

Anionic polymerization of fluorine-substituted phenyl methacrylates

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Synthesis and anionic polymerization of the fluorine-substituted phenyl methacrylates are herein reported. A series of mono-, di-, and multi-substituted fluorophenyl methacrylates $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{H}_4\text{F}-4$ (\mathbf{M}^{1a}), $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{H}_4\text{F}-3$ (\mathbf{M}^{1b}), $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{H}_3\text{F}_2-2,4$ (\mathbf{M}^2), $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{H}_2\text{F}_3-2,3,4$ (\mathbf{M}^3), $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{HF}_4-2,3,5,6$ (\mathbf{M}^4), and $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{F}_5$ (\mathbf{M}^5) were synthesized and characterized. Initially, the polymerization was carried out on the monomer \mathbf{M}^{1a} by using *n*BuLi, *t*BuLi, and KH as the respective catalysts; this approach produced the polymers in yields of 12%–50%, but with lower molecular weights. Similar results were obtained by using *t*BuLi for catalytically polymerizing the other five monomers. By introducing a co-catalyst MeAl(BHT)₂, the catalysts NaH, LiH, and *t*BuOLi each were tested to polymerize \mathbf{M}^{1a} , which gave the polymers in very low yields (3%–7%). Polymer yields of 13%–27% were obtained by each of the catalysts LiAlH₄, *n*BuLi, PhLi, and *t*BuLi in connection with MeAl(BHT)₂, but a better yield (61%) was achieved with KH/MeAl(BHT)₂. The KH/MeAl(BHT)₂ catalyst system was further employed to polymerize \mathbf{M}^{1b} and \mathbf{M}^2 , which afforded respective polymer yields of 12%–63% and 10%–53%, depending on the molar ratios of KH:MeAl(BHT)₂ as well as on the monomer concentrations. All of the polymers produced were syndiotactically rich in structure, as indicated by either ¹H or ¹⁹F NMR data. The polymerization mechanism by the combined catalyst system is proposed.

fluorophenyl methacrylates, the combined catalyst system, anionic polymerization, syndiotactic polymer, ¹H and ¹⁹F NMR data

1 Introduction

Fluorine-containing organic polymers are very important resins that exhibit excellent chemical and thermal resistance due to their C–F bonds and also have highly mechanical properties. Therefore, they have been extensively used in manufacturing special plastics, membranes, and sealing tapes [1,2]. Usually, these polymers are prepared through substitution reaction with a fluorinating agent. Such reaction often occurs under harsh conditions in terms of the transformation of the C–H bond into the C–F bond, and catalysis

is often required [3]. In such cases, maintaining a control over the content of the fluorine atom in the polymers is difficult. In comparison, polymerization with fluorine-containing monomers provides an ideal way to those materials while retaining the fluorine atom in the polymers.

Among the polymers produced via polymerization, the fluorine-containing polyacrylates exhibit higher transparency and better chemical and thermal resistance when compared to the polyacrylates [4]. The replacement of the C–H bonds by C–F bonds results in lower intrinsic light loss in the near-infrared region between 1.2 and 1.6 μm [5]. Therefore, these polymers show a more promising potential for material applications in the fields of integrated optics and transparent plastics. In recent years, polypentafluoro-

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phenyl(meth)acrylates have also been widely used as new precursor polymers in the synthesis of multifunctional materials, they are useful as biocompatible PEG analogues [6], HPMA-based self-assembled nanoaggregates [7], and so on [8], through group exchange by the activated pentafluorophenyl ester.

With regard to the fluorine-substituted aryl acrylates, due to the strong electronic negativity of the F atom, the fluoroaryl group is strongly electron-withdrawing. This effect greatly increases the polar character of the vinyl carbon-carbon double bond of the monomers. Therefore, these monomers are essentially prone to or subject to either radical or anionic polymerization [9]. Surprisingly, no anionic polymerization of these monomers has been reported although the anionic polymerization of the non-fluorine-containing acrylates was discovered early on [10]. Recently, the plasma-assisted polymerization of the pentafluorophenyl(meth)acrylate has been documented [11]. In the current experiments, we prepared a series of mono-, di-, and multi-substituted fluorophenyl methacrylates, and conducted further investigation that revealed these monomers could be polymerized by using organo-lithium or potassium reagents as the catalyst in either the presence or absence of the organoaluminum compound as the co-catalyst. Our further analysis showed the polymers to be syndiotactically rich in structure, which indicates stereochemical control by this catalyst system. This result is in sharp contrast to results obtained by the radical polymerization [5,12].

