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Living cationic polymerization of 1H,1H,2H,2H perfluorooctyl vinyl ether

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Summary

Cationic polymerization of 1H,1H,2H,2H perfluorooctyl vinyl ether (CH_2=CH-O-C_2H_4-C_6F_{13}), initiated by the HI/ZnI_2 system in 1,1,2 trichloro trifluoro ethane at -30 °C, leads to living polyvinyl ethers bearing a fluoroalkyl group. Results indicate that the polymerization is indeed free from chain transfer and termination reactions and that polyethers of controlled molecular weight and a narrow molecular weight distribution can be made available.

Introduction

Fluorine containing polymers deserve a special interest because of unique properties such as low surface energy, low refractive index, high chemical and thermal stability, ...(1-2).

Recently Higashimura and others have reported on the living carbocationic polymerization of a series of vinyl ethers by a variety of initiating systems (3-7) among which the HI/I_2 and HI/ZnI_2 initiator/activator pairs have been largely used. These remarkable contributions have paved the way to the macromolecular engineering of vinyl ethers (8-9).

In order to investigate the effect of the substituent on the cationic polymerization of vinyl ethers, Higashimura et al. have studied the polymerization of CH_2=CH-O-C_2H_4-N(nC_3H_7)$SO_2C_8F_{17}$ initiated with the HI/I_2 initiating system in 1,1,2 trichloro trifluoro ethane (CF_2Cl-$CFCl_2$, fluorocarbon 113) at a low temperature (-15 °C) (10). The use of a fluorinated solvent is necessary to keep the growing polymer chains in solution. Polymerization of this fluorinated monomer has been reported to be living but much slower than that of a non fluorinated vinyl ether. This observation has been attributed to the strong electron withdrawing effect of the fluoroalkyl substituent.

Recently, Möller et al. have mentioned that CH_2=CH-O-C_2H_4-$(CF_2)_n$-F (n = 6; 8) could be polymerized in fluorocarbon 113 at -15 °C in the presence of HI/ZnI_2 or $CH_3SO_3H/(CH_3)_2S$ (11) (Webster's initiating system (7)). However the living character of the polymerization has not been studied. By using the Webster's initiating system, Percec et al. have synthesized diblock copolymers consisting of a poly(mesogenic vinyl ether) as the first block and poly(1H,1H,2H,2H perfluorodecyl vinyl ether) as the second block (12). In this case, the living character of the polymerization of the fluorinated monomer, though possible, has not been fully demonstrated either.

In view of preparing well defined end-functional fluorinated polymers which could be part of more specialized macromolecular systems, the cationic polymerization of 1H,1H,2H,2H perFluoroOctyl Vinyl Ether (FOVE, CH_2=CH-O-C_2H_4-C_6F_{13}) has been considered in this study. The HI/ZnI_2 initiating system has been used in fluorocarbon 113 at -30 °C (13) because it has the advantage of a faster polymerization rate over the HI/I_2 pair. The purpose of this paper is to prove that FOVE can be polymerized in a living way under these experimental conditions.

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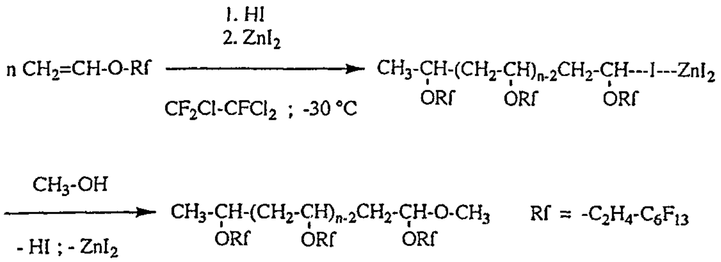
Results and Discussion

FOVE has been synthesized by the mercuric acetate catalyzed transvinylation of 1H,1H,2H,2H perfluoro 1-octanol with ethyl vinyl ether (eq. 1) according to the method reported by Boutevin et al. (14). The reaction conditions have however been slightly modified in order to increase the reaction yield as detailed in the experimental part.

