# Stereospecific Free-Radical Polymerization of Methacrylates Using Fluoroalcohols as Solvents

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**Introduction.** The stereoregularity of vinyl polymers often significantly affects the properties of the polymers. However, many industrially important vinyl polymers including poly(methyl methacrylate) (PMMA) and polystyrene are produced by radical polymerization, which is more versatile and economical compared with other types of polymerizations, but is generally poor in stereocontrol. Hence, the development of stereoregulation methods for radical polymerization can contribute to the industrial production of polymers with improved properties.[1−3]

Through our efforts to find effective methods of stereocontrol in radical polymerization,[1,4−9] we recently found that the stereochemistry of vinyl ester polymerization is affected by fluoroalcohols used as the reaction solvents. Such fluoroalcohols include 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (HFTB), and perfluoro-*tert*-butyl alcohol (PFTB).[4,5] For example, PFTB significantly improved the syndiotactic specificity of vinyl acetate polymerization and gave the highest syndiotacticity for vinyl ester polymerization under optimized conditions.[4] In the present study, to examine the applicability of this method to acrylic monomers, the radical polymerizations of methyl, ethyl, and *tert*-butyl methacrylates (MMA, EMA, and *t*-BuMA) were carried out in fluoroalcohol solvents.

**Experimental Section. Materials.** MMA, EMA, and *t*-BuMA were washed with aq NaOH (5%) and distilled. The sources and purification methods of the other reagents used in this work are the same as those reported elsewhere.[4]

**Polymerization.** Polymerization was carried out under dry nitrogen in a glass tube equipped with a three-way stopcock in a manner similar to that reported for the vinyl esters. [4] Reaction products were precipitated in a large excess of methanol or a methanol−water mixture, and the obtained polymers were isolated with a centrifuge.

**Measurements.** $^1$H NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz). The triad tacticity of PMMA and poly(EMA) was determined on the basis of the peaks of the α-methyl group in the $^1$H NMR spectra and that of poly(*t*-BuMA) was measured as PMMA derived therefrom. In the NMR spectra of poly(EMA), heterotactic (mr) and syndiotactic (rr) α-methyl signals were observed separately, but the methyl signal of ester group overlapped on the isotactic (mm) α-methyl signal. The isotactic content was estimated by subtracting the intensity of ester methyl signal. The number-average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) of the polymers were determined by size-exclusion chromatography (SEC) calibrated using standard polystyrenes on a Jasco PU-980 pump equipped with an RI-930 detector using TSKgel GMH$_{HR}$-H and G3000$_{HR}$ columns connected in series (eluent tetrahydrofuran, THF; temperature 40 °C).

**Results and Discussion. Polymerization of MMA.** The polymerization of MMA was carried out in TFE, HFIP, HFTB, and PFTB in order to examine the effects of the fluoroalcohols on the reaction stereochemistry. The polymerization in the other solvents (toluene and methanol) was also performed as control experiments. The conditions and results are shown in Table 1 (runs 1−17). In most cases, the use of fluoroalcohols resulted in higher polymer yields compared with those for the polymerization in methanol or toluene. At all temperatures, the polymerization in PFTB produced polymers having the largest triad syndiotactic content (rr). The other fluoroalcohols also were effective in enhancing the rr specificity during the polymerization at −40 °C, although their effects were not so obvious at 20 °C and 60 °C. The rr specificity observed in run 17 in Table 1 (82.9%) is considered to be the highest for the radical polymerization of MMA.[2,3] Figure 1 shows the $^1$H NMR spectrum of the PMMA obtained in run 17. The high syndiotacticity of the polymer is evidenced by the spectral pattern due to the α-methyl and β-methylene.[10] The NMR spectrum also proves that no side reactions such as ester exchange between solvent and monomer (monomeric unit) took place and the PMMA has an authentic chemical structure.