2 Experimental

2.1 Materials and methods

Air- and moisture-sensitive compounds were manipulated under dry argon or nitrogen atmosphere by using Schlenk line and glovebox techniques. Solvents toluene, *n*-hexane, and diethyl ether were dried by refluxing with sodium/potassium benzophenone under N₂ prior to use. The NMR (¹H and ¹⁹F) spectra were recorded on a Bruker Avance II 400 MHz spectrometer (Switzerland). The polymer number average molecular weight (*M_n*) and molecular weight distributions (MWD=*M_w*/*M_n*) were measured by gel permeation chromatography (GPC). MALDI-TOF mass spectra were measured on a Bruker MicroFlex MALDI-TOF-MS (USA). Commercial reagents were purchased from Aldrich (USA), Acros (Belgium), and Alfa-Aesar Chemical Co (USA), and used as received. Co-catalyst AlMe(BHT)₂ (BHT=2,6-*t*Bu-4-MeC₆H₂OH) was prepared according to the literature [13]. The preparation of mono-, di-, and multi-substituted fluorophenyl methacrylates are described or mentioned in journals [12] or patents [14] according to different procedures; the related analysis data are not always fully shown. Herein we give a detailed report on the synthesis of a series of such monomers together with a full characterization of the data.

2.2 General synthesis of monomers

2.2.1 H₂C=C(CH₃)C(O)OC₆H₄F-4 (**M^{1a}**)

To a mixture of 4-fluorophenol (27.9 mL, 300 mmol) and 2,6-lutidine (34.8 mL, 300 mmol) was added diethyl ether (500 mL). This solution obtained was cooled to 0 °C and methyl acryloyl chloride (36.9 mL, 360 mmol) was added dropwise to it while stirring. The mixture was kept at this temperature for 3 h and then warmed to room temperature, during which a solid of HCl 2,6-lutidine adduct was precipitated. After stirring for 12 h, the solid was filtered off and the filtrate was evaporated to dryness under reduced pressure to give an oily residue. The residue was extracted with *n*-hexane (200 mL) followed by purification by florisil gel chromatography. After dehydration with MgSO₄, a colorless liquid of **M^{1a}** was obtained by removal of the *n*-hexane solvent under reduced pressure. Yield: 30.2 g, 65% (based on 4-fluorophenol). ¹H NMR (400 MHz, C₆D₆, 298 K, ppm): δ=1.84 (br, 3 H, CH₃), 5.27 (d, ²J_{HH}=1.4 Hz, 1H), 6.20 (d, ²J_{HH}=1.4 Hz, 1H) (H₂C=), 6.65 (m, 2H), 6.73 (m, 2H) (C₆H₄). ¹⁹F NMR (376 MHz, CDCl₃, 298 K, ppm): δ=-117.27 (m).

2.2.2 H₂C=C(CH₃)C(O)OC₆H₄F-3 (**M^{1b}**)

The preparation of **M^{1b}** was done in a similar manner to that of **M^{1a}**; 3-fluorophenol (27.9 mL, 300 mmol) was used instead of 4-fluorophenol. After workup, **M^{1b}** was obtained as a colorless liquid. Yield: 30.2 g, 65% (based on 3-fluorophenol). ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): δ=2.07 (br, 3H, CH₃), 5.79 (br, 1H), 6.36 (br, 1H) (H₂C=), 6.90–7.00 (m, 3H), 7.34 (m, 1H) (C₆H₄). ¹⁹F NMR (376 MHz, CDCl₃, 298 K, ppm): δ=-111.17 (m).

2.2.3 H₂C=C(CH₃)C(O)OC₆H₃F₂-2,4 (**M²**)

The preparation of **M²** was done in a similar manner to that of **M^{1a}**; 2,4-difluorophenol (36.30 g, 200 mmol), 2,6-lutidine (23.2 mL, 200 mmol), and methyl acryloyl chloride (23.3 mL, 240 mmol) were used. After workup, **M²** was obtained as a colorless liquid. Yield: 34.48 g, 86% (based on 2,4-difluorophenol). ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): δ=2.07 (dd, ⁴J_{HH}=1.6 and 1.6 Hz, 3H, CH₃), 5.80 (dt, ⁴J_{HH}=1.6 and ²J_{HH}=1.6 Hz, 1H), 6.36 (dt, ⁴J_{HH}=1.6 and ²J_{HH}=1.6 Hz, 1H) (H₂C=), 6.86–6.97 (m, 2H), 7.14 (m, 1H) (C₆H₃). ¹⁹F NMR (376 MHz, CDCl₃, 298 K, ppm): δ=-123.71 (m, 1F, *p*-F), -112.91 (m, 1F, *o*-F).

