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Francis Pardal, Vincent Lapinte, Jean-Jacques Robin. Kinetics of cotelomerization of 3-(trimethoxysilyl)propylmethacrylate and perfluorodecylacrylate. *European Polymer Journal*, 2009, 45, pp.1198-1207. 10.1016/j.eurpolymj.2008.12.035 . hal-00367170

HAL Id: hal-00367170

<https://hal.science/hal-00367170>

Submitted on 14 Apr 2009

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Kinetics of cotelomerization of 3-(trimethoxysilyl)propyl methacrylate and perfluorodecylacrylate

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Keywords: copolymerization; fluorinated polyacrylate; kinetic; reactivity ratio; telomerization

Abstract

The telomerization of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) in the presence of 2-mercaptoethanol was investigated at 80°C in acetonitrile. In our case, the efficiency of 2-mercaptoethanol as telogen agent, with TMSPMA, was demonstrated and the transfer constant (C_T) was determined. Moreover, cotelomerization of TMSPMA with perfluorodecylacrylate (PFDA) using various PFDA contents was investigated in order to obtain α -hydroxy oligomers with statistical copolymer-type main chains bearing trimethoxysilyl and perfluoro pendant chains. Until 10 mol % PFDA, no phase separation occurred. In this composition, r_{TMSPMA} and r_{PFDA} reactivity ratios were calculated, thus showing a tendency for a statistical distribution of the monomer units in the copolymer.

Introduction

Reactive end-group oligomers have attracted considerable interest during 20 years owing to the possibility of further reaction to give block and graft copolymers. Telomerization is a polymerization technique providing the synthesis of such macromolecular architectures. The term telomerization defined the reactive process where a molecule YZ, named telogen, reacts onto a polymerizable compound M to form telomers of general formula $Y(M)_nZ$. The difference between telomerization and polymerization is, in the first case, the low number of monomer units in the final compound ($n < 100$) which involves an importance of the end-group of the polymer chains. Telomerization has been performed by all polymerization mechanisms: anionic, group transfer, cationic, free-radical, polyaddition and polycondensation. Radical telomerization is the most useful technique to synthesize reactive α -functional polymers. The end-group functionality comes from the transfer agent nature (Scheme 1). Transfer agents have to present an easily radically cleavable bond such C-I, C-Br, C-Cl, S-H (mercaptans) and P-H (phosphonates). Mercaptans have been extensively studied: thioglycolic acid,^[1-3] 2-mercaptoethylamine,^[4] 3-mercaptopropionic acid,^[4] and 2-mercaptoethanol.^[5-8] The efficiency of 2-mercaptoethanol in transfer reactions has been outlined and explored in several previous investigations.^[6-7] Its reactivity has been well studied in the case of the cotelomerization of methyl methacrylate with styrene in order to obtain α -hydroxyl oligomers with random type copolymer structures for a further utilization as macromonomers.^[7]

Scheme 1: Mechanism of the radical telomerization using AIBN and 2-mercaptoethanol as telogen agent.

Fluorinated polymers are unique materials since they combine chemical inertness (to acids, bases and solvents), low water absorptivity, excellent weatherability, good resistance to oxidation, aging, and very interesting surface properties with low surface energy. Among the fluorinated monomers, acrylates with long perfluoroalkyl (R_f) side chains, such as perfluorodecylacrylate (PFDA) monomer, offer interesting properties.^[9-11] Fluorinated acrylate based polymers are most often synthesized by emulsion polymerization^[11-12] and to our knowledge, no telomerization reaction involving fluorinated acrylate monomer has been attempted yet. In opposition to acrylates with long perfluoroalkyl (R_f) side chains, some ethylene units substituted by fluorine atoms were telomerized. For instance, Boutevin et al. studied radical telomerization of chlorotrifluoroethylene and cotelomerization with butyl vinyl

ether and mercaptans (2-hydroxy ethyl mercaptan, $C_6F_{13}C_2H_4SH$ or perfluorochloroalkyl iodides).^[13] Vinylidene fluoride was also telomerized with perfluoroalkyl iodides by thermal and redox processes.^[14] The main problem in the solution polymerization of this type of monomer is their low solubility in usual hydrocarbonated solvents. The cotelomerization with hydrophilic hydrogenated methacrylate comonomers can solve this lack.