$$C_6F_{13}\text{-}C_2H_4\text{-}OH + CH_2{=}CH\text{-}O\text{-}C_2H_5 \xrightarrow{Hg(OAc)_2} CH_2{=}CH\text{-}O\text{-}C_2H_4\text{-}C_6F_{13} + C_2H_5\text{-}OH$$

[1]

Due to a high fluorine content , FOVE has been polymerized in fluorocarbon 113 at -30°C (eq. 2) in order to prevent the growing chains from precipitating as it should occur in a non fluorinated solvent.



$$n\ CH_2{=}CH\text{-}O\text{-}Rf \xrightarrow[CF_2Cl\text{-}CFCl_2\ ;\ -30\ °C]{1.\ HI \quad 2.\ ZnI_2} CH_3\text{-}\underset{ORf}{CH}\text{-}(CH_2\text{-}\underset{ORf}{CH})_{n\text{-}2}CH_2\text{-}\underset{ORf}{CH}\text{---}I\text{---}ZnI_2$$

$$\xrightarrow[-\ HI\ ;\ -\ ZnI_2]{CH_3\text{-}OH} CH_3\text{-}\underset{ORf}{CH}\text{-}(CH_2\text{-}\underset{ORf}{CH})_{n\text{-}2}CH_2\text{-}\underset{ORf}{CH}\text{-}O\text{-}CH_3 \qquad Rf = \text{-}C_2H_4\text{-}C_6F_{13}$$

[2]

An α-iodo ether first results from the addition of HI onto the monomer. The carbon / iodine bond of this compound is then activated (polarized or ionized) by ZnI_2 which allows the chain propagation to occur. Polymerization is terminated by addition of an excess of methanol. Figure 1 shows the ^1H NMR spectrum of the α-iodo FOVE that has been prepared by the addition of FOVE by an equimolar amount of HI in fluorocarbon 113, at -30 °C, under nitrogen. The NMR spectrum of the α-iodo FOVE has been recorded in a mixture of dry fluorocarbon 113 / CD_2Cl_2, at -30 °C, under nitrogen. These strictly controlled conditions are requested due to the instability of the iodo compound in relation to the electron withdrawing effect of the perfluoroalkyl moiety. The 0 to 2 ppm range is not shown in figure 1 since only signals of n-hexane in which HI is dissolved can be seen.

Since FOVE bears a strongly electron withdrawing substituent, its reactivity is expected to be much lower compared to an alkyl vinyl ether. In order to ensure a polymerization rate fast enough, the $[HI]_0/[ZnI_2]_0$ molar ratio which is usually ca. 50 (15) has been decreased down to 1 so that more ZnI_2 is available for the activation of the carbon / iodine bonds. Expectedly, HI and ZnI_2 cannot initiate the FOVE polymerization when used separately ; figure 2 shows the time-conversion curve, under the aforementioned experimental conditions. It is worth noting that the polymerization is complete after one hour, compared to less than five minutes for ethyl vinyl ether under the same conditions. This observation confirms the comparatively low reactivity of FOVE.

It must also be pointed out that the polymerization medium is still homogeneous when the polymerization is carried out to completion. In contrast, the recovered polyFOVE has proved to be insoluble in common organic solvents which is a problem for the polymer characterization.

