

SUPPORTING INFORMATION :

Synthesis and Characterization of Poly(vinylidene fluoride)-*b*- poly(styrene) Block Copolymers by Iodine Transfer Polymerization.

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ITP of VDF

ITP is a process involving an iodinated transfer agent (R-I), a monomer (styrene in this present case), and a radical initiator (e.g. AIBN), the ratio $[AIBN]/[R-I]$ being lower than unity. The initiating radicals, A^\bullet , are generated by thermal decomposition of a conventional initiator, such as AIBN, in step (1), (Scheme 1 in Supporting Information). Then, A^\bullet radicals can initiate the polymerization of monomer (such as styrene) as shown in step (2). The exchange of iodine from the transfer agent, R-I, to the propagating radical, P_n^\bullet , results in the formation of the polymeric alkyl iodide, P_n-I , and a new initiating radical, R^\bullet , as shown in step (4). The generated radical R^\bullet must be able to initiate the polymerization of the monomer (step (3)). Large differences in the stability of the reactants and products involved in step (4) could result in shifting the equilibrium overwhelmingly to the right or to the left. Therefore, the ideal case is when the structure of R^\bullet closely mimics the structure of the propagating radical, resulting in a thermodynamically neutral transfer step. The exchange process described in step (5) is thermodynamically neutral, because P_n^\bullet and P_m^\bullet propagating chains as well as P_n-I and P_m-I dormant chains have the same structure (which is commonly regarded for degenerative chain transfer). Both equilibriums (steps (4) and (5)) involving dormant and propagating species are crucial for the controlled/living behavior of the polymerization. As in any radical process, termination still occurs in ITP (step (6)), but the number of dead chains is kept low compared to the number of iodine-capped polymeric chains (living chains).

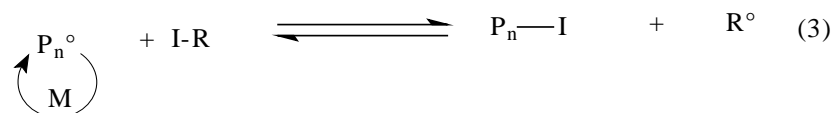
decomposition of initiator



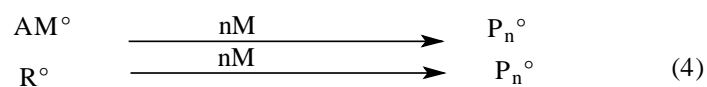
initiation :



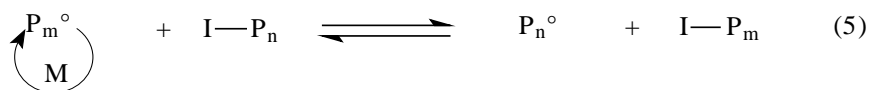
chain transfer :



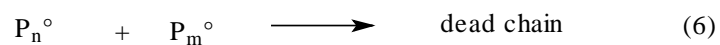
propagation :



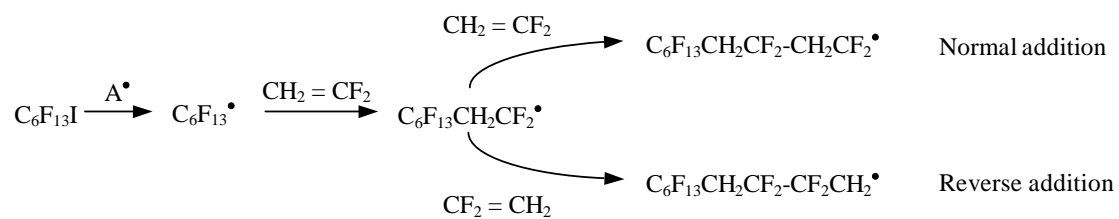
equilibrium between dormant and living species :



termination reaction



Scheme 1. Mechanism of iodine transfer polymerization of a M monomer in the presence of R-I and A₂ as chain transfer agent and initiator, respectively.



Scheme 2. Different reactions that occur in iodine transfer polymerization (ITP) of vinylidene fluoride (VDF).

