA indicates lower electron density at the β -carbon, suggesting the higher reactivity of TMSMA than that of *t*-BuMA in nucleophilic addition.

In conclusion, TMSMA could be polymerized stereospecifically with *t*-C₄H₉Li in toluene at -78°C to give highly isotactic PMAD and highly syndiotactic PMAD in the absence and presence of MeAl(ODBP)₂, respectively. These stereoregular PMADs have the same chemical structure and useful for investigation

tacticity dependences of properties such as viscosity, thermal degradation, dehydration between carboxylic acid groups along the chain, and stereocomplex formation with isotactic PMMA. The livingness of the polymerizations is now investigated to utilize these stereospecific polymerizations to the preparation of stereoblock PMAD and stereoregular amphiphilic block copolymers.

Acknowledgment. The authors thank Mr. K. Itoh for his technical assistance.

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