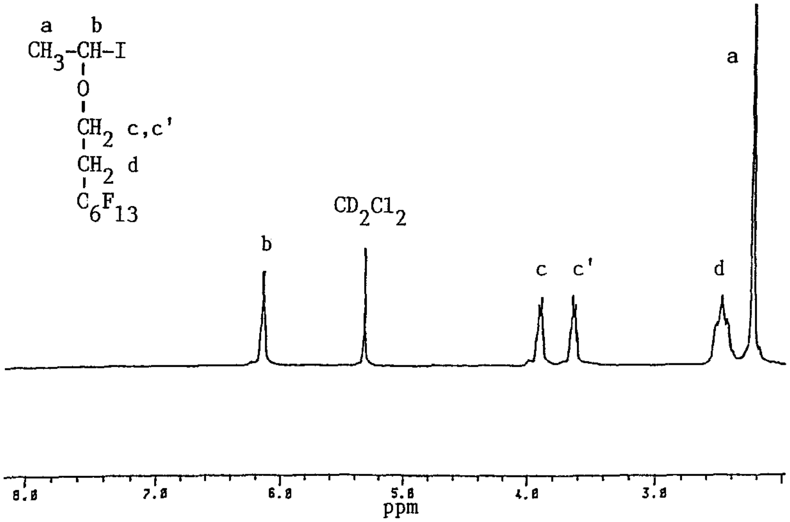


Figure 1 : 400 MHz ^1H NMR spectrum of the addition product of HI to FOVE (CD_2Cl_2/fluorocarbon 113; 50 : 50, v : v; -30 °C).

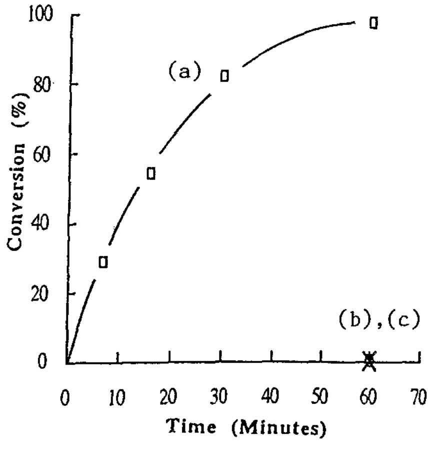


Figure 2 : Time-conversion curve for the polymerization of FOVE in fluorocarbon 113 at -30 °C. $[FOVE]_0 = 0.1$ M, (a) : $[HI]_0 = [ZnI_2]_0 = 4$ mM ; (b) : $[HI]_0 = 4$ mM, $[ZnI_2]_0 = 0$ mM ; (c) : $[HI]_0 = 0$ mM, $[ZnI_2]_0 = 4$ mM

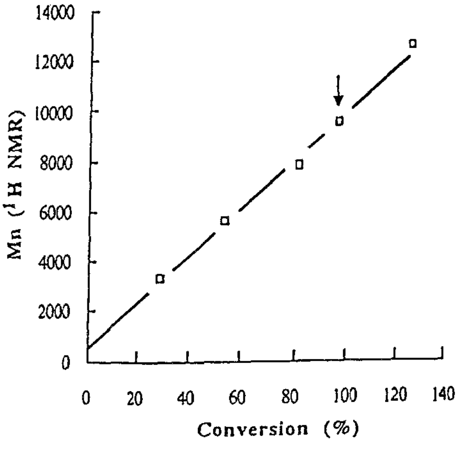


Figure 3 : Dependence of Mn (measured by ^1H NMR) on FOVE conversion in fluorocarbon 113 at -30 °C. $[FOVE]_0 = 0.1$ M, $[HI]_0 = [ZnI_2]_0 = 4$ mM. The arrow indicates the addition of a second FOVE feed to a completely polymerized solution ($[FOVE]' = 0.05$ M)

Figure 3 shows the molecular weight dependence on the FOVE conversion. The insolubility of the polyFOVE in THF has prevented it from being characterized by size exclusion chromatography (SEC). Molecular weight has accordingly been measured by ^1H NMR (in a mixture of $CDCl_3$ and fluorocarbon 113) on the basis of the relative intensities of the protons of the terminal methyl group associated with the monomer unit first polymerized : protons a in figure 6) and the protons of the repeat unit (protons g in figure 6). Molecular weight increases linearly with FOVE conversion. More importantly this linear dependence is preserved when the completely polymerized solution is added with as second feed of FOVE (correlation coefficient = 0.997). As recently discussed by Penczek et al. (16), this indicates that the FOVE polymerization is free from chain transfer reactions.