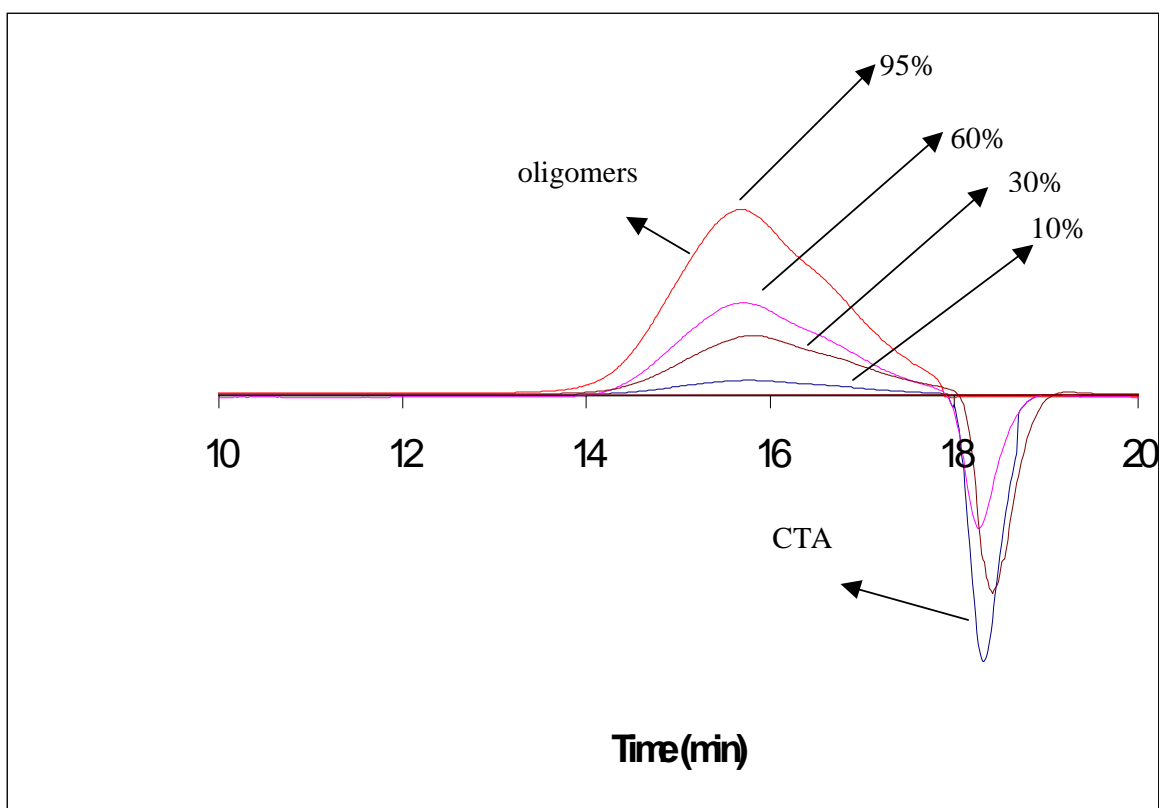


Figure 1. SEC chromatograms of oligomers obtained by Iodine Transfer Polymerization (ITP) of styrene in the presence of $C_6F_{13}CH_2CF_2I$, as the Chain Transfer Agent and Azobisisobutyronitrile (AIBN), as the initiator at 70 °C.

% represents the styrene conversions.

Experimental Conditions: $[Styrene]_0 : [C_6F_{13}-CH_2CF_2I]_0 : [Initiator]_0 = 100.00 : 2.50 : 0.25$ at 70 °C in acetonitrile.