2.2.4 H₂C=C(CH₃)C(O)OC₆H₂F₃-2,3,4 (**M³**)

The preparation of **M³** was done in a similar manner to that of **M^{1a}**; 2,3,4-trifluorophenol (4.58 g, 30 mmol), 2,6-lutidine (3.5 mL, 30 mmol), and methyl acryloyl chloride (3.3 mL, 32 mmol) were used. Yield: 5.62 g, 84% (based on 2,3,4-trifluorophenol). ¹H NMR (400 MHz, CDCl₃, 298 K, ppm):

$\delta=2.08$ (dd, $^4J_{\text{HH}} = 1.6$ and 1.6 Hz, 3 H, CH_3), 5.84 (dt, $^4J_{\text{HH}}=1.6$ and $^2J_{\text{HH}}=1.6$ Hz, 1H) ($\text{H}_2\text{C}=\text{}$), $6.89\text{--}7.04$ (m, 2H, C_6H_2). ^{19}F NMR (376 MHz, CDCl_3 , 298 K, ppm): $\delta=-157.34$ (m, 1 F, $m\text{-F}$), -146.12 (m, 1F, $p\text{-F}$), -136.77 (m, 1 F, $o\text{-F}$).

2.2.5 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{HF}_4\text{-2,3,5,6}$ (M^4)

The preparation of M^4 was done in a similar manner to that of M^{1a} ; 2,3,5,6-Tetrafluorophenol (4.98 g, 30 mmol), 2,6-lutidine (3.5 mL, 30 mmol), and methyl acryloyl chloride (3.3 mL, 32 mmol) were used. After workup, M^4 was obtained as a colorless liquid. Yield: 6.13 g, 87% (based on 2,3,5,6-tetrafluorophenol). ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): $\delta=2.10$ (br, 3 H, CH_3), 5.91 (br, 1H), 6.46 (br, 1H, $\text{H}_2\text{C}=\text{}$), 6.97–7.06 (m, 1H, C_6H). ^{19}F NMR (376 MHz, CDCl_3 , 298 K, ppm): $\delta=-153.11$ (m, 2F, $m\text{-F}$), -139.23 (m, 2F, $o\text{-F}$).

2.2.6 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OC}_6\text{F}_5$ (M^5)

The preparation of M^5 was done in a similar manner to that of M^{1a} ; pentafluorophenol (5.52 g, 30 mmol), 2,6-lutidine (3.5 mL, 30 mmol), and methyl acryloyl chloride (3.3 mL, 32 mmol) were used. After workup, M^5 was obtained as a colorless liquid. Yield: 6.22 g, 81% (based on pentafluorophenol). ^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): $\delta=2.10$ (br, 3 H, CH_3), 5.92 (br, 1H), 6.46 (br, 1H, $\text{H}_2\text{C}=\text{}$). ^{19}F NMR (376 MHz, CDCl_3 , 298 K, ppm): $\delta=-162.78$ (m, 2F, $m\text{-F}$), -158.50 (m, 1F, $p\text{-F}$), -153.00 (m, 2F, $o\text{-F}$).

2.3 General synthesis of polymers and GPC and NMR analysis

In a typical experiment, catalyst or a mixture of catalyst and co-catalyst was added to a Schlenk flask followed by the solvent. After stirring for a few minutes, monomer was added and the mixture was stirred for a required time. After workup, usually 5% HCl-contained *n*-hexane (5 mL) was added to kill the catalyst, and then the polymer was precipitated into *n*-hexane (100 mL). The polymer was collected by filtration and dried under vacuum at 50 °C for 24 h to give a constant weight. The polymers obtained were characterized by ^1H and ^{19}F NMR spectroscopy and gel permeation chromatography (GPC).

