Deeper insight into the MADIX Polymerization of Vinylidene Fluoride

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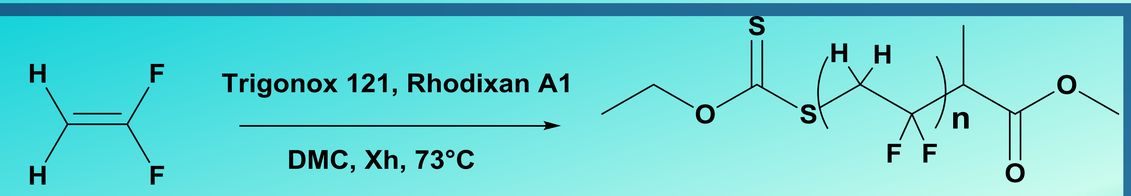
Objective:
Develop efficient controlled radical polymerization technique for the synthesis of well-defined poly(vinylidene fluoride) (PVDF) architectures.

Introduction:
- Iodine Transfer of Polymerization (ITP) of VDF is relatively well-known[1], and easy to setup, but does not afford very good control on the molecular weights and their distribution. In addition, loss of the chain end iodine atom is often observed.
- Recently, polymerization of VDF using macromolecular design via inter-change of xanthates (MADIX)[2] was reported. Promising results were shown, but this study did not provide optimized polymerization conditions or complete understanding of the phenomena observed during the polymerization.
- The present work is a much more detailed study of the polymerization of VDF under MADIX conditions: the effects of the VDF head-to-head (H-H) addition[3], and of the transfer reaction (caused by H-abstraction by fluorinated radicals) on the control of the VDF polymerization are carefully elucidated.



Scheme 1. MADIX polymerization of VDF

Run	M-DP target eq	time	% yield[a]	DP NMR[b]	M_n theo[c] (g/mol)	M_n NMR[d] (g/mol)	M_n SEC[e] (g/mol)	Đ[e]	% S-CH_2-[b]	% S-CF_2-[b]	% -CF_2H	Tm (°C)
1	48	24h	57	43	2000	3000	5000	1.42	**94**	**0**	**6**	171.7
2	50	5h	< 5	4	n.d.[f]	500	n.d	n.d	**12**	**53**	**2**	n.d
3	51	10h	25	20	1000	1500	3900	1.12	**43**	**54**	**3**	145.8
4	51	15h	35	29	1400	2100	4100	1.29	**66**	**31**	**3**	159
5	54	20h	75	47	2700	3200	7200	1.40	**100**	**0**	**6**	170.9

Table 1. MADIX polymerization of VDF
[a]Determined by gravimetry. [b]Determined by ^{1}H NMR. [c]Calculated using yield as conversion. [d]Calculated from DP. NMR and theoretical molecular. [e]Determined by SEC in DMF. [f]not determined.

Microstructure determination using ^{1}H-and ^{19}F NMR Spectroscopies:

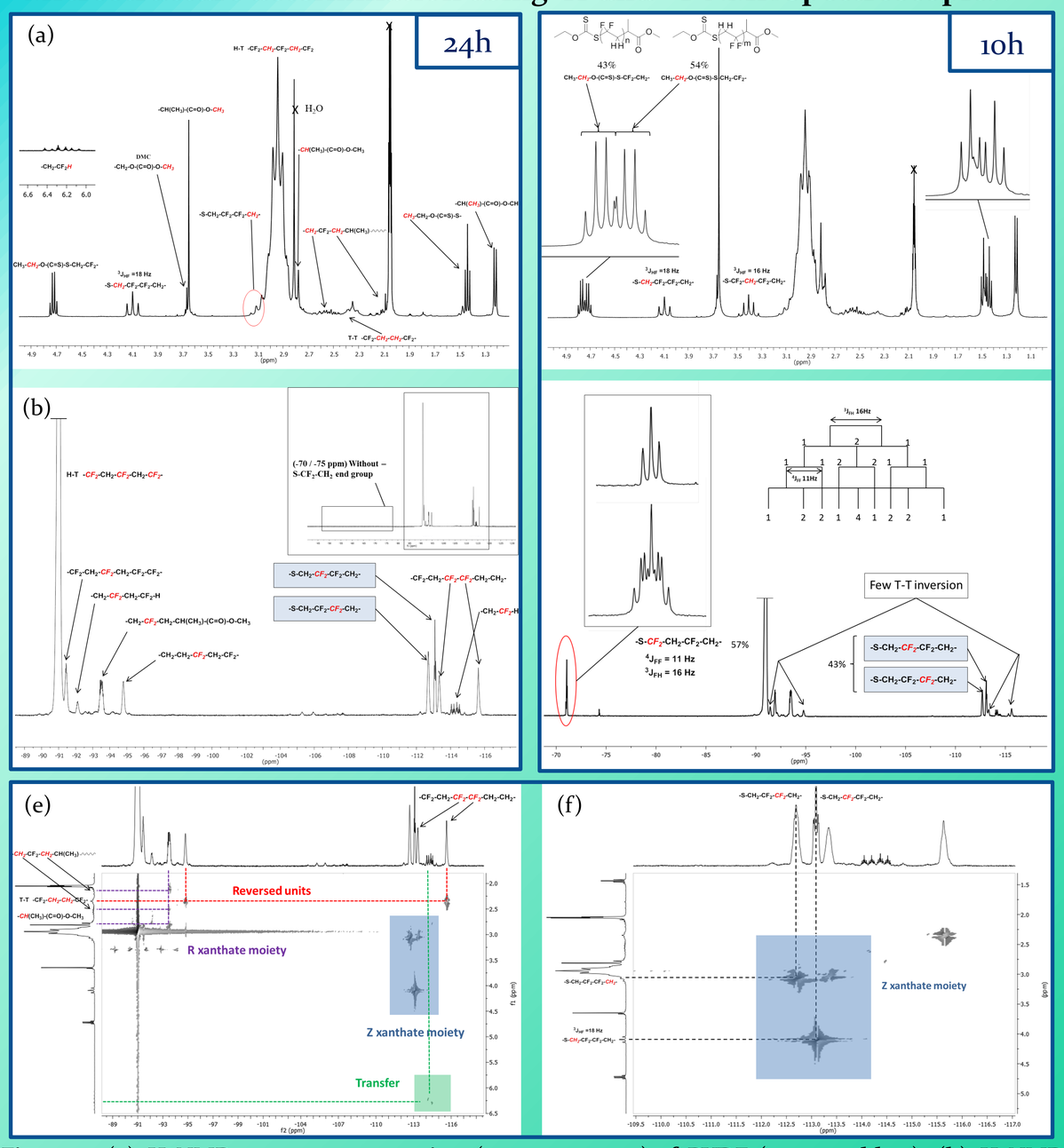


Figure 3. (a) ^{1}H NMR spectrum expansion (1.2 to 4.9 ppm) of PVDF (run 1, table 1). (b) ^{1}H NMR spectrum expansion (1.2 – 4.9 ppm) of PVDF (run 3, table 1). (c) ^{19}F NMR spectrum expansion (-89 to -128 ppm) spectrum of PVDF (run 1, table 1). (d) ^{19}F NMR spectrum expansion (-70 to -117) of PVDF (run 3, table 1). (e) HETCOR ^{1}H-^{19}F NMR spectrum of PVDF (run 1, table 1). (f) HETCOR ^{1}H-^{19}F NMR spectrum of PVDF (run 1, table 1) expanded around the Xanthate end-group signals.

Kinetics :

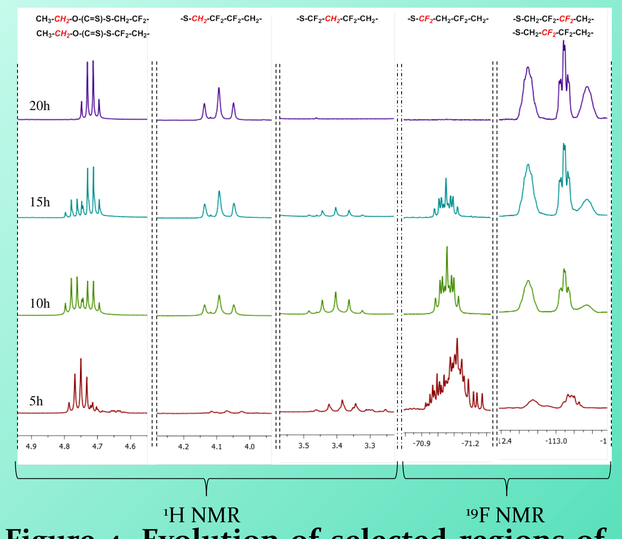


Figure 4. Evolution of selected regions of ^{1}H NMR and ^{19}F NMR spectra of MADIX polymerization of VDF versus time

