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Synthesis

Synthesis of a poly(vinylidene fluoride) macromonomer

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Summary

Methacrylate-type poly(vinylidene fluoride) macromonomer was synthesized from vinylidene fluoride via hydroxy-ended poly(vinylidene fluoride). The macromonomer copolymerized easily with methyl methacrylate, but homopolymerization did not proceed completely.

Introduction

The new field of macromonomer chemistry has expanded rapidly in recent years.[1,2,3] Macromonomers derived from many of the common monomers are now available, and research continues to make more such useful intermediates. In this work we describe the synthesis of a macromonomer of poly(vinylidenefluoride) ($PVDF_2$).

Experimental

Materials - Vinylidene fluoride (VDF_2) was purchased from SCM Specialty Chemicals. Methanol used for telomerization of VDF_2 was distilled over magnesium. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Dimethylsulfoxide (DMSO) was distilled under reduced pressure and kept with Molecular Sieve Type-4A. Vinyl acetate (VOAc) and methyl methacrylate (MMA) were distilled immediately before usage. All other chemicals were used without further purification.

Instruments - In a telomerization of VDF_2, a 300 mL stainless steel autoclave made by Autoclave Engineers Inc. was used. It was equipped with a magnetically driven stirrer. The temperature of the autoclave was controlled by a thermo-couple and temperature-power regulator. ^1H nmr spectra were obtained in DMSO-d_6 on a Varian EM-360 Analytical NMR spectrometer. The proton decoupled ^{13}C nmr spectrum was measured on a Bruker Model WM-250 Multinuclear FT spectrometer. Ir spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer (Model 983). Size exclusion chromatography (SEC) was done on DuPont ZORBAX PSM 60-S, PSM 300-S, and IBM Type A columns (250 mm). Detector was Waters Assoc. differential refractometer. The eluent was dimethylformamide (DMF). Molecular weights were calibrated with standard polystyrene.

Synthesis of Hydroxy-ended $PVDF_2$ - A 300 mL stainless steel autoclave was charged with 1.20 g (8.02 mmol) of di-t-butyl peroxide and 70 mL of methanol (1.74 mol), and was then sealed. The autoclave was degassed with argon. It was cooled by dry ice-acetone to condense additional VDF_2 into the reactor. The weight of VDF_2 used, 94 g (1.47 mol), was calculated from the change in weight of the cylinder. The reaction was carried out at 180°C for 10 hrs. The pressure in the autoclave at 180°C was 2020 psi initially.

After the reaction the autoclave was cooled to room temperature. The reaction mixture of light brown solid and brown liquid was filtered, and the insoluble part was washed with methanol. Drying the methanol-insoluble part in vacuum gave 31.8g of slightly yellow solid. The filtrate was concentrated and added to distilled water. The precipitate was filtered and dried to give 7.1g of white fine powder (methanol-soluble part). Total yield was 41%. Ir's of both parts, 3415 (s, broad, OH), 3017 (s, CH_2), 2980 (s, CH_2), 1407 (s, CH_2), 1274 (s, CF_2) cm^{-1}; ^1H nmr's of both parts, δ ~2.3 (m, $-CF_2CH_2CH_2CF_2-$), 2.9 (t, $-CF_2CH_2CF_2-$), 3.6 (d, $-\underline{CH_2}OH$). ^{13}C nmr of the methanol-insoluble part, δ 42.85 (quintet, J = 24 Hz, $-CF_2\underline{C}H_2CF_2-$, Jcal = 21 Hz); 54.64 (t, J = 6.3 Hz, $HO\underline{C}H_2-$, Jcal = 8 Hz); 62.26 (t, J = 31 Hz, $HOCH_2\underline{C}H_2CF_2-$); 119.88 (t, J = 246 Hz), $-CH_2\underline{C}F_2CH_2-$, Jcal = 245 Hz). Calculated values (Jcal) are those from standard nmr tables.[4] SEC's methanol-insoluble part - a unimodal broad peak having its maximum at 16.8 count (M.W. 3.6×10^3), methanol-soluble part - a unimodal broad peak having its peak at 18.2 count (M.W. 2.2×10^3). End group determination of methanol-insoluble part by 250 MHz nmr gave 1.8×10^3, in reasonable agreement.