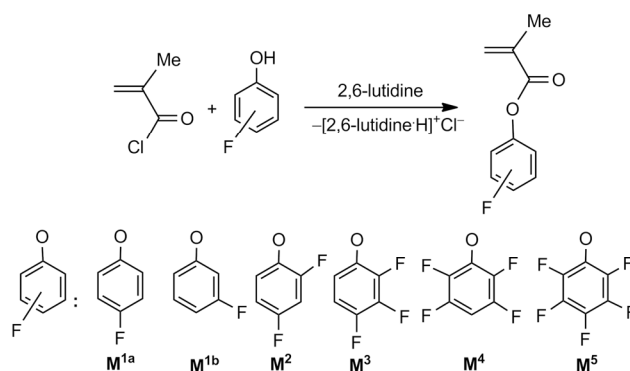
GPC analysis of the polymers was performed at 40 °C and a flow rate of 1.0 mL/min, with THF as the eluent, on a Waters University 1500 GPC instrument (USA) equipped with four 5 μm PL gel columns (Polymer Laboratories, USA) and calibrated using 10 PMMA standards. Chromatograms were processed with Waters Empower software (v. 2002, USA). NMR spectra for the polymers were recorded in CDCl_3 and analyzed according to procedures in the literature [15].

3 Results and discussion

3.1 Monomer synthesis

Fluorine-substituted phenyl methacrylates can be generally prepared via HCl elimination by using methyl acryloyl chloride and fluorine-substituted phenol. In these reactions, the organic Lewis base is usually used as the HCl-acceptor. As shown in Scheme 1, the monomers M^{1a} , M^{1b} , and $\text{M}^2\text{--M}^5$ were prepared according to the literatures [12] with slight modifications. When organometallic compounds are used as catalyst, these monomers must be extremely both moisture- and air-free. Therefore, the raw products obtained must be subjected to careful dehydration over anhydrous MgSO_4 after purification through a column filled with high-temperature-treated florisil gel. In our experiments, whether or not H_2O has contaminated the monomers can be detected from the IR spectrometry by the O–H bond vibration absorption around $\tilde{\nu}$ 3400 cm^{-1} . We noted that bulk homopolymerization often happened if the prepared monomer was not pure. Blazejewski *et al.* [5] observed the cross-linking of M^5 in bulk during its preparation, but the exact reason for this cross-linking is not clear. The impurity of these monomers can be detected from both the ^1H and ^{19}F NMR data. We note that these monomers appear easier to polymerize than the methyl methacrylate (MMA) by standing at room temperature. This is probably due to the presence of the electron-withdrawing fluorophenyl group, which increases the polarity of the vinyl carbon-carbon double bond and then enhances its polymerization reactivity.

The monomers M^{1a} , M^{1b} , and $\text{M}^2\text{--M}^5$ are all colorless liquid at room temperature, and turn into crystalline solid when kept at low temperature (–20 °C). These compounds are soluble in organic solvents such as aliphatic, aromatic, and halogenated hydrocarbons, as well as diethyl ether and THF. They have been clearly characterized by the NMR (^1H and ^{19}F) spectroscopy. In the ^1H NMR spectra, the methyl protons of these monomers resonate at a region of δ 1.84–2.10 ppm. The two vinyl protons give signals at δ 5.27–5.92 and 6.20–6.46 ppm, as multiplets or broad peaks, which



Scheme 1 Synthesis of fluorophenyl methacrylate monomers.

indicate couplings with both the germinal and the remote methyl H atoms. The ^{19}F NMR spectra show one resonance for $\text{M}^{1\text{a}}$ and $\text{M}^{1\text{b}}$ and multiplet resonances for M^2 – M^5 , consistently with the fluorine atom(s) attached to each phenyl ring.

3.2 Polymerization

In 2005, Théato and coworkers [12b]) reported on the radical polymerization of M^5 and pentafluorophenyl acrylate by using AIBN as initiator, here the polymers were produced in 80%–85% yields at 80 °C in benzene or dioxane within 6 h. These two polymers were analyzed by GPC to give molecular weights (M_n) of 24050 and 26680 g/mol, respectively, with both molecular weight distributions (MWD, M_w/M_n) close to 2. The ^{19}F NMR data suggest that these two polymers are atactic in structure, as indicated by their very broad resonances (in comparison to the sharp resonances observed for the corresponding monomers). In 2007, Okamoto and coworkers [12c]) conducted the polymerization of M^4 and M^5 using AIBN but in the presence of alkylthiol as the chain transfer agent (CTA). They obtained the polymers, PM^4 and PM^5 with M_n of 2.2×10^4 – 9.0×10^4 g/mol. No PDI or tacticity data were reported. Investigation of such monomers by means of anionic polymerization has not yet been attempted.