Figure 2 shows the temperature dependence of tacticity during the polymerization of PFTB (Fordham plots[11]). The difference in activation enthalpy ($\Delta H^\ddagger$) and that in activation entropy ($\Delta S^\ddagger$) between the isotactic- and syndiotactic-specific propagations can be determined by the plot according to the following equation:[11]

$$\ln\left(\frac{P_i}{P_s}\right) = \frac{\Delta S_i^\ddagger - \Delta S_s^\ddagger}{R} - \frac{\Delta H_i^\ddagger - \Delta H_s^\ddagger}{RT} \qquad (1)$$

where $P_i$ and $P_s$ are the mole fractions of isotactic and syndiotactic dyads, respectively, $R$ is a gas constant (1.987 cal/mol·K), and $T$ is the polymerization temperature (K). The obtained values of $\Delta H_i^\ddagger - \Delta H_s^\ddagger$ and $\Delta S_i^\ddagger - \Delta S_s^\ddagger$ for the MMA polymerizations are summarized in Table 2. The positive values of $\Delta H_i^\ddagger - \Delta H_s^\ddagger$ and the negative values of $\Delta S_i^\ddagger - \Delta S_s^\ddagger$ in all cases indicate that syndiotactic propagation is favored by both enthalpy and entropy.

The solvent effects observed here may be reasonably ascribed to the hydrogen bonding between the solvent and monomer (monomeric) unit as proposed for the polymerization of vinyl esters.[4] The interaction can make the monomer and growing polymer chain apparently bulkier than the original monomer and can change

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**Table 1. Free-Radical Polymerization of MMA and EMA**[a]

| | | | | | | | | triad tacticity[d] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| run | monomer | solvent | temp (°C) | time (h) | yield[b] (%) | $\bar{M}_n$[c] ($\times 10^{-4}$) | $\bar{M}_w/\bar{M}_n$[c] | mm | mr | rr |
| 1 | MMA | toluene | 60 | 3 | 31 | 4.18 | 1.40 | 3.2 | 33.3 | 63.5 |
| 2 | MMA | methanol | 60 | 3 | 52 | 8.34 | 1.52 | 3.6 | 31.9 | 64.4 |
| 3 | MMA | TFE | 60 | 3 | 60 | 5.33 | 1.41 | 3.6 | 33.1 | 63.4 |
| 4 | MMA | HFIP | 60 | 3 | 56 | 4.90 | 1.41 | 3.0 | 32.2 | 64.8 |
| 5 | MMA | HFTB | 60 | 3 | 73 | 6.79 | 1.44 | 2.9 | 31.2 | 65.9 |
| 6 | MMA | PFTB | 50 | 5 | 60 | 9.19 | 1.41 | 1.7 | 27.3 | 71.0 |
| 7 | MMA | toluene | 20 | 24 | 36 | 2.34 | 1.57 | 1.9 | 29.2 | 68.9 |
| 8 | MMA | methanol | 20 | 24 | 69 | 3.57 | 2.57 | 2.5 | 31.5 | 66.0 |
| 9 | MMA | TFE | 20 | 24 | 66 | 2.80 | 1.57 | 2.1 | 29.2 | 68.7 |
| 10 | MMA | HFIP | 20 | 24 | 70 | 2.33 | 1.45 | 1.8 | 27.0 | 71.1 |
| 11 | MMA | HFTB | 20 | 24 | >99 | 8.56 | 2.66 | 2.3 | 28.0 | 69.8 |
| 12 | MMA | PFTB | 20 | 24 | 76 | 2.27 | 1.58 | 1.2 | 23.6 | 75.3 |
| 13 | MMA | toluene | −40 | 24 | 4 | 5.29 | 2.01 | 1.0 | 23.0 | 76.0 |
| 14 | MMA | methanol | −40 | 24 | 7 | 11.54 | 3.14 | 1.6 | 23.4 | 74.9 |
| 15 | MMA | TFE | −40 | 24 | 14 | 7.62 | 2.09 | 0.9 | 21.6 | 77.5 |
| 16 | MMA | HFIP | −40 | 24 | 26 | 6.01 | 1.52 | 1.3 | 19.6 | 79.1 |
| 17 | MMA | PFTB | −40 | 24 | 13 | 6.12 | 3.27 | 0.5 | 16.6 | 82.9 |
| 18 | EMA | toluene | 60 | 3 | 14 | 8.22 | 1.13 | 10.6 | 29.1 | 60.2 |
| 19 | EMA | methanol | 60 | 3 | 35 | 6.73 | 1.29 | 5.8 | 33.7 | 60.4 |
| 20 | EMA | TFE | 60 | 3 | 39 | 9.90 | 1.19 | 3.9 | 32.2 | 63.9 |
| 21 | EMA | HFIP | 60 | 3 | 26 | 9.13 | 1.14 | 4.3 | 30.6 | 65.1 |
| 22 | EMA | HFTB | 60 | 3 | 52 | 8.17 | 1.26 | 3.7 | 28.1 | 68.2 |
| 23 | EMA | methanol | 20 | 24 | 58 | 1.78 | 2.09 | 16.1 | 22.6 | 61.3 |
| 24 | EMA | TFE | 20 | 24 | 70 | 2.38 | 2.23 | 5.7 | 25.5 | 68.3 |
| 25 | EMA | HFIP | 20 | 24 | 67 | 1.96 | 1.73 | 4.1 | 24.6 | 71.3 |
| 26 | EMA | HFTB | 20 | 24 | 88 | 2.84 | 1.70 | 2.2 | 23.5 | 74.3 |
| 27 | EMA | PFTB | 20 | 24 | 59 | 2.02 | 2.05 | 4.3 | 19.4 | 76.3 |
| 28 | EMA | toluene | −40 | 48 | 3 | 11.33 | 1.19 | 4.7 | 18.2 | 77.1 |
| 29 | EMA | methanol | −40 | 48 | 12 | 9.47 | 2.29 | 11.8 | 16.2 | 72.0 |
| 30 | EMA | TFE | −40 | 48 | 26 | 9.81 | 1.33 | 2.8 | 17.4 | 79.8 |
| 31 | EMA | HFIP | −40 | 48 | 36 | 8.91 | 1.49 | 4.4 | 15.3 | 80.3 |
| 32 | EMA | HFTB | −40 | 48 | 49 | 18.84 | 1.78 | 1.9 | 11.2 | 86.9 |
| 33 | EMA | PFTB | −40 | 48 | 64 | 11.63 | 1.37 | 0.9 | 14.7 | 84.4 |