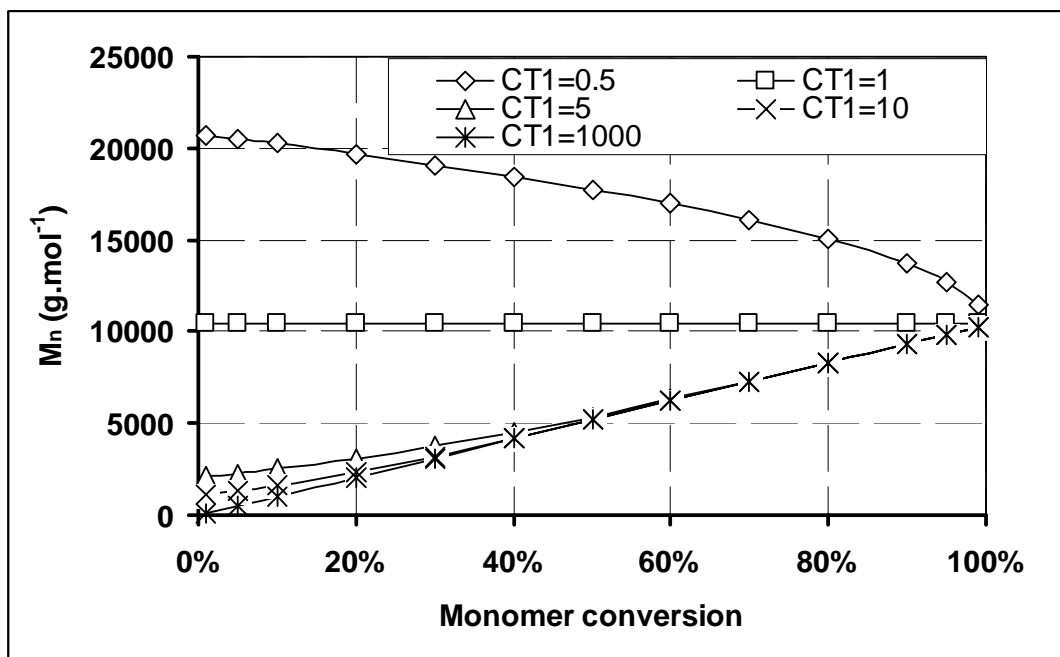


Figure 2. Evolution of molecular weight M_n *versus* the monomer conversion for different values of transfer constant, CT_1 , according to the equation $M_n = (p[M]_0 M_{\text{monomer}}) / ([CTA]_0 (1 - (1 - p)^{CT_1}))$ (conditions: $[M]_0/[CTA]_0 = 100$, $M_{\text{monomer}} = 104 \text{ g.mol}^{-1}$).

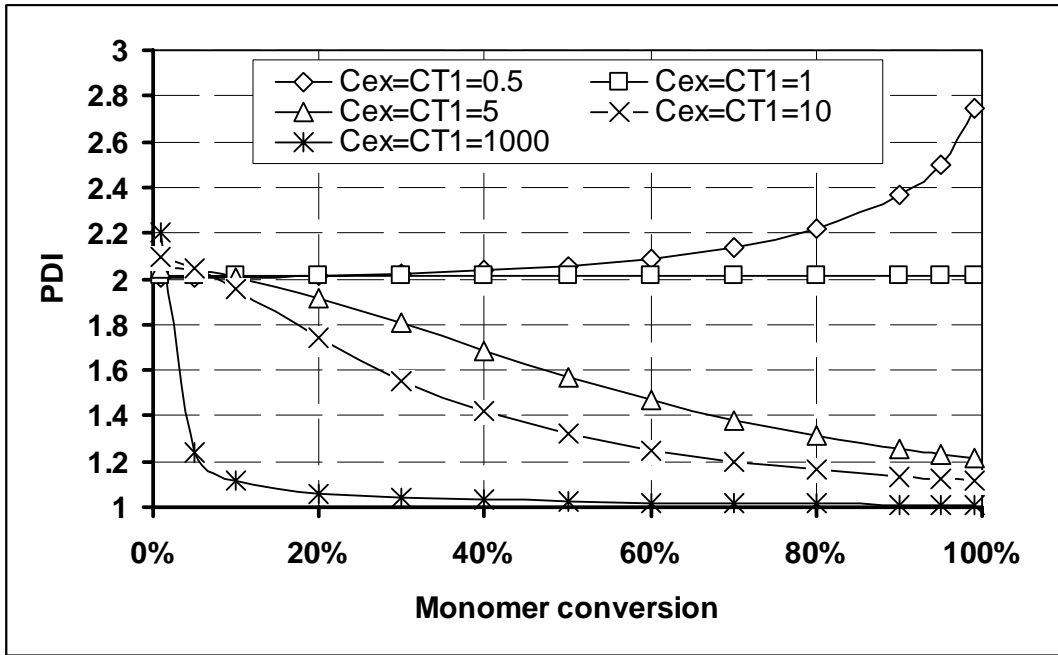


Figure 3. Evolution of polydispersity index (PDI) with monomer conversion for different values of degenerative transfer constant, C_{ex} , in the particular case where $C_{ex}=C_{T1}$, according to the equation $PDI=(1+([M]_0/[CTA]_0)(2+(2-p)(1-C_{ex})/C_{ex}))/((p[M]_0)/([CTA]_0(1-(1-p)^{C_{ex}})))$ (conditions: $[M]_0/[CTA]_0=100$).