During dehydration of the monomer $\text{M}^{1\text{a}}$, we used CaH_2 , a powerful reagent. As a consequence, gelation of $\text{M}^{1\text{a}}$ occurred. By precipitation into 5% HCl-acidified *n*-hexane [16], an off-white solid polymer was obtained in a low yield whereas removal of all volatiles of the solution after separation of the solid polymer gave oily residue. Both the solid and the oily residue were analyzed to give lower molecular weights. In consideration of this result, we further screened similar organometallic compounds such as *n*BuLi, *t*BuLi, and KH as the catalyst for polymerizing $\text{M}^{1\text{a}}$ (catalyst: $\text{M}^{1\text{a}}$, 0.16 mmol:8 mmol (1:50); toluene solvent, 10 mL; room temperature). The polymers produced were in yields of 10%–50%, but with lower molecular weights [17]. Similar results were obtained by selecting *t*BuLi for

polymerizing the other five monomers. We noted that the multi-substituted fluorophenyl metacrylates seemed easy to occur by self-polymerization probably due to strong electron-withdrawing of the related ester groups of the monomers. Figure 1 shows a MALDI-TOF analysis result of the polymer produced by using *t*BuLi as the catalyst. The m/z values of the major set of peaks are calculated to be 180.82 (MW of $\text{M}^{1\text{a}} \times n$ (the number of $\text{M}^{1\text{a}}$ repeat units) + 57.11 (MW of *t*Bu of the *t*BuLi catalyst) + 23.00 (MW of Na^+ of NaI added in the measurement). This suggests initiation of the polymerization of $\text{M}^{1\text{a}}$ by the anionic *t*Bu group of the *t*BuLi catalyst, even though the M_n of the polymer is not large.

In 2005, Chen and Rodriguez-Delgado [18] demonstrated that by introducing Lewis acidic aluminum or boron compound as the co-catalyst into the catalyst isopropyl α -lithioisobutyrate a single-site anionic polymerization of MMA can be realized that gives an almost quantitative conversion of the monomer with M_n of 1.49×10^4 – 11.9×10^4 g/mol and MWD of 1.08–1.51.

Based on this result, we prepared an aluminum compound $\text{MeAl}(\text{BHT})_2$ (BHT=2,6-*t*Bu₂-4-MeC₆H₂O) [13] together with other commercially available aluminum compounds [17] and used them with the main catalyst. Typical results of $\text{M}^{1\text{a}}$ polymerization by the organometallic compound/ $\text{MeAl}(\text{BHT})_2$ in a molar ratio of 1:2 in toluene at 25 °C for a required time of 12 h (in a similar way to previous reports) are summarized in Table 1. Here we see that NaH, LiH, and *t*BuOLi, each combined with $\text{MeAl}(\text{BHT})_2$ to produce $\text{PM}^{1\text{a}}$ in very low yields (3%–7%). Polymer yields of 13%–27% were obtained by LiAlH_4 , *n*BuLi, PhLi, and *t*BuLi in combination with $\text{MeAl}(\text{BHT})_2$, and that a better yield (61%) was achieved with KH/ $\text{MeAl}(\text{BHT})_2$. Although these polymer yields varied largely, the number-average molecular weights (M_n , 1.01×10^4 – 4.25×10^4 g/mol) of these polymers are comparable to those obtained by the radical polymerization described above [12]. These values are also close to those of the PMMA generated with the similar anionic catalyst system. But, with respect to the fluorophenyl versus methyl group linkage, the polymer-