Thus, this paper is focused on the synthesis on additives for applications in organic/inorganic hybride materials. Oligomers bearing two functionalities were prepared: a fluorinated part for surface properties and a silane one for grafting onto silica particles. The oligomers were choosen since they allow low viscosities and facilitate their processing. So, this paper describes the cotelomerization of heptadecafluorodecyl acrylate with a reactive acrylate offering grafting onto inorganic matrix.^[15-19] A well-known candidate for the organic/inorganic hybrid applications is 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). None investigation on copolymerization of TMSPMA with PFDA has already been reported in the literature. Although, few references exist on homopolymerization of TMSPMA^[20-22] and copolymerization^[22-23] with others acrylate and methacrylate comonomers. Koh et al.^[23] have synthesized amphiphilic block copolymers by atom-transfer radical polymerization (ATRP) with TMSPMA, methyl methacrylate and poly(ethylene oxide) methyl ether methacrylate in order to form organic/inorganic hybrid nanocapsules used in the encapsulation of substances into confined spaces. Ritz et al. reported the copolymerization by ATRP of TMSPMA with methyl methacrylate and generated gradient copolymers for applications as compatibilizers for polymer blends or pressure sensitive adhesives.^[24] D'Agosto et al. also synthesized amphiphilic block copolymers by RAFT technique which can self-assemble into a variety of nano-objects and can be used as colloid stabilizers, nanoreactors, or templates for making inorganic solids.^[20]

The aim of the work was firstly, the determination of the transfer constant (C_T) of TMSPMA in the presence of 2-mercaptoethanol by telomerization and the check of non-attendance of the side reactions between trimethylsilyl groups and the functional telogen. Secondly, the free-radical cotelomerization of TMSPMA with PFDA in the presence of 2-mercaptoethanol was studied in order to prepare α -hydroxy terminated statistical oligomer-type backbone which may be further used to obtain graft copolymers. Finally, the monomer reactivity ratios of TMSPMA (monomer M1) and PFDA (monomer M2) were determined according to Macret's and Jaack's methods.

Experimental

Materials

Perfluorodecyl acrylate (PFDA) (Fluorochem, 98%) was distilled under vacuum (8 mbar, 130°C). 2,2'-Azobisisobutyronitrile (AIBN) was purified twice by recrystallization in methanol and dried under vacuum. 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) (Aldrich, purity 98%), 2-mercaptoethanol (ME) (Aldrich, 99%), mercaptoacetic acid (Aldrich, 97%), acetonitrile (Acros), iodine solution (0.1049 mol.L⁻¹; Aldrich) and CDCl₃ (Aldrich, 99.8%) were used as received.

TMSPMA, ¹H NMR (CDCl₃) δ (ppm): 6.09 (s, H_{e cis}), 5.54 (s, H_{e trans}), 4.11 (t, O-CH₂), 3.57 (s, Si-O-CH₃), 1.93 (s, C-CH₃), 1.86-1.63 (m, O-CH₂-CH₂), 0.69 (m, CH₂-CH₂-Si). ¹³C NMR (CDCl₃) δ (ppm): 166.95 (COO), 136.23 (C=CH₂), 124.78 (CH₂=C), 66.19 (O-CH₂), 50.15 (Si-O-CH₃), 27.80 (C-CH₃), 17.95 (CH₂-CH₂-CH₂), 166.95 (CH₂-Si). FTIR (cm⁻¹): 2944 (CH), 2841 (OCH₃), 1717 (C=O), 1638 (C=C), 1100 (Si-O).