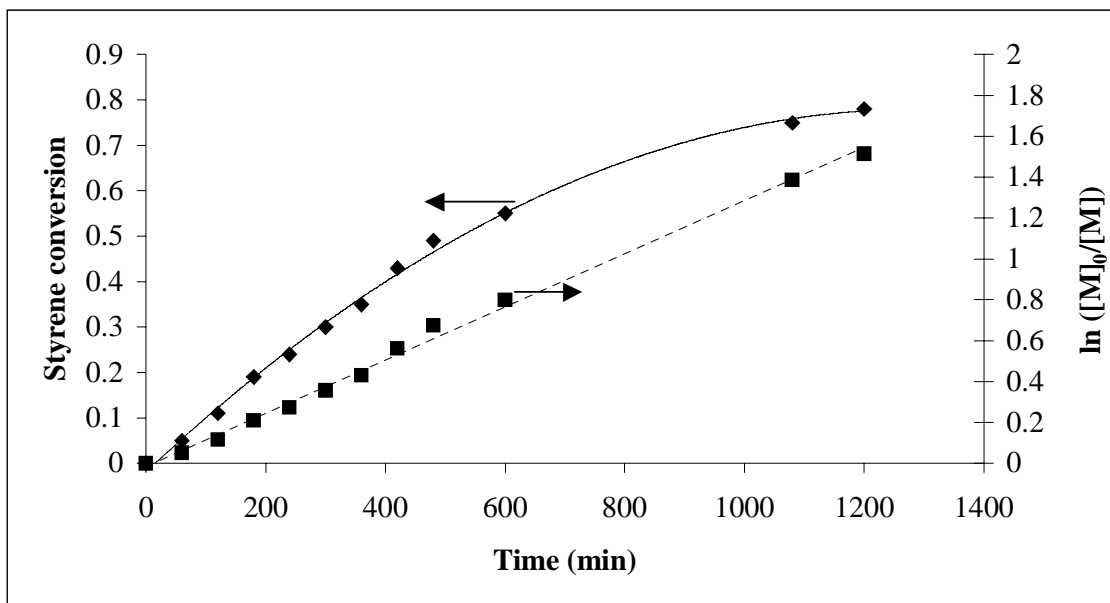


Figure 4. Styrene conversion and $\ln [M]_0 / [M]$ versus time for iodine transfer polymerization of styrene, initiated with azobisisobutyronitrile (AIBN) and in the presence of $C_6F_{13}-CH_2-CF_2-I$ as the chain transfer agent (CTA) performed at 70 °C.

Experimental Conditions: $[Styrene]_0:[C_6F_{13}-CH_2CF_2-I]_0:[Initiator]_0 = 100.00:2.50:0.25$ at 70 °C in acetonitrile.

