

Synthesis and characterization of semifluorinated polymers via group transfer polymerization

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Abstract

Group transfer polymerization (GTP) was used to prepare semifluorinated polymers based on acrylic and methacrylic monomers. In the first case, electrophilic catalyzed GTP was applied with 1-methoxy-2-methyl-1-trimethylsilyloxy-1-propene (MMTP) as initiator, zinc iodide as catalyst and 1H,1H,2H,2H-perfluorooctyl acrylate as monomer. In this way it has been possible to obtain oligomers. Higher molecular weight polymers were prepared by means of the nucleophilic tetrabutylammonium benzoate as catalyst. With MMTP as initiator, 1H,1H,2H,2H-perfluoroalkyl methacrylates, $F(CF_2)_m(CH_2)_2OCOC(CH_3)=CH_2$, were polymerized to molecular weights $> 4.5 \text{ kg mol}^{-1}$. The polydispersity was found to depend strongly on the length of the perfluoroalkyl side chain, i.e. M_w/M_n decreases with increasing m .

Keywords: Electrophilic and nucleophilic catalyzed group transfer polymerization (GTP); 1H,1H,2H,2H-perfluoroalkyl acrylates and methacrylates; Low polydispersity semifluorinated polymers

1. Introduction

Control over polymeric material properties implies controlling the molecular structure of the constituent macromolecules. Living polymerization techniques allow the preparation of polymers with narrow molecular weight distribution and the synthesis of block copolymers by the sequential addition of different monomers. Anionic and cationic polymerization are widely applied methods. More recently, group transfer polymerization (GTP) [1] and living radical polymerization [2–7] have been developed as a route to well controlled polymers.

All living polymerizations have in common that they have originally been designed for systems with nonfluorinated monomers. Solvents and initiators cannot always be simply modified for fluorinated compounds. Among the reported anionic polymerizations of fluorinated monomers encountered in literature is the successful synthesis of poly(hexafluoro-1,3-butadiene) from hexafluoro-2-butyne [8] and hexafluoro-1,3-butadiene [9]. Another important class of fluorine containing monomers consists of amphiphilic semifluorinated monomers. Polymers based on semifluorinated monomers have been polymerized anionically, e.g. 1,2,2-trifluorostyrene [10], *o*-, *m*- and *p*-trifluoromethylstyrene [11,12] and fluoroalkyl acrylates and methacrylates with small perfluoroalkyl chains [13]. However, in this case yields are relatively low. The cationic polymerization of

semifluorinated vinyl ethers yields polymers with low polydispersity as well as fair yields [14]. Also radical reactions have been used to prepare controlled polymeric architectures containing fluorinated monomers. Tatamoto reported the preparation of triblock copolymers consisting of fluorinated vinylidene-hexafluoropropylene copolymers and tetrafluoroethylene-ethylene based copolymers by using radical iodine transfer polymerizations [6].

Polymers containing fluorinated (meth)acrylates comprise an important class of fluorinated materials. A number of applications is known, e.g. as low dielectric constant polymers in electronic industry [15], friction modifiers in lubrication oil [16], optical fiber claddings [17], membranes [18], low surface energy coatings [19] and anti fouling agents. Most applications originate from the special surface properties of these type of macromolecules e.g., low surface energy as determined by contact angle measurements [20,21].

Previous work on the synthesis of semifluorinated diblock copolymers by nucleophilic catalyzed GTP has shown that this polymerization technique can be successfully applied for the preparation of methacrylate based semifluorinated diblock copolymers [22].

In this paper we present a detailed study on the synthesis of acrylate and methacrylate based semifluorinated polymers by GTP. This polymerization method was used because it

allows good controlled polymerizations of acrylates and methacrylates. Two routes are described: (1) electrophilic catalyzed GTP and (2) nucleophilic catalyzed GTP. The latter is commonly employed in the GTP of methacrylate monomers [1] while the former is exclusively used in the polymerization of acrylates [23].

2. Experimental details

2.1. General techniques

2.1.1. NMR

^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC 200 spectrometer at 200 MHz and 50 MHz, respectively. CDCl_3 was used as solvent. The CHCl_3 signal at 7.24 ppm was used as internal standard. For the monomers with longer perfluoroalkyl chains 1,1,2-trichlorotrifluoroethane was added to improve solubility.