Synthesis of Methacrylate-Ended $PVDF_2$-MA

A mixture of 10.8 g (3.0 mmol) of hydroxy-ended $PVDF_2$ (methanol-insoluble part), 107 mg (0.30 mmol) of 3-tert-butyl-4-hydroxy-5-methylphenyl sulfide, 98 mg (0.31 mmol) of tetra-butyl ammonium bromide, and 30.0 mL (312 mmol) of methacryloyl chloride was allowed to react with stirring under nitrogen flow at 60°C for 19 hrs. The hydroxy-ended $PVDF_2$ became swollen in methacryloyl chloride shortly after starting the reaction. Ether, 20 ml, was added to dark brown, gel-like reaction mixture. The diluted solution was poured into a large amount of ether. The flask was rinsed with a small amount of DMF and added into the ether. Precipitated polymer was collected by filtration followed by washing with ether. After drying, it was reprecipitated from DMF into distilled water. Washing with water, water-methanol, methanol, and drying gave 9.88 g (2.7 mmol, 90%) of slightly yellow powder. Ir, 3418 (m, broad, OH), 3019 (s, CH_2), 2980 (s, CH_2), 1726 (s, C=O), 1634 (m, C=C conj), 1409 (s, CH_2), 1273 (s, CF_2)cm^{-1}; ^1H nmr, δ 1.8 (s, $CH_3-C=$), 2.3 (m, $-CF_2CH_2CH_2CF_2-$) 2.8 (t, $-CF_2CH_2CF_2-$), 4.2 (s, $-COOCH_2-$), 5.6 and 6.0 (s, $CH_2=$); SEC, the same shape peak as that of starting hydroxy-ended polymer, the peak at 16.8 count (M.W. 3.5×10^3) based on polystyrene standards. End group determination by 250 MHz nmr gave 2.2×10^3, in reasonable agreement.

Polymerization of $PVDF_2$-MA - Homopolymerization and copolymerization were carried out in vacuum. After charging monomer(s), AIBN, and DMSO, the reaction mixture was degassed three times with repeated freeze-thaw cycles.

(i) Homopolymerization of $PVDF_2$-MA - In 6 mL of DMSO, 1.82 g (0.52 mmol) of $PVdF_2$-MA was polymerized using 2.9 mg (0.018 mmol) of AIBN at first. After 191 hrs., 3.4 mg (0.021 mmol) of AIBN was added and the polymerization was continued for 70 hrs more. Polymerization temperature was 70°C. At this temperature the reaction mixture was homogeneous. It was poured into 250 mL of ether. Precipitate was filtered then washed with ether. Drying in vacuum gave 1.43 g (78%) of white powder. ^1H nmr, δ 4.0-4.4 (broad, $-COOCH_2-$), no olefinic proton at 5.6 nor 6.0. SEC exhibited a broad peak at 16.1 count (M.W. 6.3×10^3) and a bimodal trace whose peaks were at 12.8 count (M.W. 1.2×10^5) and at 13.6 count (M.W. 4.3×10^4).

ii) Copolymerization between $PVDF_2$-MA and VOAc - The polymerization was carried out at 70°C, and the results are summarized in Table I. The reaction mixture was poured into large amount of ether. When polymer was obtained as a sticky lump, ether was decanted and the polymer was reprecipitated with DMF-distilled water. The precipitate was filtered, washed with non-solvent, then dried in vacuum. The color of the resulting polymer was white or slightly yellow. ^1H nmr, 0.7-1.2 (CH_3 in methacryl group), 1.5-2.0 (CH_2 in main chain and CH_3COO-), 2.1-3.3 ($-CH_2CF_2-$), 4.5-5.0 (CH in main chain).