It is known that the propagation rate (Rp) of the living polymerization of vinyl ethers (M) initiated with a HI/zinc halide (ZnX_2) system obeys (17-18) equation 3.

$$Rp = - d[M]/dt = k_p [HI]_0 [ZnX_2]_0 [M] = k' [M] \qquad [3]$$

Figure 4 shows that the cationic polymerization of FOVE is in agreement with equation 3. Indeed the time dependence of ln ($[M]_0$ / $[M]_t$) is linear which means that the number of growing chains does not change versus time (16). Thus, linearity of the plot in figure 4 (correlation coefficient = 0.999) supports the absence of termination reaction in the course of the FOVE polymerization.

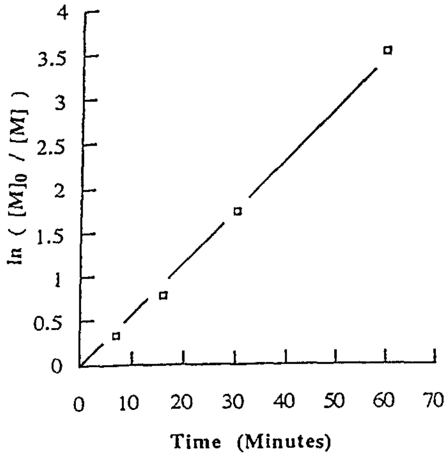


Figure 4 : Plot of ln ($[FOVE]_0$ / [FOVE]) versus time in fluorocarbon 113 at -30 °C. $[FOVE]_0$ = 0.1 M, $[HI]_0$ = $[ZnI_2]_0$ = 4 mM.

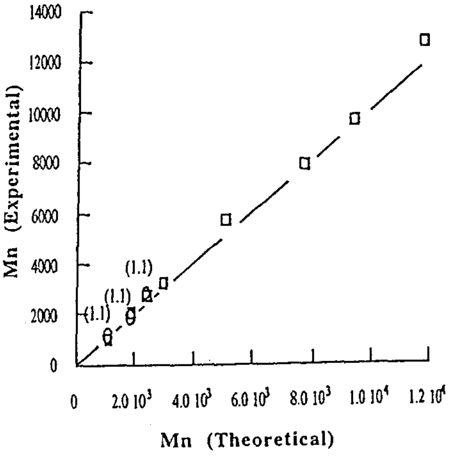


Figure 5 : Plot of experimental Mn versus the theoretical ($[FOVE]_0$.Conv./$[HI]_0$). Fluorocarbon 113 at -30 °C. $[HI]_0$ / $[ZnI_2]_0$ = 1. □ : ^1H NMR; O : SEC, polystyrene calibration; ( ) : Mw / Mn. The straight line is the theoretical relationship.

Figure 5 shows a very good agreement between the experimental molecular weight and the value expected for a living polymerization. Polymers of a predicted size can thus be obtained at least in a range extending to 14 000. It must be noted that when the molecular weight of polyFOVE is smaller than ca. 2 500, the polymer is soluble in common solvents and can be analyzed by SEC (THF, polystyrene calibration). Figure 5 shows that the molecular weights determined by SEC match very well values obtained by ^{1}H NMR spectroscopy. Moreover, the molecular weight distribution is quite narrow (M_w/M_n = 1.1).

From the aforementioned results it appears that FOVE can be polymerized in a living way under the reported experimental conditions at least in the investigated molecular weight range. As a result, fluorinated polyethers of controlled molecular weight and a narrow molecular weight distribution can be made available.