2.1.2. Size exclusion chromatography (SEC)

SEC was performed in toluene or tetrahydrofuran (polymer concentration of ca. 8 mg ml^{-1}) at room temperature. The setup consisted of a Waters 590 programmable HPLC pump, a HP Ti-Series 1050 autosampler, a set of Waters μ -Styragel columns (10^5 , 10^4 , 10^3 , 10^6 \AA) and a Waters 410 differential refractometer. The flow rate was 1.5 ml min^{-1} . Narrow poly(styrene) standards (PSS) were used for calibration. GPC-WIN version 2.54 software from PSS was used for the evaluation.

2.1.3. GC/MS

A Finnigan MAT SSQ 7000 mass spectrometer was coupled to a Varian 3400 gas chromatograph. The GC-column (DB-5 MS from J & W Scientific), had a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 μm . Methane was used as carrier gas at a flow rate of ca. 1 ml min^{-1} .

2.2. Materials

Acryloyl chloride (Aldrich) was used as received. Methacrylic anhydride (Aldrich) was distilled in vacuo before use. 1H,1H,2H,2H-Perfluorohexan-1-ol and 1H,1H,2H,2H-perfluorooctan-1-ol (Riedel de Haen) were distilled under reduced pressure. 1H,1H,2H,2H-Perfluorodecan-1-ol (Hoechst) was sublimated. Zinc iodide (Aldrich, 99.99%) was dried by evacuating ($<0.1 \text{ mbar}$) at 160°C overnight and stored in a nitrogen recirculated glovebox. Benzoic acid (Fluka) and tetrabutylammonium hydroxide (Aldrich, 40 wt% in water) were used as received. Dichloromethane (technical quality) was distilled on the rotary evaporator and then distilled over P_2O_5 under nitrogen. Methanol (technical quality) was distilled over a 70 cm column. Acetonitrile (Merck, p.a.) was distilled over P_2O_5 . Tetrahydrofuran (Merck, p.a.) was distilled from potassium benzophenone

and stored over molecular sieves (4 \AA) in a glovebox under nitrogen atmosphere. Toluene (Merck, p.a.) and 1,1,2-trichlorotrifluoroethane (Merck, p.a.) were used as received. 1-Methoxy-2-methyl-1-trimethylsilyloxy-1-propene (MMTP, Aldrich) was distilled over a spinning band column and stored over 4 \AA molecular sieves in a glovebox. 4-Dimethylaminopyridine (Aldrich) and triethylamine (Fluka) were used as received.

2.3. Syntheses

2.3.1. Tetrabutylammonium benzoate (TBAB)

TBAB was prepared as reported in the literature [24].

2.3.2. 1H,1H,2H,2H-perfluorooctyl acrylate (F6H2A)

30.0 g (82 mmol) of 1H,1H,2H,2H-perfluorooctan-1-ol was weighed into a 500 ml three-necked flask and dissolved in 150 ml 1,1,2-trichlorotrifluoroethane. The flask was cooled with an ice bath and after 10 min 16 ml (198 mmol) of acryloyl chloride was slowly added. After 20 min, 18 ml (130 mmol) of triethylamine was added dropwise. The ice bath was removed and the solution was heated at 55°C overnight. The solution was washed four times with water, dried, filtered and the solvent removed to yield 22 g of a light yellow liquid. The monomer was purified and dried by passing it over a short column with neutral aluminum oxide (ICN) and molecular sieves (4 \AA). The monomer was stored under nitrogen at -20°C over 4 \AA molecular sieves.