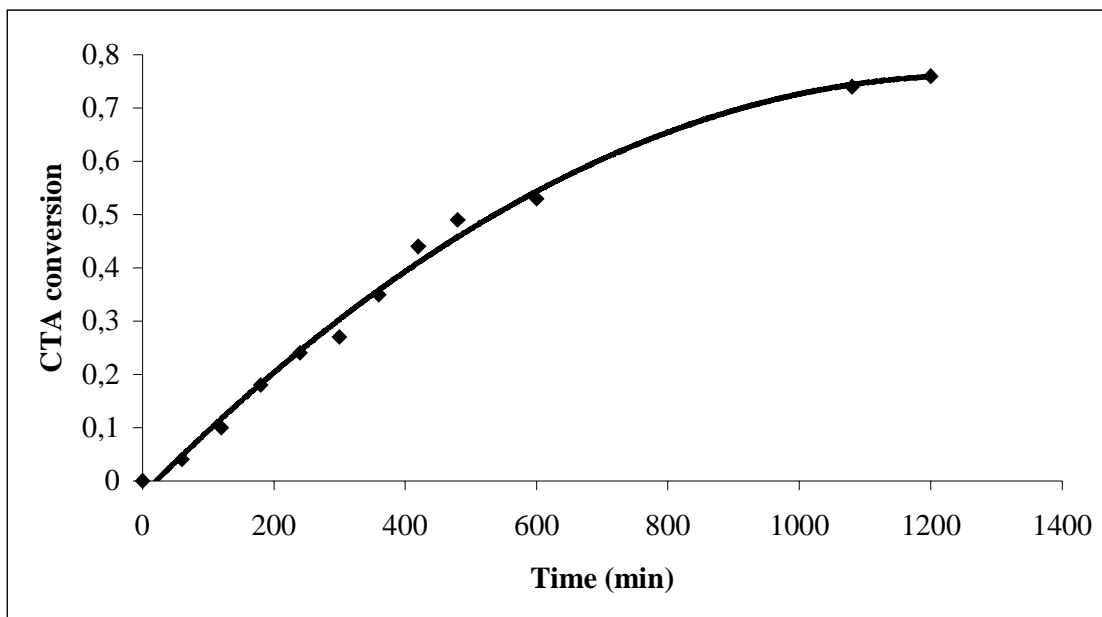


Figure 5. Evolution of the $\text{C}_6\text{F}_{13}\text{-CH}_2\text{CF}_2\text{I}$ (chain transfer agent, CTA) consumptions *versus* time for the iodine transfer polymerization (ITP) of styrene initiated by azobisisobutyronitrile (AIBN) at 70 °C.

Experimental Conditions: Iodine transfer polymerization (ITP) of styrene performed in the presence of $[\text{Styrene}]_0: [\text{C}_6\text{F}_{13}\text{-I}]_0: [\text{AIBN}]_0 = 100.00:2.50:0.25$ at 70 °C in acetonitrile.

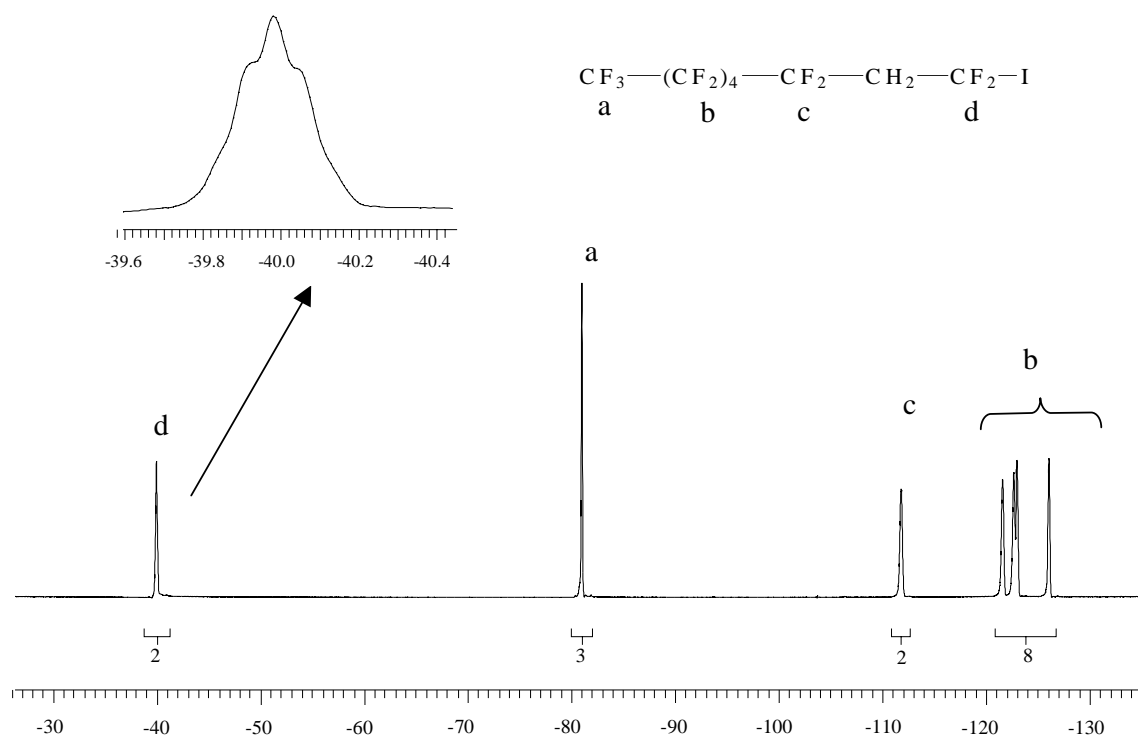


Figure 6. ^{19}F NMR spectrum of monoadduct $\text{C}_6\text{F}_{13}\text{---}(\text{CH}_2\text{CF}_2)_1\text{---I}$ (200 MHz, 298 K), recorded in CDCl_3 .