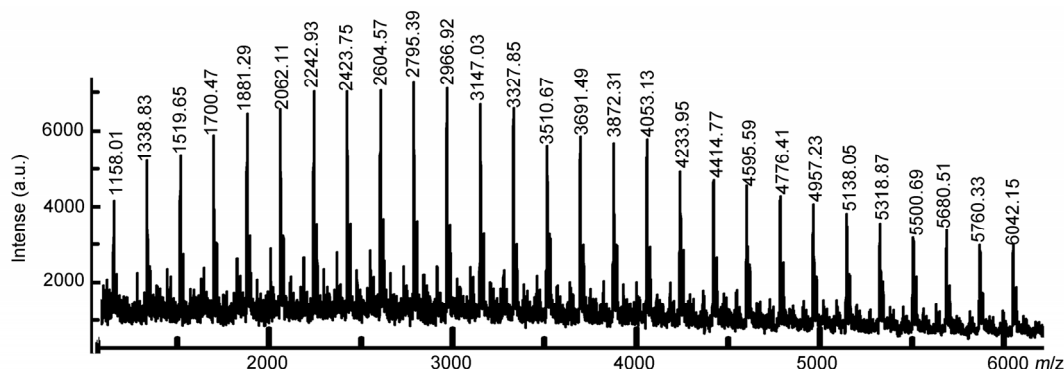


Figure 1 Portion of the MALDI-TOF mass spectrum of the low-molecular-weight $\text{PM}^{1\text{a}}$ at 25 °C in CH_2Cl_2 .

ization degree of PM^{1a} appears lower than that of PMMA. This result implies the probable influence of the size of the ester group upon the chain growth. A similar effect on the stereochemical polymer structure has been discussed [19]. It is noted that all the polymers obtained were syndiotactically rich, which appears to be a common feature of the anionic polymerization using the combined catalyst system [18].

Clearly, the $\text{KH}/\text{MeAl}(\text{BHT})_2$ catalyst is more effective in polymerizing M^{1a} in terms of the better monomer conversion as well as the polymer M_n (4.25×10^4 g/mol) and MWD (1.25) than the others (Table 1). Chen and coworkers [20] found in their work on a catalyst system related to the MMA polymerization that, the formation of the ‘ate’-type compound coupled with the large size K^+ is crucial. They also found that a 1:2 molar ratio of $\text{KH}/\text{aluminum}$ compound gave better results than 1:1 or without the aluminum co-catalyst.

Therefore, upon further investigation on the M^{1b} and M^2 polymerization, we selected KH and $\text{MeAl}(\text{BHT})_2$ to form the catalyst system but with different molar ratios. The polymerization results obtained under reaction conditions similar to those described above are shown in Table 2. It can be seen that the $\text{KH}/2 \text{ MeAl}(\text{BHT})_2$ catalyst system gave better polymer yields (63% for M^{1b} and 53% for M^2) and higher M_n (4.39×10^4 g/mol for M^{1b} and 3.65×10^4 g/mol for M^2) than the $\text{KH}/\text{MeAl}(\text{BHT})_2$ system, which yielded

12% for M^{1b} and 10% for M^2 ; M_n of 1.59×10^4 g/mol for M^{1b} and 2.14×10^4 g/mol for M^2 . When the $\text{MeAl}(\text{BHT})_2$ was increased to three equivalents, a slightly lower monomer conversion was observed. The $\text{KH}/2 \text{ MeAl}(\text{BHT})_2$ catalyst system is also effective for double amounts of the monomers used. In all of our tests, the polymers produced had a narrow MWD (1.08–1.19) and a good syndiotacticity of 59.0%–69.0%.

With KH as the main catalyst, the initiation of the polymerization might undergo a nucleophilic reaction of KH with the monomer to form the potassium ester enolate (Scheme 2). The employment of the Lewis acidic aluminum species helps to coordinatively stabilize the ester enolate and also to activate the monomer. This process allows a chain propagation reaction by the facile Michael addition between the ester enolate produced back and forth and the incoming monomer. All of the chain growing can be viewed as a continuation of the Michael additions under coordination interactions by the aluminum compounds (Scheme 3). Accordingly, the use of the double equivalents of the aluminum compounds is crucial for the polymerization, as the experimental results affirm. This reaction mechanism has also been discussed in the anionic polymerization of MMA and the related acrylate derivatives [18,20].

Table 1 M^{1a} polymerization results using the combined organometallic compounds as the catalyst system