1H,1H,2H,2H-Perfluorooctyl acrylate (F6H2A): yield 65%; purity $>98\%$ (GC); ^1H NMR (CDCl_3) δ : 2.49 (tt, 2H, $-\text{CF}_2-\text{CH}_2-$, $^3J_{\text{H-H}} = 6.3 \text{ Hz}$, $^3J_{\text{H-F}} = 18.3 \text{ Hz}$); 4.43 (t, 2H, $-\text{CH}_2-\text{O}$, $^3J_{\text{H-H}} = 6.3 \text{ Hz}$); 5.83 (dd, 1H, $\text{H}_2\text{C}=\text{CH}-$, *trans* to carbonyl, $^2J_{\text{H-H}} < 1 \text{ Hz}$, $^3J_{\text{H-H}} = 10.3 \text{ Hz}$); 6.08 (dd, 1H, $\text{H}_2\text{C}=\text{CH}-$, $^3J_{\text{H-H, vic}} = 10.3 \text{ Hz}$, $^3J_{\text{H-H, trans}} = 17.2 \text{ Hz}$); 6.41 (dd, 1H, $\text{H}_2\text{C}=\text{CH}-$, *cis* to carbonyl, $^2J_{\text{H-H}} < 1 \text{ Hz}$, $^3J_{\text{H-H}} = 17.2 \text{ Hz}$) ppm. ^{13}C NMR (CDCl_3) δ : 30.6 (t, $-\text{CF}_2-\text{CH}_2-$, $^2J_{\text{C-C}} = 21.8 \text{ Hz}$); 56.3 (s, $-\text{CH}_2-\text{O}-$); 100–125 (fluorinated carbon region); 127.7 (s, $\text{CH}_2=\text{C}<$); 131.5 (s, $\text{CH}_2=\text{C}<$); 165.5 (s, $>\text{C}=\text{O}$) ppm. GC/MS (field-ionization): $m/z = 418$ (100%, M^+), 55 (3.5, $\text{CH}_2=\text{CH}-\text{CO}^+$).

2.3.3. 1H,1H,2H,2H-perfluoroalkyl methacrylate (FmH2MA)

A typical esterification reaction is described. A 250 ml three-necked flask fitted with a nitrogen inlet, a septum and a cooler was filled with 20.0 g (43 mmol) of 1H,1H,2H,2H-perfluorodecan-1-ol, 0.6 g (5 mmol) of 4-dimethylaminopyridine and flushed with nitrogen. Then, 100 ml of freshly distilled dichloromethane and 20 ml of 1,1,2-trichlorotrifluoroethane were brought into the flask. 6.2 ml (40 mmol) of methacrylic anhydride was slowly added through the septum followed by 5.5 ml (45 mmol) of triethylamine. The solution was stirred for 18 h at 30°C and then washed consecutively with water, diluted hydrochloric acid, a 4% aqueous sodium bicarbonate solution and water. After drying and filtering, the solvent was removed and 19.3 g of a clear colorless liquid

was obtained. The monomer was purified and dried by passing it over a short column with neutral aluminum oxide (ICN) and molecular sieves (4 Å) which had been purged and eluted with THF. The monomer solution in THF was stored under nitrogen at -20°C over 4 Å molecular sieves.

1H,1H,2H,2H-Perfluorohexyl methacrylate (F4H2MA):
Yield: 80%; purity > 98% (GC); ^1H NMR (CDCl_3) δ : 1.94 (s, 3H, $-\text{CH}_3$); 2.49 (tt, 2H, $-\text{CF}_2-\text{CH}_2-$, $^3J_{\text{H-H}} = 6.3$ Hz, $^3J_{\text{H-F}} = 18.9$ Hz); 4.45 (t, 2H, $-\text{CH}_2-\text{O}-$, $^3J_{\text{H-H}} = 6.3$ Hz); 5.59 (s, 1H, vinylic hydrogen *cis* to methyl group); 6.12 (s, 1H, vinylic hydrogen *trans* to methyl group) ppm. ^{13}C NMR (CDCl_3) δ : 18.0 (s, $-\text{CH}_3$); 30.5 (t, $-\text{CF}_2-\text{CH}_2-$, $^2J_{\text{C-C}} = 21.7$ Hz); 56.4 (s, $-\text{CH}_2-\text{O}-$); 100–125 (fluorinated carbon region), 126.2 (s, $\text{CH}_2=\text{C}$); 135.7 (s, $\text{CH}_2=\text{C}$); 166.8 (s, $>\text{C}=\text{O}$) ppm. GC/MS (CI, CH_4): $m/z = 333$ (MH^+).