PFDA, ¹H NMR (CDCl₃) δ (ppm): 6.50-6.40 (dd, H_{d cis}-CH=CH), 6.19-6.05 (dd, H_{d'}-CH₂=CH), 5.91-5.85 (dd, H_{d trans}-CH=CH), 4.47 (t, O-CH₂), 2.52 (m, CH₂-CH₂-CF₂). ¹³C

NMR (CDCl_3) δ (ppm): 165.63 (COO), 131.41 ($\text{CH}_2=\text{CH}$), 127.78 ($\text{CH}=\text{CH}_2$), 125-108 ($(\text{CF}_2)_7\text{-CF}_3$), 56.37 (O- CH_2), 27.80 ($\text{CH}_2\text{-CF}_2$). FTIR (cm^{-1}): 2944 (CH), 1735 (C=O), 1200-1000 (C-F).

2-Mercaptoethanol, ^1H NMR (CDCl_3) δ (ppm): 3.71 (dt, HO- CH_2), 2.70 (dt, HS- CH_2), 2.18 (s, OH), 1.38 (t, SH). ^{13}C NMR (CDCl_3) δ (ppm): 63.41 (HO- CH_2), 26.71 (HS- CH_2).

Analytical techniques

^1H NMR spectra were recorded using a Bruker AC 200 with CDCl_3 as solvent. Chemical shifts were referenced to the peak of residual CHCl_3 at 7.26 ppm. ^{13}C NMR spectra were recorded using a Bruker AC 300 with CDCl_3 as solvent. Chemical shifts were referenced to CDCl_3 at 77 ppm. Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal.

Synthesis of the TMSPMA telomer: P(TMSPMA)

Telomerizations were performed with TMSPMA monomer in acetonitrile with different molar ratios R_0 ($R_0 = n_{\text{telogen}}/n_{\text{monomer}}$) from 0.05 to 0.3. In a typical telomerization of TMSPMA using 2-mercaptoethanol, 12.41 g (0.05 mol) of TMSPMA, 0.39 g (0.005 mol) of 2-mercaptoethanol were introduced in a 50 mL two necked flask equipped with a condenser and a septum and the solution was diluted to 50 mL with anhydrous acetonitrile. The solution was bubbled with nitrogen for 30 min before heating at 80 °C. Finally, 0.041 g ($2.5 \cdot 10^{-4}$ mol) of AIBN ($C_0 = n_{\text{initiator}}/n_{\text{monomer}} = 0.5\%$) in 1 mL of anhydrous acetonitrile were added through the septum with a syringe. After 10 h of reaction, the polymer was washed three times with anhydrous n-hexane to remove the unreacted monomer and telogen, and was dried under vacuum.

Synthesis of P(TMSPMA-stat-PFDA) cotelomer

Cotelomerizations of TMSPMA with PFDA comonomer were performed in acetonitrile with various initial molar contents of PFDA (5%, 10%, 15%). In a typical cotelomerization, 2.235 g (0.009 mol) of TMSPMA, 0.518 g (0.001 mol) of PFDA, 0.078 g (0.001 mol) of 2-mercaptoethanol were introduced in a 10 mL two necked flask equipped with a condenser and a septum and the solution was diluted to 10 mL with anhydrous acetonitrile. The solution was bubbled with nitrogen for 30 min before heating at 80°C. Finally, 0.0082 g (5.10^{-5} mol) of AIBN ($C_0 = n_{\text{initiator}}/n_{\text{monomer}} = 0.5\%$) in 0.2 mL of anhydrous acetonitrile were added through the septum with a syringe. At the conclusion of the reaction, the copolymer was washed three times with anhydrous n-hexane to remove the unreacted monomer and telogen, and was dried under vacuum.