[a] Condition: $[\mathrm{MMA}]_0 = 1.87$ mol/L, $[\mathrm{EMA}]_0 = 1.61$ mol/L, $[\mathrm{AIBN}]_0 = 0.02$ mol/L, $[n\text{-}\mathrm{Bu_3B}]_0 = 0.1$ mol/L. Initiator: runs 1−6, 18−22, AIBN; runs 7−12, 23−27, AIBN/UV; runs 13−17, 28−33, $n$-$Bu_3B$/air. [b] Methanol−insoluble part (runs 1−19, 22), water/methanol (=1: 1)−insoluble part (runs 20, 21, 23−33). [c] Determined by SEC (polystyrene standard) in THF. [d] Determined by $^1$H NMR (400 MHz) in $CDCl_3$.

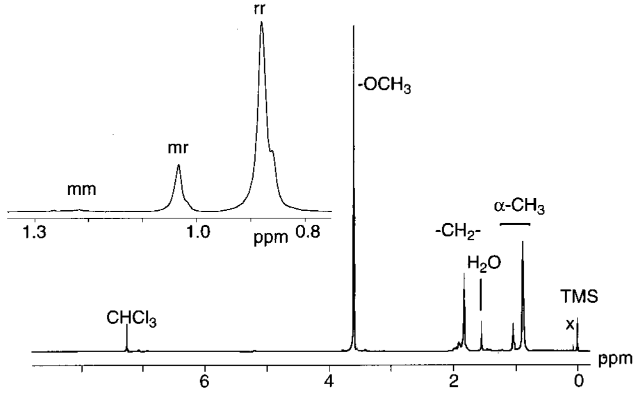

**Figure 1.** $^1$H NMR spectrum of PMMA prepared by free-radical polymerization in PFTB at −40 °C (Table 1, run 17). Conditions: 400 MHz, $CDCl_3$, and 50 °C.

the stereochemistry of the polymerization.[4] This can explain the larger effect of PFTB compared with those of the other fluoroalcohols because PFTB is the bulkiest and the most acidic among the solvents used in this work. The hydrogen-bonding interaction between the C=O group of MMA and the −OH group of the fluoroalcohols was confirmed by NMR analyses whose details will be described elsewhere.