1H,1H,2H,2H-Perfluorooctyl methacrylate (F6H2MA):
Yield 76%; purity > 98% (GC); ^1H NMR (CDCl_3) δ : 1.94 (s, 3H, $-\text{CH}_3$); 2.50 (tt, 2H, $-\text{CF}_2-\text{CH}_2-$, $^3J_{\text{H-H}} = 6.3$ Hz, $^3J_{\text{H-F}} = 18.9$ Hz); 4.45 (t, 2H, $-\text{CH}_2-\text{O}-$, $^3J_{\text{H-H}} = 6.3$ Hz); 5.59 (s, 1H, vinylic hydrogen *cis* to methyl group); 6.12 (s, 1H, vinylic hydrogen *trans* to methyl group) ppm. ^{13}C NMR (CDCl_3) δ : 17.9 (s, $-\text{CH}_3$); 30.6 (t, $-\text{CF}_2-\text{CH}_2-$, $^2J_{\text{C-C}} = 21.7$ Hz); 56.5 (s, $-\text{CH}_2-\text{O}-$); 100–125 (Fluorinated carbon region); 126.2 (s, $\text{CH}_2=\text{C}$); 135.8 (s, $\text{CH}_2=\text{C}$); 166.9 (s, $>\text{C}=\text{O}$) ppm. GC/MS (CI, CH_4): $m/z = 433$ (MH^+).

1H,1H,2H,2H-Perfluorodecyl methacrylate (F8H2MA):
Yield 84%; purity > 98% (GC); ^1H NMR (CDCl_3) δ : 1.92 (s, 3H, $-\text{CH}_3$); 2.48 (tt, 2H, $-\text{CF}_2-\text{CH}_2-$, $^3J_{\text{H-H}} = 6.3$ Hz, $^3J_{\text{H-F}} = 18.9$ Hz); 4.43 (t, 2H, $-\text{CH}_2-\text{O}-$, $^3J_{\text{H-H}} = 6.3$ Hz); 5.58 (s, 1H, vinylic hydrogen *cis* to methyl group); 6.10 (s, 1H, vinylic hydrogen *trans* to methyl group) ppm. ^{13}C NMR (CDCl_3): 17.9 (s, $-\text{CH}_3$); 30.5 (t, $-\text{CF}_2-\text{CH}_2-$, $^2J_{\text{C-C}} = 21.8$ Hz); 56.4 (s, $-\text{CH}_2-\text{O}-$); 100–125 (Fluorinated carbon region); 126.2 (s, $\text{CH}_2=\text{C}$); 135.7 (s, $\text{CH}_2=\text{C}$); 166.8 (s, $>\text{C}=\text{O}$) ppm. GC/MS (CI, CH_4): $m/z = 533$ (MH^+).

2.4. Polymerizations

2.4.1. Electrophilic catalyzed GTP

Freshly distilled dichloromethane (60 ml) was put in a 100 ml three-necked flask and brought into a glovebox. There, 2.2 g (6.9 mmol) of zinc iodide and 0.2 ml (1.0 mmol) of MMTP were added. The flask was cooled in a refrigerator inside the glovebox to -13°C . After 30 min 4.0 ml (ca. 6.3 g, 15 mmol) of F6H2A was added at once. The temperature rose to -10°C in 6 min and was allowed to decrease again to -12°C . After 25 min the flask was stirred at room temperature for another 2 h. The suspension was put into a separating funnel and washed six times with water. The dichloromethane layer was dried, filtered and the solvent was removed on a rotary evaporator. The light yellow viscous material was dried in vacuo at 50°C until constant weight.

2.4.2. Nucleophilic catalyzed GTP

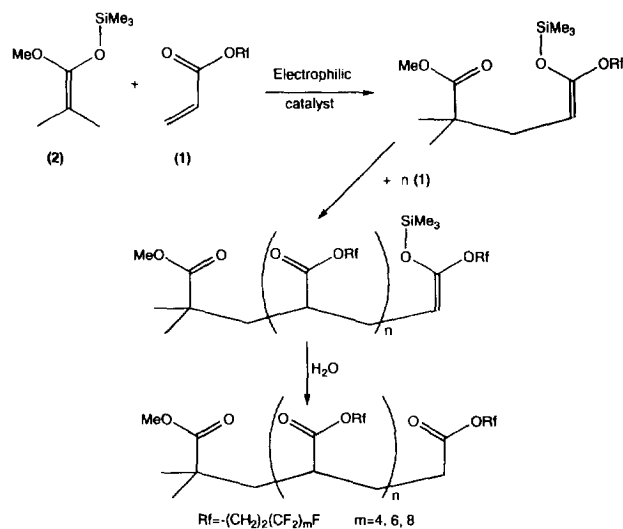
A typical experiment is described. All polymerizations were carried out in a nitrogen recirculated glovebox at room temperature. A 25 ml round bottomed flask was filled with 10 ml of THF. The desired amounts of MMTP and monomer were added. The solution was stirred for 5 min. Then polymerization was started by the addition of TBAB solution. At a certain time a sample was drawn from solution and terminated with methanol. Molecular weight was measured directly from the terminated polymerization solution by SEC.