Telomerization kinetics

All the kinetics were studied following the monomer and telogen concentrations versus reaction time. Each reaction was monitored by sampling and each aliquot was quenched in ice in order to stop the reaction. The thiol conversion of each sample was evaluated using titration of SH groups with a 0.002 mol.L^{-1} iodine solution prepared from iodine standard solution ($0.1049 \text{ mol.L}^{-1}$) according to the following equation:

The thiol concentration ($[\text{RSH}]$) versus time is given by the following equation:

$$[\text{RSH}]_t = \frac{V_{\text{eq}}(0) \times [\text{RSH}]_0}{V_{\text{eq}}(t)} \quad (2)$$

where $V_{\text{eq}}(0)$ and $V_{\text{eq}}(t)$ are equivalent to the volume of iodine solution added to the thiol solution at the beginning of the reaction and at t min, respectively. $[\text{RSH}]_t$, $[\text{RSH}]_0$ are the thiol

concentrations at different times of reaction and at $t=0$, respectively. $[I_2]$ is the concentration of the iodine solution used for the titration.

The monomer consumption was calculated by ^1H NMR with CDCl_3 as deuterated solvent. Each sample was analyzed by comparing the integration ratio of the monomer to that of polymer one.

Results and discussion

Telomerization of TMSPMA: P(TMSPMA)

Free-radical telomerization of TMSPMA: P(TMSPMA) was performed with AIBN as initiator in acetonitrile at 80°C (Scheme 2, way 1).

Scheme 2: Telomerization of TMSPMA using AIBN as initiator and 2-mercaptoethanol as telogen agent without PFDA (way 1) or with PFDA (way 2).

In the kinetic study of radical telomerization of TMSPMA, two functional mercaptans were tested as telogen: mercaptoacetic acid and 2-mercaptoethanol. The influence of the carboxylic

acid or hydroxyl end-group of the two telogens on the control of molecular weights was undertaken. Boutevin et al. have shown that mercaptoacetic acid has a high transfer constant for acrylic acid and methyl methacrylate even if the transfer process could be minimized using a mixture of solvents such as water/THF (80/20).^[1-3] In our case, the utilization of mercaptoacetic acid as telogen agent to polymerize TMSPMA yielded monoadduct and non-polymeric products. Furthermore, side reactions based on trimethylsilyloxy groups reactivity occurred like their hydrolysis and the reaction with carboxylic acid groups. In addition, the cleavage of S-H bond is less important with an alcohol en-group than an acid owing to its smaller electron withdrawing effect. Consequently, transfer reactions are less significant for 2-mercaptoethanol and allow a better control of molecular weights.

In the kinetic study, P(TMSPMA)s were synthesized using various R_0 ratios ($R_0 = n_{\text{telogen}}/n_{\text{monomer}}$). The chain transfer constant C_T ($C_T = k_{tr}/k_p$) is the driving parameter for the control of the molecular weights and their distribution. In systems with $C_T > 1$, “telomerization” will result in a complex mixture of telomers and polymers whereas a value smaller than 1 involves a better consumption of monomer and desired oligomers are obtained. Among the various methods for the determination of the C_T ,^[1] Mayo’s method^[25] requires the plot of the inverse of the $\overline{DP}_{n_0}$ versus R_0 as follows:

$$\frac{1}{\overline{DP}_{n_0}} = C_T \frac{[T]_0}{[M]_0} = C_T R_0 \quad (3)$$

where $[T]_0$ and $[M]_0$ are the concentration of telogen and monomer at $t = 0$, respectively. Thus, if $1/\overline{DP}_{n_0}$ is plotted as a function of the R_0 ratio, C_T value can be directly deduced. Experimentally, C_T values are determined at very low conversion. The O'Brien method^[26] takes into account the conversion rate of the reactants and consists in following the monomer and the telogen conversions during the reaction. C_T value was deduced at high conversion yield from the straight line of $\ln([T]_0/[T]_t)$ versus $\ln([M]_0/[M]_t)$:

$$\ln \frac{[T]_0}{[T]_t} = C_T \ln \frac{[M]_0}{[M]_t} \quad (4)$$

Both monomer and telogen concentrations are required to determine the C_T values according to O'Brien method. The consumption of the chain transfer agent was followed by iodide titration of aliquots of the samples taken during the reaction. The monomer conversion was determined by ^1H NMR analysis through the integration of the peaks located at 4.10 ppm (H_a : attributed to CH_2 in α position of the ester function of TMSPMA) and at 3.91 ppm (H_b : CH_2 in α position of the ester function of the telomer) (Figure 1) using the following equation:

$$\frac{[\text{TMSPMA}]_t}{[\text{TMSPMA}]_0} = \frac{\int H_a \text{ (at 4.10 ppm)}}{\int H_a \text{ (at 4.10 ppm)} + \int H_b \text{ (at 3.91 ppm)}} \quad (5)$$