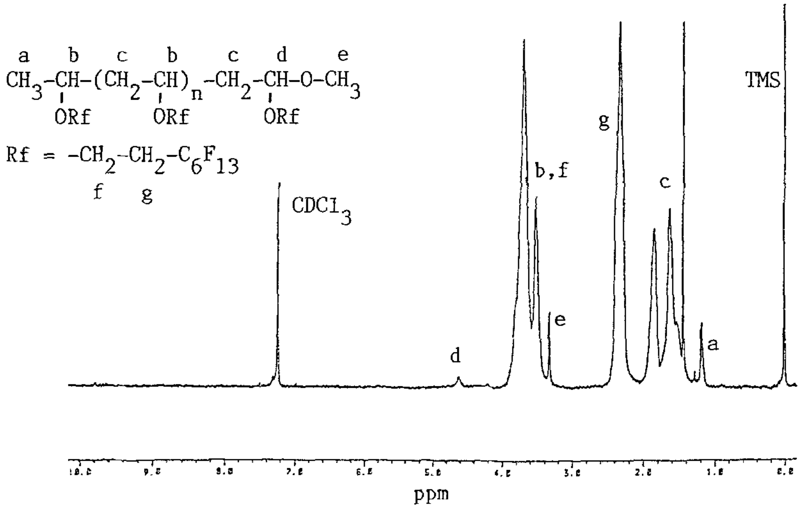


Figure 6 : 400 MHz ^{1}H NMR spectrum of a polyFOVE obtained in fluorocarbon 113 at -30 °C. ($[HI]_0$ / $[ZnI_2]_0$ = 1). Mn = 7700 (^{1}H NMR).

Nevertheless ^{1}H NMR spectra of pFOVE (Figure 6) show that the intensity of the signal of the methoxy end group resulting from the quenching of the living chains with methanol (protons e at 3.3 ppm) is ca. 75 % the intensity of the signal of the CH_3 end-group generated by the initiation step (protons a at 1.2 ppm). This most likely results from some ill-defined side reactions during the termination step. Whatever these side reactions are, they are completely prevented from occurring by decreasing the amount of ZnI_2 used. Indeed, when a $[HI]_0/[ZnI_2]_0$ ratio of 10 or more is used, deactivation with methanol is quantitative since as many methoxy end-groups as methyl end-groups are observed. Although control of the molecular weight is preserved, the polymerization rate is slower as predicted by equation 3. For instance, a theoretical molecular weight of 2400 is reached after ca. 60 minutes when the initiator/activator ratio is 10 . It is also worth noting that polyFOVE of a predicted length can be prepared at -30 °C ($[HI]_0/[ZnI_2]_0$ = 10) when fluorocarbon 113 is replaced by a solvent of comparable dielectric constant (ε), such as toluene (ε_{f113} = 2.41, $\varepsilon_{toluene}$ = 2.44 (19)). Of course, polymerization is then limited to low molecular weight (lower than ca.2500) due to a restricted solubility.

Since living character of the FOVE polymerization is now well established, synthesis of well defined end functional polyFOVE may be considered by deactivation of the living active centers with various functional nucleophiles (8). This will be the topic of a forthcoming report.

Experimental

Synthesis of 1H,1H,2H,2H perfluorooctyl vinyl ether (FOVE) : 85 g of 1H,1H,2H,2H perfluoro 1-octanol (Atochem), 120 g of ethyl vinyl ether (Merck) and 6,7 g of mercuric acetate (Janssen) were mixed in a Pyrex ampoule under stirring and frozen in liquid nitrogen. After sealing, the ampoule was heated up to 100 °C and the content stirred for three hours. Conversion of the fluorinated alcohol into fluorinated vinyl ether was 70 % (GC). The reaction mixture was fractionally distilled twice under reduced pressure (18 mm Hg) to give the fluorinated vinyl ether (Bp : 55 °C). It was however contaminated by ca 10 % (GC) of fluorinated alcohol. It was further purified by addition of an excess of n-butyl lithium (Aldrich,
1.5 molar excess compared to the undesired fluorinated alcohol). The mixture was fractionally distilled to yield the pure fluorinated vinyl ether (purity > 99.5 %, GC, yield : 40 %).

Polymerization : Polymerization was carried out under dry nitrogen in a vessel equipped with a three-way stopcock. All glassware was flamed under vacuum prior to use. Solutions were transferred with stainless steel capillaries using standard vacuum techniques or with glass syringes equipped with capillaries. Solutions of HI (Aldrich) and ZnI_2 (Aldrich), in n-hexane (Lab Chemistry) and diethyl ether (Lab Chemistry) respectively were prepared as reported elsewhere[3,17]. They were kept in the dark at -18 °C under dry nitrogen until use.