3. Results and discussion

Using semifluorinated alcohols as starting material the corresponding acrylic and methacrylic esters were synthesized in good yield by a normal esterification reaction from acryloyl chloride and methacrylic anhydride. Using the anhydride instead of methacryloyl chloride resulted in 50–60% better yields [22]. The prepared semifluorinated monomers were employed in the group transfer polymerization (GTP) of low molecular weight polymers.

3.1. Electrophilic catalyzed GTP

The acrylate monomer was used in the electrophilic catalyzed group transfer polymerization (GTP). Scheme 1 shows a general outline for the GTP of semifluorinated acrylates (1) with 1-methoxy-2-methyl-1-trimethylsilyloxy-1-propene (MMTP, (2)) as initiator. The 1H,1H,2H,2H-perfluoroalkyl group is denoted by Rf. Table 1 gives the properties of the reaction product (3) of the GTP of 1H,1H,2H,2H-perfluorooctyl acrylate (F6H2A). The molecular weight obtained according to polystyrene standards appears to be significantly lower compared with the theoretical molecular weight as determined from the initial monomer to initial initiator ratio. Furthermore, the absence of any major side reac-



Scheme 1.

Table 1
Group transfer polymerization of F6H2A, with $[MMTP] = 0.016 \text{ mol l}^{-1}$ and $[ZnI_2] = 0.11 \text{ mol l}^{-1}$, and FmH2MA, with $[MMTP] = 3.9 \text{ mmol l}^{-1}$ and $[TBAB] = 0.4 \text{ mmol l}^{-1}$

No.	Monomer	$[M]$ (mol l^{-1})	$M_{n,th}^a$ (kg mol^{-1})	$M_{n,exp}^{b,c}$ (kg mol^{-1})	M_w/M_n^c	Yield c (%)	$M_{n,exp}^d$ (kg mol^{-1})	M_w/M_n^d	Yield d (%)
1	F6H2A	0.25	6.3	1.9 e	1.10	37	–	–	–
2	F4H2MA	0.05	4.4	3.9	1.33	55	4.0	1.32	63
3	F4H2MA	0.07	6.1	4.1	1.38	50	4.0	1.39	59
4	F6H2MA	0.07	7.9	4.5	1.17	15	4.5	1.16	20
5	F8H2MA	0.05	7.0	3.1 f	1.06	46	–	–	–

a Theoretical molecular weights were determined from the monomer to initiator ratio $[M]_0/[I]_0$.

b Molecular weights were determined by SEC in toluene and calculated according to PS standards.

c Polymerization time: 3 min.

d Polymerization time: 10 min.

e Molecular weight was determined by SEC in tetrahydrofuran and calculated according to PS standards.

f Polymerization time: 4 min.

tions is reflected by the low polydispersity of 1.10 indicating that a fast initiation reaction took place relative to the rate of propagation. However, it has to be noted that the actual or true molecular weights are expected to be higher than the values obtained by SEC experiments, because of the generally bad solubility of the semifluorinated polymers in THF and a presumably rather collapsed coil structure. Narrow molecular weight distributions and fast polymerizations have been reported also for the GTP of nonfluorinated acrylates and are a peculiar feature of electrophilic catalyzed GTP [23]. No further attempts to optimize solvent quality for the GTP of semifluorinated acrylates were undertaken.

The ^1H NMR spectrum of the polymer obtained is given in Fig. 1. Double bond signals at 5.83, 6.08 and 6.41 ppm due to unreacted monomer are absent in this spectrum.

Furthermore, the ^1H NMR spectrum confirms that the polymerization occurs according to the general mechanism

as given in Scheme 1. Both methyl groups (e) of the initiator molecule at the chain end result in the signals around 1.15 ppm. The methoxy group in the initiator molecule gives signal (b) at 3.60 ppm. The molecular weight as calculated from the ratio of the integral of peak (a) at 4.35 to the integral of peak (b) at 3.60 ppm is 3.9 kg mol^{-1} . This is about two times higher than the number average molecular weight as determined by SEC with polystyrene calibration standards.