Figure 1: ^1H NMR spectra (CDCl_3) of P(TMSPMA) ($R_0=1$) versus time, before precipitation.

Figure 2 reports monomer and telogen concentrations versus time. The monomer concentration decreases faster than telogen concentration until the first fourth hours of reaction. After this reaction time, linear behaviour of TMSPMA and telogen consumptions with the same slope occurs. C_T value was deduced from the slope of $\ln([ME]_0/[ME]_t)$ versus $\ln([TMSPMA]_0/[TMSPMA]_t)$ (Figure 3). The C_T values range from 0.57 for $R_0=0.3$ to 0.73 for $R_0=0.05$ with a correlation coefficient of the linear relationship (R^2) close to 0.99-0.98 (Table 1). The C_T value of TMSPMA telomerization with 2-mercaptoethanol ($C_T=0.65 \pm 0.08$) means that transfer reactions occur and that a control of the molecular weights can be achieved. Moreover a C_T value inferior to 1 means that the relative rate of consumption of the transfer agent is lower than the propagation rate which is in agreement with the shift between the plots in Figure 2. Chain transfer constant depends on the structures of monomer and telogen^[4] and it is therefore difficult to compare our results with the C_T values found in the literature. However, the values measured ($C_T=0.65$) are in the same order of magnitude as those found by Robin et al.^[6] who reported a C_T value of 0.72 for 2-(dimethylamino)ethyl methacrylate in acetonitrile and 0.57 in benzene at 70°C. Teodorescu et al. also obtained a C_T value of 0.62 for methyl methacrylate in benzene at 60°C.^[7] Finally acetonitrile was a solvent able to provide an efficacious transfer avoiding strong hydrogen bonds or dipole-dipole interactions between the solvent and the monomer. Moreover acetonitrile is a good solvent for PFDA co-units for further study of copolymerisation of TMSPMA with PFDA.

Figure 2: Evolution of monomer and telomer concentrations versus time ($R_0=0.1$).

Figure 3: $\ln([ME]_0/[ME]_t)$ versus $\ln([TMSPMA]_0/[TMSPMA]_t)$ for the polymerization of TMSPMA for different R_0 (● $R_0=0.05$, ◆ $R_0=0.1$, ■ $R_0=0.2$, ▲ $R_0=0.3$).

Table 1: C_T and $\overline{DP}_n$ values according to R_0 for the telomerization of TMSPMA by 2-mercaptoethanol.

R_0	C_T	R^2	$\overline{DP}_n^{th}$	$\overline{DP}_n^{exp*}$
0.05	0.73	0.999	20	26.3
0.1	0.70	0.983	10	12.8
0.2	0.60	0.984	5	6.7
0.3	0.57	0.988	3.3	4.3

*obtained from 1H NMR analysis.

After 10h of reaction, the synthesized oligomers were washed three times with anhydrous n-hexane and dried under vacuum to remove the both unreacted monomer and telogen. The experimental number-average polymerization degree ($\overline{DP}_n^{exp}$) was determined by 1H NMR analysis (Figure 4) through the integration of the peaks located at 3.91 ppm (H_b : CH_2 in α position of the ester function of the telomer) and at 2.68 ppm (H_c : CH_2 in β position of hydroxyl function of the telomer) following the equation:

$$\overline{DP}_n^{exp} = \frac{\int H_b \text{ (at 3.91 ppm)}}{\int H_c \text{ (at 2.68 ppm)}} \quad (6)$$