Run No.	Initiator/activator/monomer	Ratio ^{a)}	Yield (%)	M_n^b (10^4 g/mol)	MWD (M_w/M_n) ^{b)}	[mm] ^{c)} (%)	[mr] ^{c)} (%)	[rr] ^{c)} (%)
1	<i>t</i> BuLi/MeAl(BHT) ₂ /M ^{1a}	1:2:100	27	1.01	1.29	13.2	16.6	70.2
2	<i>n</i> BuLi/MeAl(BHT) ₂ /M ^{1a}	1:2:100	19	1.04	1.26	14.8	17.8	67.4
3	PhLi/MeAl(BHT) ₂ /M ^{1a}	1:2:100	27	1.71	1.71	13.2	23.4	63.4
4	KH/MeAl(BHT) ₂ /M ^{1a}	1:2:100	61	4.25	1.25	9.5	27.4	63.1
5	NaH/MeAl(BHT) ₂ /M ^{1a}	1:2:100	3	1.62	1.80	12.1	25.8	62.1
6	LiH/MeAl(BHT) ₂ /M ^{1a}	1:2:100	3	1.62	1.88	10.2	23.2	66.6
7	<i>t</i> BuOLi/MeAl(BHT) ₂ /M ^{1a}	1:2:100	7	4.07	1.91	8.9	26.4	64.7
8	LiAlH ₄ /MeAl(BHT) ₂ /M ^{1a}	1:2:100	13	2.04	1.32	9.2	27.6	63.2

a) M^{1a} , 1.44 g, 8 mmol; catalyst, 0.08 mmol; $\text{MeAl}(\text{BHT})_2$, 0.077 g, 0.16 mmol; toluene, 10 mL; polymerization temperature, 25 °C; polymerization time, 12 h; b) determined by GPC; c) measured by ¹H NMR spectroscopy.

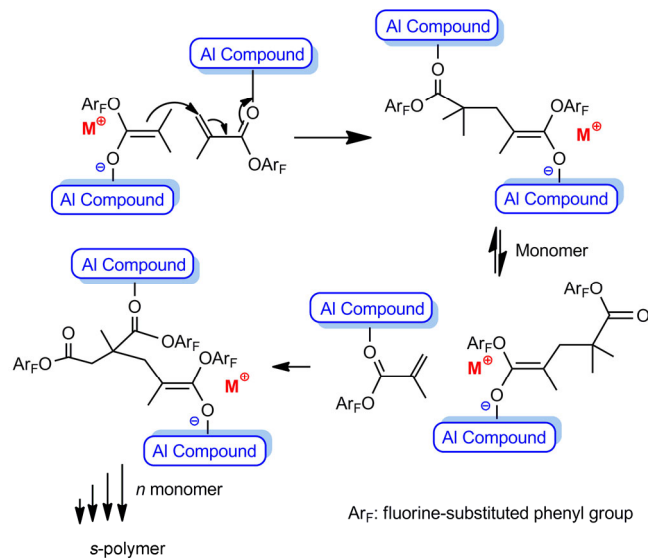
Table 2 M^{1b} and M^2 polymerization results by $\text{KH}/\text{MeAl}(\text{BHT})_2$ catalyst system

Run No.	Initiator/activator/monomer	Ratio ^{a)}	Yield (%)	M_n^b (10^4 g/mol)	MWD (M_w/M_n) ^{b)}	[mm] ^{c)} (%)	[mr] ^{c)} (%)	[rr] ^{c)} (%)
1	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^{1b}$	1:1:100	12	1.59	1.08	9.9	24.3	65.8
2	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^{1b}$	1:2:100	63	4.39	1.11	9.9	25.5	69.0
3	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^{1b}$	1:3:100	57	2.22	1.19	9.7	25.8	64.5
4	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^{1b}$	1:2:200	56	2.19	1.08	9.8	26.2	64.0
5	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^2$	1:1:100	10	2.14	1.08	5.6	32.7	61.7
6	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^2$	1:2:100	53	3.65	1.11	5.1	31.2	63.7
7	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^2$	1:3:100	49	2.79	1.09	5.5	35.5	59.0
8	$\text{KH}/\text{MeAl}(\text{BHT})_2/\text{M}^2$	1:2:200	50	2.62	1.09	6.2	31.7	62.1

a) M^{1b} , 1.44 g, 8 mmol; M^2 , 1.65 g, 8 mmol; KH , 0.0032 g, 0.08 mmol; $\text{MeAl}(\text{BHT})_2$, 0.077 g, 0.16 mmol; toluene, 10 mL; polymerization temperature, 25 °C; polymerization time, 12 h; b) determined by GPC; c) measured by ¹H NMR spectroscopy.



Scheme 2 Possible initial reaction of KH with monomer to form the monomer initiator, potassium ester enolate.



Scheme 3 Plausible mechanism for anionic polymerization with the combined catalyst system.