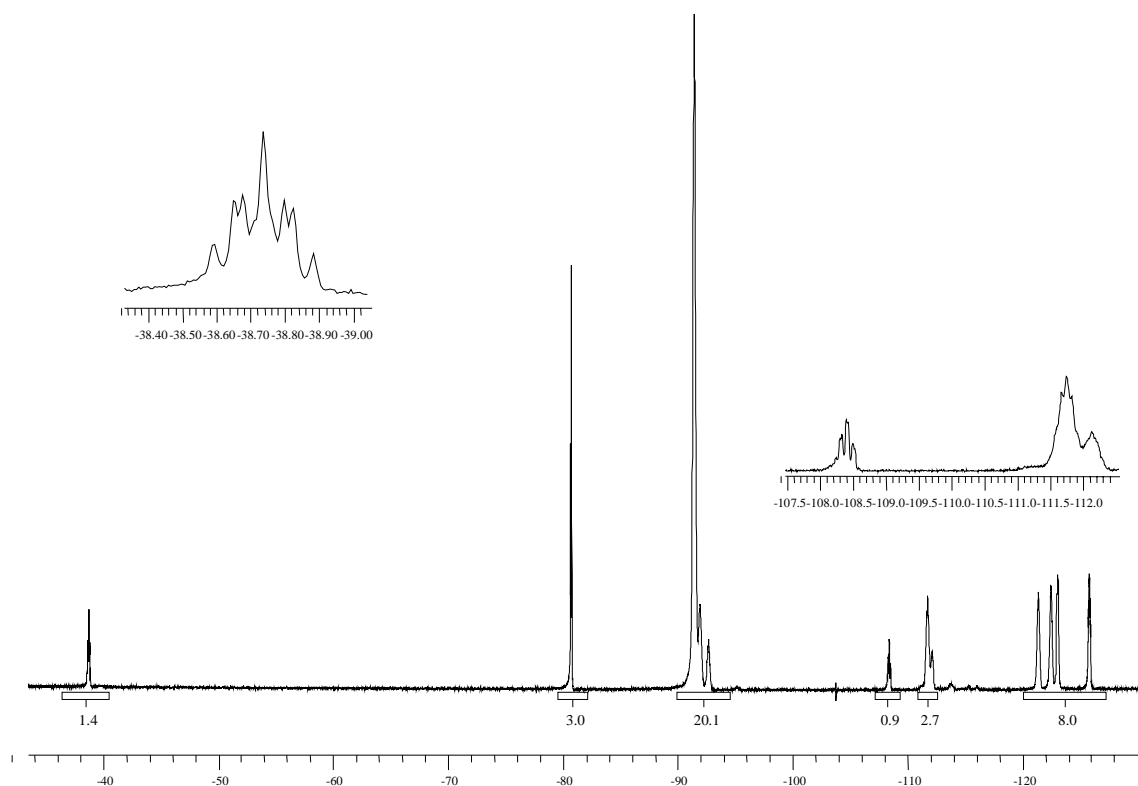


Figure 7. ^{19}F NMR spectrum of the poly(vinylidene fluoride)-I (recorded in deuterated acetone) (Average degree of polymerization ($\overline{\text{DP}}_n$) = 10) obtained by ITP of vinylidene fluoride (VDF) with $\text{C}_6\text{F}_{13}\text{I}$.

Experimental conditions of Iodine Transfer Polymerization of vinylidene fluoride with $\text{C}_6\text{F}_{13}\text{I}$ initiated by tert-butylperoxide pivalate at 75 °C in 1,1,1,3,3-pentafluorobutane : $[\text{VDF}]_0 : [\text{C}_6\text{F}_{13}\text{I}]_0 : [\text{Tert-butylperoxypivalate}]_0 = 100.0 : 10.0 : 0.6$ at 75 °C.