^{13}C NMR spectra of both monomer and oligomer are plotted in Fig. 2(A) and (B), respectively. All signals of the double bonds disappeared in the oligomer spectrum. The signals (b) in Fig. 2(B) are mainly due to the presence of 1,1,2-trichlorotrifluoroethane. An attempt has been made to designate the signals arising from the proposed oligomer structure ((3), Fig. 2(B)).

3.2. Nucleophilic catalyzed GTP

Higher molecular weight semifluorinated polymers were synthesized using nucleophilic catalysis applicable for methacrylate monomers. In this case too, the theoretical molecular weights were chosen in the range mentioned in Table 1 because this allows the formation of low molecular weight polymers and subsequent SEC analysis. As the molecular weight is determined by the monomer to initiator ratio, a very high initiator concentration would lead to the formation of oligomers only. At very low initiator concentrations on the other hand, molecular weights are expected to be high which would result in solubility problems.

Monomers with the following side groups have been polymerized: 1H,1H,2H,2H-perfluorohexyl methacrylate (F4H2MA), 1H,1H,2H,2H-perfluorooctyl methacrylate (F6H2MA) and 1H,1H,2H,2H-perfluorodecyl methacrylate (F8H2MA). The results of the characterization are summarized in Table 1. The data demonstrate that the polymerization is very fast, as usually observed for group transfer polymerizations of methacrylates, i.e. in the order of tens of seconds [25]. This follows from comparison of the SEC data after 3 min and 10 min, respectively (Table 1), where neither

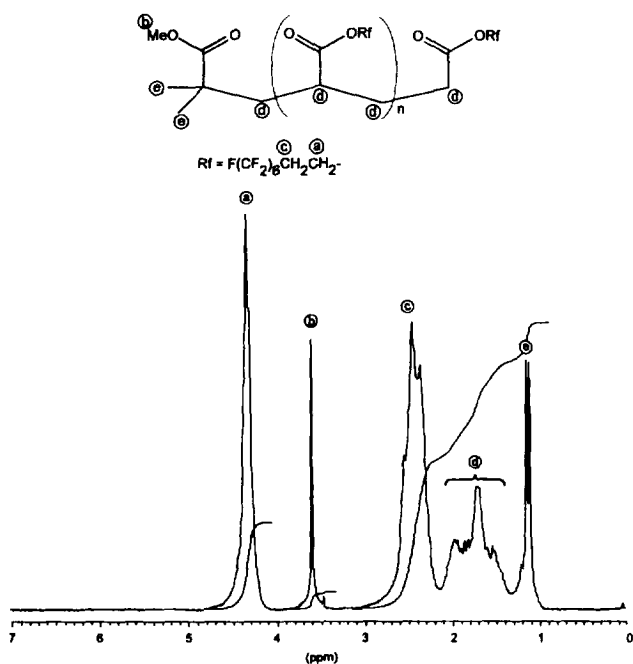


Fig. 1. ^1H NMR spectra of PF6H2A recorded in CDCl_3 .