The theoretical number-average polymerization degree $\overline{DP}_n^{th}$ was calculated as the molar ratio of initial monomer and transfer agent i.e. the inverse of R_0 . The equation (7) could be used because the calculations were achieved at the end of the reaction after 10 hours of reaction for conversion rate close to one:

$$\overline{DP}_n^{th} = \frac{1}{R_0} = \frac{[M]_0}{[T]_0} \quad (7)$$

The theoretical ($\overline{DP}_n^{th}$) and experimental ($\overline{DP}_n^{exp}$) values are listed in Table 1 where it can be seen that higher experimental values in respect to theoretical ones are obtained. These results are in good agreement with the C_T values which are lower than 1 meaning that the transfer process is less efficient than the propagation process (Figure 2).

Figure 4: ^1H NMR spectrum of P(TMSPMA) in CDCl_3 after precipitation in n-hexane ($R_0=0.1$).

Cotelomerization of TMSPMA with PFDA: P(TMSPMA-stat-PFDA)

To determine the higher content in PFDA fluoromonomer that can be incorporated in the P(TMSPMA-stat-PFDA) copolymer, cotelomerizations were carried out with different initial molar ratios in PFDA fluoromonomer (5%, 10% and 15%) (Scheme 2, way 2). Experiments were performed using 2-mercaptoethanol as transfer agent and AIBN as initiator in acetonitrile at 80°C . A kinetic study of the homotelomerization of PFDA and the calculation of C_T value could not be realized owing to the poor solubility of fluorine moieties in organic

solvents and their precipitation. Consequently, these copolymers could not be analysed by size-exclusion chromatography because of their insolubility in the solvents usually employed as eluent. Perrier et al. observed the same phenomenon when studying the synthesis of statistical copolymers of methyl methacrylate with PFDA where a 20% maximum content could be reached.^[9-10] In our case, the phase separation did not occur until 10% of PFDA in P(TMSPMA-stat-PFDA). Thus, TMSPMA co-units might have a twofold beneficial role, that is, the improvement of solubility in usual solvents and the availability of SiOMe₃ groups for further grafting from process.

In both case, the conversion of PFDA and TMSPMA monomers versus time were linear throughout the first hour of reaction with a faster consumption of PFDA than TMSPMA (Figure 5). After this reaction time a gradual decrease of PFDA consumption has been observed. For 10% of initial PFDA content, the final composition of P(TMSPMA-stat-PFDA) (at t=5h) is 92% of TMSPMA moieties and 8% of PFDA moieties. It confirms that for high monomers conversion TMSPMA reacts preferentially than PFDA and thus the copolymer is enriched in TMSPMA units.

Figure 5: $\ln[M]_0/[M]_t$ as a function of time for TMSPMA and PFDA monomers (10 mol. % of initial PFDA content).

Monomer reactivity ratios are very important parameters for the elucidation of copolymer structure (copolymer composition, monomer sequence distribution) and kinetics (propagation rate coefficients), so, the reactivity ratios of TMSPMA and PFDA were determined. Given the diminution of PFDA consumption, kinetic study was limited to the first hour of reaction (Figure 5). The r_1 and r_2 ratios indicate the reactivity of a given free radical face to monomers 1 and monomer 2. The ratios depend on the structure of the two monomers and of the corresponding radicals. They are independent of the copolymerization rate and of the structure of the initiator. Among the numerous calculation methods of the reactivity ratio in radical copolymerization, Jaacks^[27] and Macret^[28] methods were selected to evaluate the reactivity ratios of TMSPMA and PFDA ($r_{\text{TMSPMA}}=r_1$, $r_{\text{PFDA}}=r_2$). Jaacks's method is based on the approximation of the quasi-stationary state where the concentrations of both radicals are quasi-constant. Furthermore, this method requires a great excess in one monomer in respect with the other one to consider only one type of radical. If M_1 is in excess in regard to M_2 , the instantaneous composition of the copolymer is described by the following equation:

$$\frac{\delta(M_1)}{\delta(M_2)} = r_1 \frac{M_1}{M_2} \quad (8)$$

that can be integrated under the following form:

$$\ln \frac{[M_1]_t}{[M_1]_0} = r_1 \ln \frac{[M_2]_t}{[M_2]_0} \quad (9)$$

Thus, plotting $\ln \frac{[M_1]_t}{[M_1]_0}$ versus $\ln \frac{[M_2]_t}{[M_2]_0}$ allows to calculate r_1 as the slope of the straight line. Jaacks's method was only used to determine the reactivity ratio of TMSPMA owing to polymer precipitation which prevents the study of the cotelomerization with an excess of PFDA and the calculation of the reactivity ratio of PFDA. The reactivity ratio r_1 was obtained from a monomer molar ratio TMSPMA/PFDA: 90/10. The evolution of the reaction versus

time was monitored using ^1H NMR analysis, measuring the integration of double bonds of each monomer signal ($\text{H}_{\text{d cis}}$ and H_{e}), and calculating their corresponding theoretical values according to the reference peak (Si-OCH_3 : H_{f}) at 3.57 ppm (Figure 6). In the equation (11) the integration from $\text{H}_{\text{d cis}}$ to H_{f} was successively divided by 9 corresponding to the three Si-OMe by molecule and by 9 because the initial monomer molar ratio TMSPMA/PFDA is 90/10. The conversion rates for TMSPMA and PFDA were expressed by these equations:

$$\frac{[\text{TMSPMA}]_{\text{t}}}{[\text{TMSPMA}]_0} = \frac{\int \text{H}_{\text{e}} \text{ (at 5.54 ppm)}}{\int \text{H}_{\text{f}}/9 \text{ (at 3.57 ppm)}} \quad (10)$$

$$\frac{[\text{PFDA}]_{\text{t}}}{[\text{PFDA}]_0} = \frac{\int \text{H}_{\text{d cis}} \text{ (at 6.40 ppm)}}{\int \text{H}_{\text{f}}/81 \text{ (at 3.57 ppm)}} \quad (11)$$

Figure 6: ^1H NMR spectrum of P(TMSPMA-*stat*-PFDA) in CDCl_3 before precipitation.

The reactivity ratio r_1 was given by the value of the plot of $\ln([TMSPMA]_0/[TMSPMA]_t)$ versus $\ln([PFDA]_0/[PFDA]_t)$ as illustrates in Figure 7. A value of 0.65 for r_1 was found which means that radicals from TMSPMA moieties react preferentially on PFDA monomer.

Figure 7: $\ln[TMSPMA]_0/[TMSPMA]_t$ versus $\ln[PFDA]_0/[PFDA]_t$ for the copolymerization of TMSPMA with PFDA (9/1 mol/mol).

Macret's method was also used to confirm this r_1 value and to determine the r_2 value.^[28] This graphical method is issued from Ezrielev et al. works^[29] with the following equation:

$$\frac{X}{Y}(Y-1) = r_1 \frac{X^2}{Y} - r_2 \quad (12)$$

where $X = \frac{[M_1]}{[M_2]}$ and $Y = \frac{dM_1}{dM_2}$ represent the monomer concentration ratio in the medium and

the monomer concentration ratio inserted in the copolymer respectively as a function of time.

In contrast with Y value, X value can be easily calculated. Assuming that consumption of monomer is a first order reaction, one can write equations 13 and 14:

$$[M_i]_t = [M_i]_0 e^{-\alpha_i t} \quad (13)$$

$$Y = \frac{dM_1}{dM_2} = \frac{\alpha_1 [M_1]}{\alpha_2 [M_2]} \quad (14)$$

with α_1 and α_2 representing the conversion rate of M_1 and M_2 respectively.