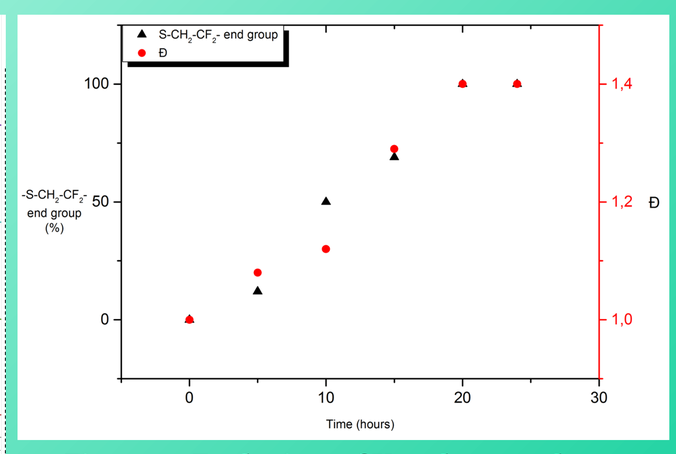
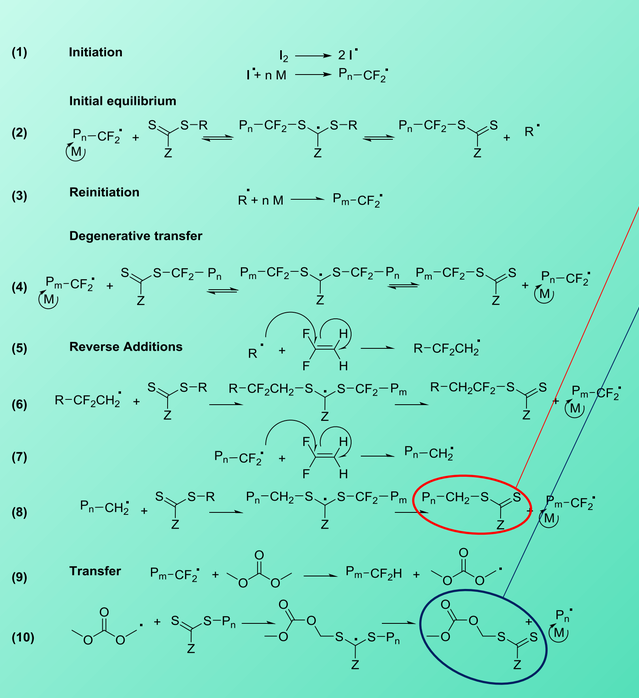


Figure 5. Evolution of Xanthate end-group and polydispersity index versus time

Mechanism of the MADIX of VDF:



Scheme 2. Detailed mechanism of the MADIX polymerization of VDF

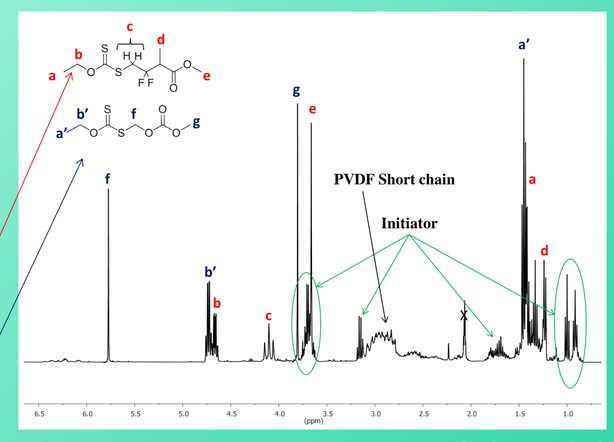


Figure 6. ^{1}H NMR spectrum of the soluble residue after precipitation of PVDF synthesized using MADIX (Run 1, Table 1)

- 10 % of Z end-group lost by transfer
  ⇒ *10% of deads chains*
- 31 % of Z- and R-group lost by radical attack of R· on the CF_2 carbon of VDF
  ⇒ *Higher Mn targeted*

Conclusion:

This work led to a deeper understanding of the reactions at work during the MADIX polymerization of VDF.
- Transfer reaction to DMC followed by irreversible transfer to the chain transfer agent (CTA) leads to a loss of xanthate group (ca. 10%).
- Head-to-head (HH) addition of one unit of VDF followed by irreversible transfer to the CTA leads to a loss of CTA (ca. 30%).
- HH addition of VDF in the course of polymerization followed by irreversible transfer to the CTA leads to accumulation of non reactive chains and this an increase of the PDI

References:

[1] G. David, C. Boyer, J. Tonnar, B. Ameduri, P. Lacroix Desmazes; B. Boutevin, *Chem Rev,* 2006, *106*, 3936–3981.
[2] E. Girard, J.D. Marty, B. Ameduri; M. Destarac, *ACS Macro Lett*, 2012, *1*, 270-274.
[3] A.D. Asandei, O.I. Adebolu; C.P. Simpson, *J Am Chem Soc,* 2012, *134*, 6080-6083.).