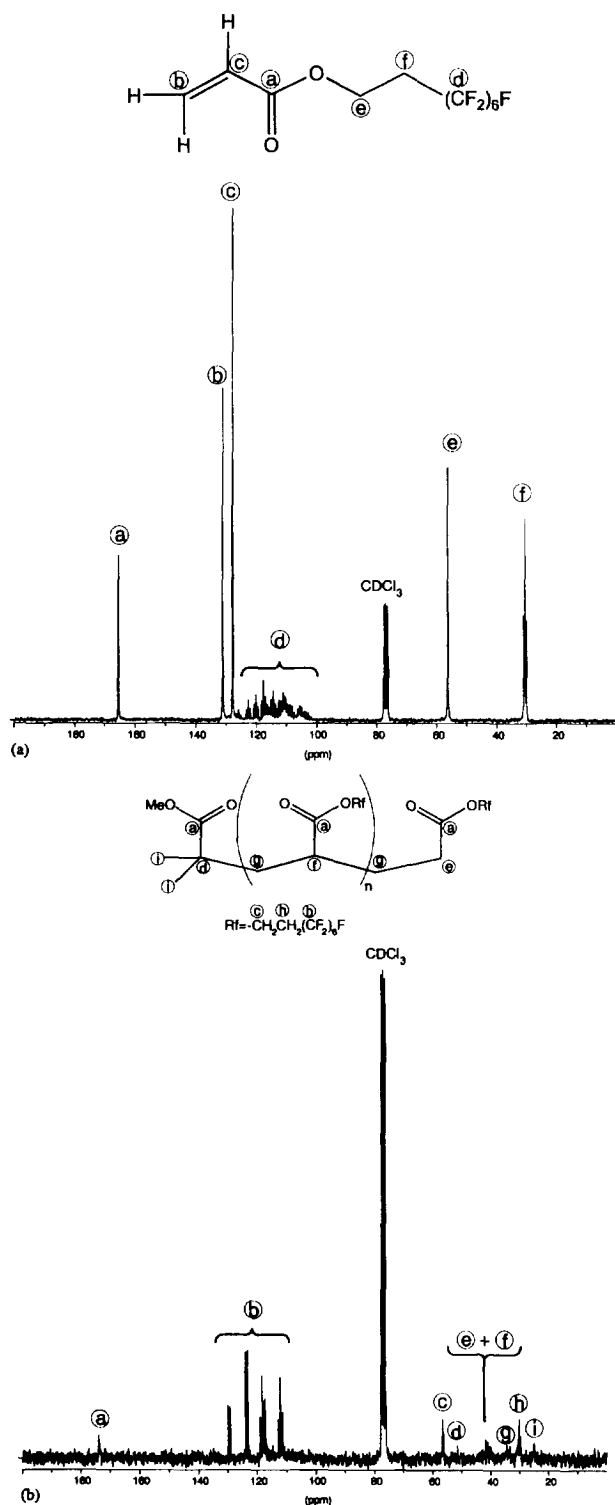


Fig. 2. ¹³C NMR spectra of (A) F6H2A and (B) PF6H2A recorded in CDCl₃.

increase in molecular weight nor polydispersity occurs. In general, only a minor increase in yield was observed at prolonged reaction times. Thus it seems that the presence of perfluorinated side chains does not affect the polymerization.

Typical for the nucleophilic catalyzed GTP was the strong dependence of polydispersity on the length of the perfluoro-

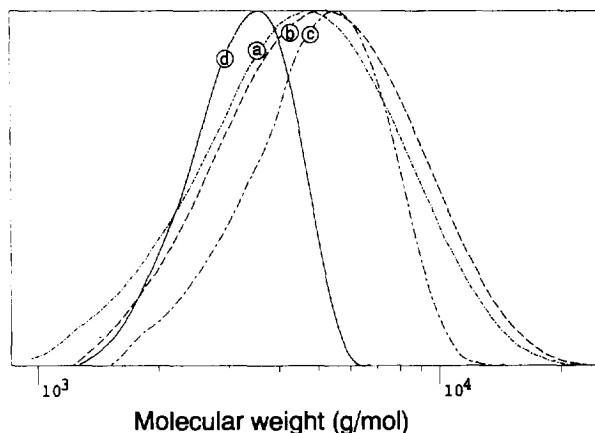


Fig. 3. Molecular weight distributions of (a) PF4H2MA after 3 min ($[F4H2MA] = 0.05 \text{ mol l}^{-1}$), (b) PF4H2MA after 3 min ($[F4H2MA] = 0.07 \text{ mol l}^{-1}$), (c) PF6H2MA after 3 min and (d) PF8H2MA after 4 min measured by GPC in tetrahydrofuran.

roalkyl side chain. Polydispersity decreased as follows: PF4H2MA > PF6H2MA > PF8H2MA. This is demonstrated in Fig. 3, where the molecular weight distributions are plotted for all methacrylate based polymers. This result may be explained because molecular weights are impeded by the limited solubility of fluorinated polymers in nonfluorinated solvents. As molecular weight increases, the solubility of the resulting polymer decreases drastically and polymerization ceases. The effect is expected to increase with the length of perfluorinated residue. Solubility problems might be overcome by performing the reactions in fluorinated solvents. However, our experiments of nucleophile catalyzed GTP in 1,1,2-trichlorotrifluoroethane were not successful. This was attributed to the low solubility of the nucleophilic catalyst in the halogenated solvent.

In conclusion, semifluorinated low polydispersity poly-methacrylates can be prepared by nucleophilic GTP under normal conditions, i.e. nonfluorinated solvent and initiator. Oligomers based on perfluoroalkyl acrylate are obtained when zinc iodide is used as an electrophilic catalyst.

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