From the plot of $\ln \frac{[TMSPMA]_t}{[TMSPMA]_0}$ and $\ln \frac{[PFDA]_t}{[PFDA]_0}$ as a function of time, $\alpha_{TMSPMA}=0.0045$ and $\alpha_{PFDA}=0.0068$ were deduced from the coefficient of the slopes as shown in Figure 5. These values allow to calculate Y and thus to report the plot $X(Y-1)/Y$ versus X^2/Y . Thus, r_1 and r_2 values were obtained using the slope (r_{TMSPMA}) and the origin of the curve (r_{PFDA}) of Macret's equation (Figure 8). In addition, $r_{TMSPMA} \times r_{PFDA}$ value close to 1 indicates that statistical copolymers are synthesized. The comparison of the r_{TMSPMA} values ensuing of Macret's and Jaacks' methods reveals a good agreement between these two methods (Table 2). For cotelomerization of TMSPMA with PFDA, Macret's method provides $r_{TMSPMA} < 1$ and $r_{PFDA} > 1$. The first value means that the TMSPMA terminated propagating chain reacts preferentially with PFDA monomer according cross-propagation reaction whereas the r_{PFDA} value means PFDA terminated propagating chain reacts preferentially with PFDA monomer according homopolymerization reaction. Consequently, the copolymer composition should be enriched in PFDA content at the beginning of the reaction. Moreover we have shown that after one hour of reaction, consumption of PFDA decreases (Figure 5). In conclusion at the early stage of the polymerization (first hour), the resulting chains are enriched in PFDA monomer, forming short sequences of PFDA units. At higher monomer conversion, the monomer feed is enriched in less reactive TMSPMA radicals, so that longer sequences of TMSPMA units are formed. All of these results indicate a drift of the copolymer composition with increasing conversion. The determination of the reactivity ratios of TMSPMA or PFDA with other monomer has not been attempted yet. One example of copolymerization of 2-

(trimethoxysilyloxy)ethyl methacrylate (TMSEMA) with PFDA by ATRP has been found.^[24] The extended Kelen-Tüdös method was used to determine $r_{\text{TMSEMA}}=1.58$ and $r_{\text{MMA}}=0.59$ and illustrated that the copolymers had only a soft gradient composition. Perrier et al. reported the kinetic study of copolymerization of MMA with PFDA and they showed that conversion of each monomer was almost identical throughout the reaction indicating similar reactivity ratios.^[9-10] Thus, it is difficult to compare these results according to the different experimental conditions and the different methods to determine the reactivity ratios.

Figure 8: $X/Y(Y-1)$ as a function of X^2/Y for the copolymerization of TMSPMA with PFDA (9/1 mol/mol).

Table 2: Comparison of the reactivity ratios of TMSPMA and PFDA.

Method	r_{TMSPMA}	r_{PFDA}	$r_{\text{TMSPMA}} \times r_{\text{PFDA}}$
Macret	0.66	1.51	0.99
Jaacks	0.65	---	---

Conclusion

Hydroxyl terminated copolymers were prepared by free-radical telomerization of monomers bearing perfluoro pendant chains and SiOCH_3 reactive groups. Homotelomerization of TMSPMA reveals the efficiency of 2-mercaptoethanol as transfer agent in acetonitrile and the inert nature of SiOCH_3 groups since no by-products were observed. Further, synthesis of copolymers based on TMSPMA and PFDA was successfully achieved. The incorporation of PFDA moieties in P(TMSPMA-stat-PFDA) was limited to 10% due to the insolubility of copolymers with higher contents. Then, the reactivity ratios were determined by Jaacks and Macret's methods. These methods show that $r_{\text{PFDA}} > 1$ and $r_{\text{TMSPMA}} < 1$: a statistical P(TMSPMA-stat-PFDA) copolymer. Thus, telomerization seems to be a convenient way to synthesize functionalized end-group copolymers by incorporating fluorine groups. Thus, these preliminary results will be applied to the surface treatment of silica particles in order to modify their properties and their processing. These results will be published in a further paper.

Acknowledgements: The authors thank the financial support by CREAT - Centre de Recherche de la Division Chargeurs Interlining du groupe Chargeurs.

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