N-hexane, toluene (Lab Chemistry), 1,1,2 trichloro trifluoro ethane (fluorocarbon 113, Janssen), ethyl vinyl ether and FOVE were dried over calcium hydride (Aldrich) and distilled before use. Diethyl ether was dried over sodium prior to distillation. All chemicals were of an analytical grade.

The desired amount of HI was added to a fluorocarbon 113 solution of FOVE at -30 °C. After 15 minutes, ZnI_2 was added and the polymerization allowed to proceed. When desired, the polymerization medium was quenched with a large excess of methanol (Lab Chemistry), containing ca. 5 % dimethyl 2-6 pyridine (Janssen) or aqueous ammonia (UCB) in view of trapping the released HI. The organic solution was washed first with a 10 % sodium thiosulphate (Baker) aqueous solution and then with deionized water until a neutral pH was reached. It was then dried over sodium sulphate (Baker) and filtered. Solvent was removed under vacuum and the isolated polymer was weighted in order to calculate the monomer conversion.

Characterization of polyFOVE : ^1H NMR spectra were recorded at 400 MHz (in a 1:1 v:v mixture of $CDCl_3$ and fluorocarbon 113, at room temperature unless otherwise specified) on a Bruker AM 400 spectrometer with a TMS internal reference. Gas chromatography (GC) was carried out with a Delsi 30 chromatograph equipped with a Flame Ionization Detector (FID) and a FFAP type column. Size exclusion chromatography was performed, in THF at 45 °C, with a Hewlett Packard HP 1090 Liquid Chromatograph, equipped with a Refractive Index Detector HP 1037A and with 4 polystyrene gel columns of a 100, 500, 10 000, 100 000 angstroms porosity respectively, Polymer Laboratories) . Columns were calibrated with 16 polystyrene standards (Polymer Laboratories) covering a large range of Mn (580 to 570 000).

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References

1. B.Boutevin, Y. Pietrasanta, "Les Acrylates et Polyacrylates Fluorés", Erec, Paris (1988)
2. M. Yamabe, Makromol. Chem., Macromol. Symp., 64, 11 (1992)
3. M. Miyamoto, M. Sawamoto, T. Higashimura, Macromolecules, 17, 265 (1984)
4. M. Sawamoto, C. Okamoto, T. Higashimura, Macromolecules, 20, 2693 (1987)
5. M. Sawamoto, Trends Polym. Sci., 1, 111 (1993)
6. O. Nuyken, H. Kröner, S. Aechtner, Makromol. Chem., Macromol. Symp., 32, 181 (1990)
7. C. Cho, B.A. Feit, O.W. Webster, Macromolecules, 23, 1918 (1990)
8. M. Sawamoto, Prog. Polym. Sci., 16, 111 (1991)
9. B. Ivan, J.P. Kennedy, "Designed Polymers by Carbocationic Macromolecular Engineering : Theory and Practice", Hanser, Munich (1991)
10. W. O. Choi, M. Sawamoto, T. Higashimura, Polym. J., 20, 201 (1988)
11. J. Höpkens, M. Möller, M. Lee, V. Percec, Makromol. Chem., 193, 275 (1992)
12. V. Percec, M. Lee, J. Macromol. Sci., Pure Appl. Chem, A29(9), 723 (1992)
13. Part of this paper has been presented at the "Meeting on New Developments in Cationic Polymerization of Vinyl Ethers", 22nd October 1991, Ghent, Belgium
14. B. Boutevin, B. Youssef, J. Fluor. Chem, 44, 395 (1989)
15. K. Kojima, M. Sawamoto, T. Higashimura, Polym. Bull., 23, 149 (1990)
16. S. Penczek, P. Kubisa, R. Szymanski, Makromol. Chem., Rapid Commun., 12, 77 (1991)
17. K. Kojima, M. Sawamoto, T. Higashimura, Macromolecules, 22, 1552 (1989)
18. V. Héroguez, A. Deffieux, M. Fontanille, Makromol. Chem., Macromol. Symp., 32, 199 (1990)
19. CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton (1988)

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