A small portion of the polymer was extracted in a Soxhlet extractor with methanol to remove as much as possible of homo-PMMA. ^1H nmr of the polymer after the extraction showed a considerable increase in the intensity of the peak caused by $PVDF_2$ units.

iii) Copolymerization between $PVDF_2$-MA and MMA - In 6 mL of DMSO, 990 mg (0.28 mmol) of $PVDF_2$-MA and 940 mg (9.4 mmol) of MMA were copolymerized using 10.2 mg (0.075 mmol) of AIBN at 55°C in homogeneous solution. After 4 hrs. the reaction mixture was poured into 250 mL of methanol. Since the polymer was obtained as a sticky lump, methanol was decanted and the polymer was reprecipitated from DMF into methanol. After filtration and drying, 1.12 g (58%) of white powder was obtained. ^1H nmr, δ 0.6-1.2 (CH_3- in methacryl group), 1.7-2.0 ($-CH_2-$ in main chain), 2.1-3.3 (CH_2 in $PVDF_2$-MA unit), 3.4-3.7 ($-OCH_3$).

Soxhlet extraction of 225 mg of the resulting polymer with chloroform for 20 hrs gave only 12 mg of extract, which consisted of mostly PMMA. SEC of the polymer after the extraction showed two peaks with different signs of RI (reference: DMF). One was at 12.1 count (M.W. $\sim 1 \times 10^6$), the other was at 16.0 count (M.W. 6.6×10^3). The former mainly consists of MMA unit, the latter mainly consists of $PVDF_2$-MMA unit which was not extracted.

Results and Discussion. The hydroxy-ended poly(vinylidene fluoride) was prepared by telomerization of vinylidene fluoride with methanol and di-t-butyl peroxide, analogously to the procedure reported for tetrafluoroethylene.[5] Reaction on a 1.47 mole scale gave 41% yield. The molecular weight of the methanol-insoluble part was 3.6×10^3, based on polystyrene standard. Nmr's, especially ^{13}C nmr of the polymer, supports the structure $HOCH_2(CH_2CF_2)_nH$. The methanol-insoluble part was used for the following reaction because it is more convenient for purification after the reaction.

Table 1 Copolymerization between Methacrylate Macromonomer and Vinyl Acetate

Run	macromonomer g (mmol)	vinyl acetate g (mmol)	AIBN mg (mmol)	DMSO mL	Time hrs	Product g,[a]	Yield[a] %	Yield[b] %
1	0.99 (0.28)	1.06 (12.3)	25 (0.15)	3	22	1.7	83	53
2	1.50 (0.42)	0.60 (7.0)	25 (0.15)	4.5	19	1.5	72	53
3	1.00 (0.28)	1.06 (12.3)	2.3 (0.014)	3	22	0.99	49	40

[a] As precipitated

[b] After soxhlet extraction with methanol

Conversion to the methacrylate was readily carried out. The resulting macromonomer was characterized by SEC, ir, and ^{1}H nmr. The infrared spectrum still exhibited a small OH absorption, but ^{1}H nmr showed no remaining methylene protons adjacent to hydroxyl group. This OH absorption in the ir spectrum may be caused by a trace of water adsorbed by the macromonomer.

Homopolymerization proceeded only partially, and did not give high molecular weight polymer. This result could be attributed to a low molar concentration of the macromonomer.

Copolymerizations with two vinyl monomers were performed. Reaction conditions and results of the copolymerization with vinyl acetate are shown in Table 1. Also it shows the results of the extraction with methanol. SEC's of the polymers after the extraction revealed broad peaks with maxima located at slightly higher molecular weight range, such as; run 1 at 16.2 count (M.W. 5.9 x 10^3), run 2 at 15.6 count (M.W. 9.1 X 10^3), run 3 at 15.7 count (M.W. 8.1 X 10^3). These results can be expected from the nature of these comonomers. Vinyl acetate is a non-conjugated vinyl monomer, whereas the macromonomer is a conjugated vinyl monomer. This difference causes the methacrylate macromonomer to behave as an inhibitor in this case.

^{1}H Nmr of the copolymer between the macromonomer and methyl methacrylate did not show the methylene protons of the main chain. This is explained by the broadness of that peak due to the restricted mobility of methylene protons of the main chain in the graft-type copolymer. Nevertheless, even after extraction of homopolymer, the copolymer showed high molecular weight as shown by size exclusion chromatography. This result indicates that the macromonomer copolymerized well with methyl methacrylate.

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