**Polymerization of EMA.** The conditions and results of the polymerization of EMA are summarized in Table 1 (runs 18−33). In addition to the stereochemical effects described hereafter, the fluoroalcohols resulted in higher polymer yields than those of toluene or methanol in most cases, which was similar to the polymerization of MMA. The fluoroalcohols also enhanced the rr-specificity during the polymerization of EMA. In this case, the solvent effects were obvious even at 20 and 60 °C. At 20 and 60 °C, the degree of the solvent effects seems roughly proportional to the bulkiness of the solvents; TFE exhibited the smallest effect and PFTB showed the a largest effect. It is interesting that at −40 °C HFTB showed a larger rr-enhancing effect than that of PFTB. This is probably because the hydrogen-bonding interaction between HFTB and EMA is stronger than that between PFTB and EMA at this temperature. The additional bulkiness of EMA compared with MMA might prevent an effective hydrogen-bonding interaction with the bulky PFTB under certain conditions. The polymerization of EMA in HFTB at −40 °C resulted in

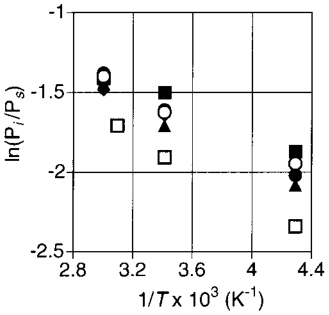

**Figure 2.** Fordham plots for the polymerizations of MMA in toluene (○), methanol (■), TFE (●), HFIP (▲), HFTB (◆), and PFTB (□).

**Table 2. Activation Parameters for the Free-Radical Polymerization**[a]

| monomer | solvent | $\Delta H_i^‡ - \Delta H_s^‡$ (cal/mol) | $\Delta S_i^‡ - \Delta S_s^‡$ (cal/mol·K) |
|---|---|---|---|
| MMA | toluene | 740 | −0.68 |
| MMA | methanol | 700 | −0.70 |
| MMA | TFE | 900 | −0.16 |
| MMA | HFIP | 830 | −0.58 |
| MMA | PFTB | 960 | −0.52 |
| EMA | toluene | 1120 | 1.19 |
| EMA | methanol | 1040 | 1.71 |
| EMA | TFE | 1090 | 0.64 |
| EMA | HFIP | 990 | 0.22 |
| EMA | HFTB | 1530 | 1.59 |
| EMA | PFTB | 1290 | 0.81 |

[a] See text for the method of determination.

a syndiotactic specificity of 86.9% (run 32 in Table 1), which is the highest for the radical polymerization of methacrylates to the best of our knowledge.[2,3]

Table 2 indicates the values of $\Delta H^‡$ and $\Delta S^‡$ between the isotactic- and syndiotactic-specific propagations determined in the same manner as that described for the MMA polymerization. The syndiotactic propagation in the EMA polymerizations is favored by enthalpy.

**Polymerization of *t*-BuMA.** The effects of PFTB were also investigated for the polymerization of *t*-BuMA, a bulkier monomer than MMA and EMA. The polymerizations in toluene at +20 and −40 °C produced polymers with triad tacticities of mm/mr/rr = 1.7/33.4/64.9 and 2.7/22.8/74.4, respectively, whereas that in PFTB at the corresponding temperatures led to the polymer with mm/mr/rr = 1.7/35.3/63.0 and 1.4/33.2/65.4, respectively. Thus, at 20 °C, the effects of PFTB were much less obvious than those in MMA and EMA under similar conditions, and at both temperatures, PFTB reduced the rr-specificity contrary to the results so far described. Analogous results have been found in the polymerization of a bulky vinyl ester, vinyl pivalate, in PFTB.[5] PFTB enhanced the syndiospecificity in the vinyl acetate polymerization, but it reduced the value for the vinyl pivalate polymerization. Although the results of the *t*-BuMA polymerization cannot be immediately rationalized, the difference in the strength of the monomer−PFTB interaction or the structure of the hydrogen-bound complex depending on the monomer−solvent combination should be responsible for the variation in the solvent effects.

**Conclusions.** The stereochemistry of the MMA, EMA, and *t*-BuMA polymerizations was affected by the use of fluoroalcohols as solvents. The polymerization of MMA in PFTB and that of EMA in HFTB at −40 °C resulted in the highest rr content for PMMA and poly(EMA), respectively, synthesized by the radical polymerization. Efforts are under way to optimize the reaction conditions in order to maximize the effects of the fluoroalcohols. The mechanism of the solvent effects is also currently being studied.

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