3.3 Polymer structure

The tacticity of the polymers is determined from either the ^1H or ^{19}F NMR data. As with PMMA obtained by anionic polymerization, the protons of the Me group directly attached at the polymer chain exhibited three sets of resonances; these corresponded to the triads rr, mr, and mm, according to the statistic stereochemical array of the Me along the chain [15]. For our samples, aside from the indication of the tacticity from the ^1H NMR spectrum, we were able to find a similar estimation from the ^{19}F NMR data. As pictured in Figures 2 and 3, three sets of the fluorine resonances were observed in close ratio to those of the proton ones, which gave a general syndiotacticity character for each polymer. Apparently, the informations gained from either the Me or the fluorophenyl ester groups arrayed along the main chain can provide insight into the stereochemical structure of the polymers. It is reasonable to predict that indications given by the ^{19}F NMR signals could have a more widespread application for copolymers, because in such polymers the Me proton resonances would be easily disturbed or submerged by the resonances from the other groups of the copolymerized monomers.

4 Conclusions

We prepared a series of mono-, di-, and multi-substituted

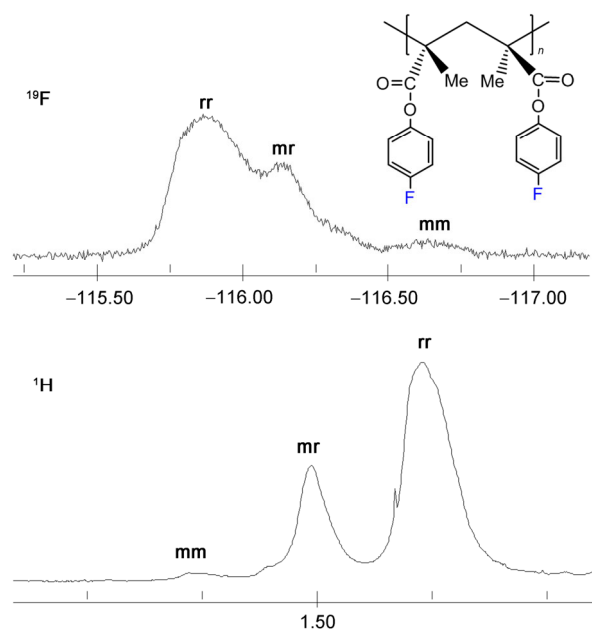


Figure 2 Enhanced ^1H and ^{19}F NMR spectra of the polymer PM^{1a} obtained in Run 1 in Table 1.

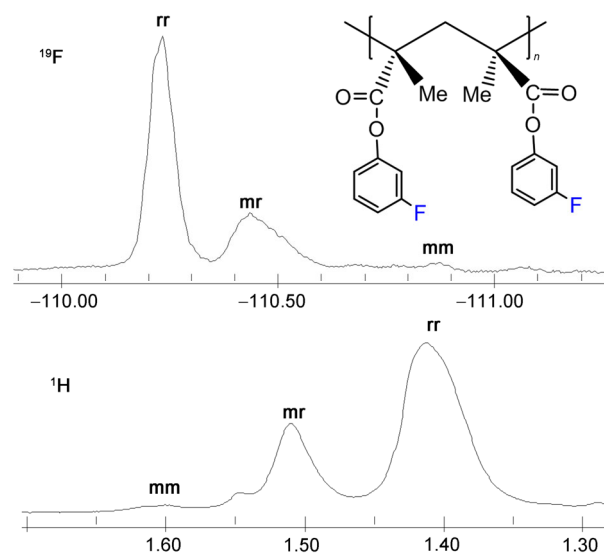


Figure 3 Enhanced ^1H and ^{19}F NMR spectra of the polymer PM^{1b} obtained in Run 2 in Table 2.

fluorophenyl metacrylates, and investigated, for the first time, the anionic polymerization of these monomers with combined organometallic compounds as the catalyst system. This catalyst system included *t*BuLi, *n*BuLi, PhLi, KH, NaH, LiH, *t*BuOLi, and LiAlH₄, all combined with MeAl(BHT)₂ as well as some of the former ones individually. All were found to be active in polymerization reaction. We conducted a detailed study of the KH/MeAl(BHT)₂ system in terms of both M^{1b} and M² polymerization, and found that this system exhibits not only better activity but also control over the syndiotactic stereochemistry of the polymers. The

probable polymerization mechanism may undergo an initial nucleophilic reaction of KH with monomer to give a potassium ester enolate followed by the consecutive Michael addition to the monomers. The tacticity of the polymers produced can be detected from either ^1H or ^{19}F NMR data.

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