
**Xanthates as Chain-Transfer Agents in Controlled Radical Polymerization (MADIX): Structural Effect of the O-Alkyl Group**

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**Experimental Part**

**Materials**

Styrene, ethyl acrylate and toluene were distilled over CaH₂ prior to use. 2,2’-Azoisobutyronitrile (AIBN) was recrystallized from methanol. The synthesis of xanthate $X_1$ was described previously.[3a]

**Synthesis of Xanthate 2**

Carbon disulfide (2.4 ml, 40 mmol) was added to a solution of trifluoroethanol (2.0g, 20 mmol) in $N,N$-dimethylformamide (DMF; 40 ml) with cooling to 0 °C. Sodium hydride (0.96g, 20 mmol) was added. The resulting mixture was stirred for 1 h at 0 °C and then treated with ethyl 2-bromopropionate (2.34 ml, 18 mmol). After stirring for an additional 1 h at 0 °C and 2 h at room temperature, the mixture was diluted with diethyl ether, washed with water, then with brine, and finally concentrated under partial vacuum. The residue was purified by chromatography on silica gel using heptane/ethyl acetate (9:1) to give pure xanthate 2 (3.4g, 69%).

$^1$H NMR (200 MHz, CDCl₃): $\delta = 4.90$ (q, $J = 8$ Hz, 2 H), 4.37 (q, $J = 8.4$ Hz, 1 H), 4.20 (q, $J = 7.0$ Hz, 2 H), 1.55 (d, $J = 8$ Hz, 3 H), 1.25 (t, $J = 7$ Hz, 3 H).
\[ \text{Synthesis of Xanthate 3} \]

Synthesis of Diethyl 2,2,2-trifluoro-1-hydroxyethylphosphonate (3a)

A solution of fluor hydrate (10.0 g of a 75\% aqueous solution, 64.6 mmol) and diethylphosphite HP(O)(OEt)\textsubscript{2} (64.6 mmol) in triethylamine (9.0 ml, 64.6 mmol) was stirred at room temperature for 15 h. The mixture was rapidly concentrated under partial vacuum while keeping the temperature below 40 °C. The residue was purified by flash chromatography (petroleum ether/acetone: 10:1, then diethyl ether, then diethyl ether/methanol: 10:1) to give adduct 3a in 82\% yield.

\[ ^{1}\text{H NMR (200 MHz, CDCl}_{3} \] \( \delta = 6.08 \text{ (bs, 1 H), 4.12-4.38 (m, 5 H), 1.33 (t, J = 7.1 Hz, 3 H).} \]

IR (film) : 3400, 2992, 2918, 1640, 1268 cm\textsuperscript{-1}.

MS (IC) \( m/z = 237 [\text{MH}]^+ \).

Synthesis of Ethyl 2-[1-Diethoxyphosphoryl-2,2,2-trifluoroethoxythio carbonylsulfanyl] Propionate (3)

A solution of alcohol 3a (5.0 g 21.18 mmol) in DMF (6 ml) was added dropwise to a suspension of sodium hydride (1.03 g of a 60\% dispersion in mineral oil, 25.75 mmol) in DMF (30 ml), cooled to 0 °C. After 30 min at 0 °C, carbon disulfide (2.65 ml, 44 mmol) was added and stirring was continued for another 15 min. Ethyl 2-bromopropionate (3.51 ml, 26.7 mmol) was added and the mixture kept at 0 °C for 23 h. It was then neutralized with saturated aqueous ammonium chloride, extracted three times with ethyl acetate, and the combined organic layers were dried over magnesium sulfate. The solvent was removed under partial
vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to give xanthate 3 in 21% yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 4.03$-4.37 (m, 7 H), 1.75 (d, $J = 6.8$ Hz, 3 H), 1.20-1.56 (m, 9 H).

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 198.0, 170.3, 64.8, 64.7, 61.9, 40.2, 28.4, 15.9, 15.8, 13.8.$

IR (film): 2982, 2931, 1736, 1450, 1158 cm$^{-1}$.

General Procedure for Polymerization Experiments

Xanthate, monomer, initiator and solvent were placed in a glass tube equipped with magnetic stirrer. The reaction content was degassed by three freeze-thaw cycles and sealed under vacuum. The flask was then placed in an oil bath thermostated at 110 °C for styrene polymerization and at 80 °C for ethyl acrylate polymerization. All polymerizations were performed in batch under homogeneous conditions. After a given time (see article, Table 1), the reaction was quenched by cooling the tubes in cold water. Residual monomer was removed by submitting the reaction mixture to a constant flow of nitrogen overnight and then by drying the recovered polymer under vacuum for several hours. The crude product was analyzed by means of GPC and $^1$H NMR spectroscopy. In a typical experiment, 0.1 g (2.5×10$^{-4}$ mol) of $X_3$ was reacted with 2 g (1.99×10$^{-2}$ mol) of ethyl acrylate and 1.2 mg (7.5×10$^{-6}$ mol) of AIBN in 1.88 g of toluene for 0.42 h. This gave poly(ethyl acrylate) in 49.6% yield with $M_n = 4400$ g·mol$^{-1}$ and PDI = 1.12.

Characterization

Molar masses ($M_n$) and polydispersities ($M_w/M_n$) were determined by GPC, using the following Phenogel columns: Guard, linear, 1000 Å and 100 Å (eluent: THF (1 ml·min$^{-1}$). A
differential refractive index detector was used, and molecular weights were calculated based on PS standards. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using a Biflex III (Bruker) time-of-flight mass spectrometer. The instrument was equipped with a nitrogen laser (337 nm) and a delayed extraction. It was operated at an accelerating potential of 20 kV in linear mode. The MALDI mass spectra represent averages over 100 consecutive laser shots (1 Hz repetition rate). The polymer solutions (20 g·L⁻¹) were prepared in THF. The matrix, 4-(4-nitrophenylazo)resorcinol, was also dissolved in THF (10 g·L⁻¹). The poly(ethyl acrylate) solution (100 µl) was mixed with potassium chloride (500 µl of a 0.01 M solution in C₂H₅OH/H₂O 90:10 v/v) which was added to favor ionization by cation attachment. Then 20 µl of the resulting solution were added to 20 µl of the matrix solution. A 1.5 µl portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (ethoxylated nonylphenol) were used to calibrate the mass scale using calibration software from Biflex III.