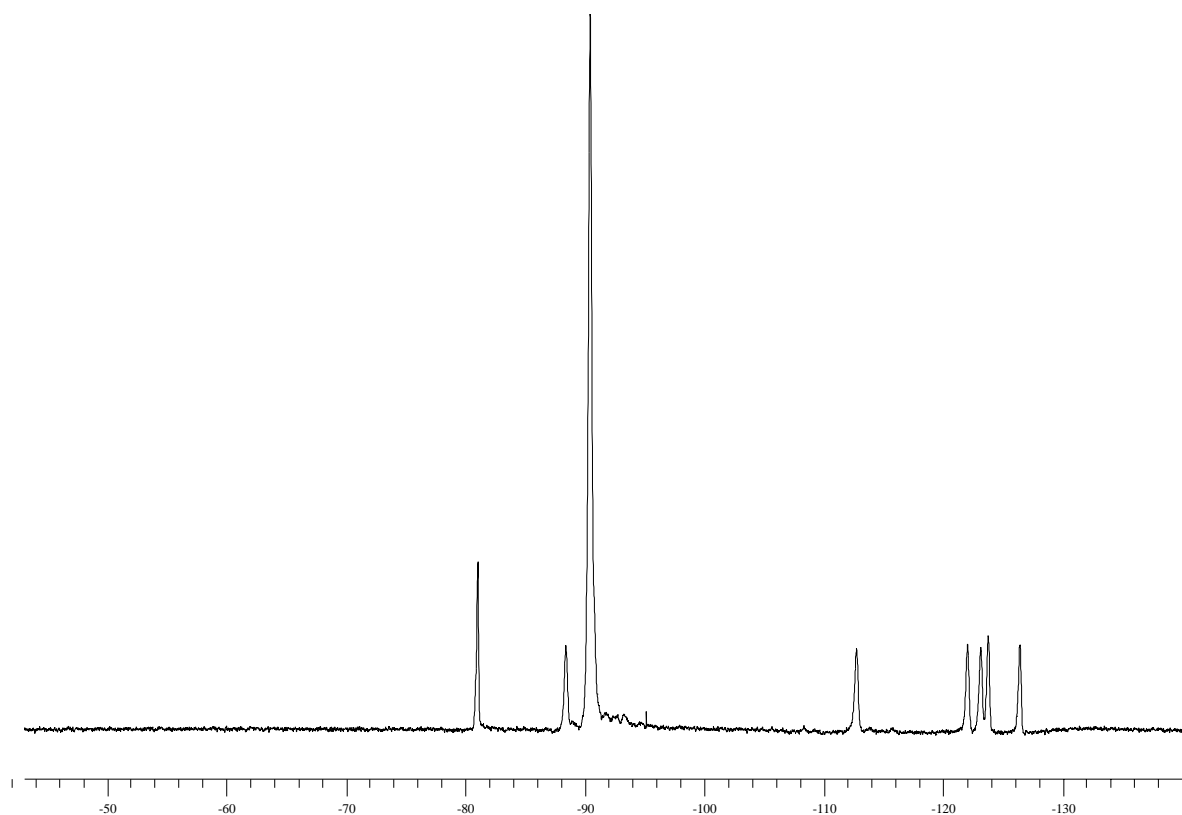


Figure 8. ^{19}F NMR spectrum of $\text{C}_6\text{F}_{13}-(\text{CH}_2-\text{CF}_2)_{10}-(\text{PS})_{60}\text{-I}$ block copolymers obtained by iodine transfer polymerization (ITP) of styrene with $\text{C}_6\text{F}_{13}-(\text{CH}_2-\text{CF}_2)_{10}\text{-I}$, as the macromolecular chain transfer agent (400 MHz, deuterated DMF).

Experimental Conditions: Iodine transfer polymerization (ITP) of styrene performed in the presence of macro Chain Transfer Agent at 70 °C in acetonitrile $[\text{Styrene}]_0:[\text{C}_6\text{F}_{13}-(\text{CH}_2-\text{CF}_2)_{10}\text{-I}]_0:[\text{AIBN}]_0 = 100.0:1.5:1.0$.

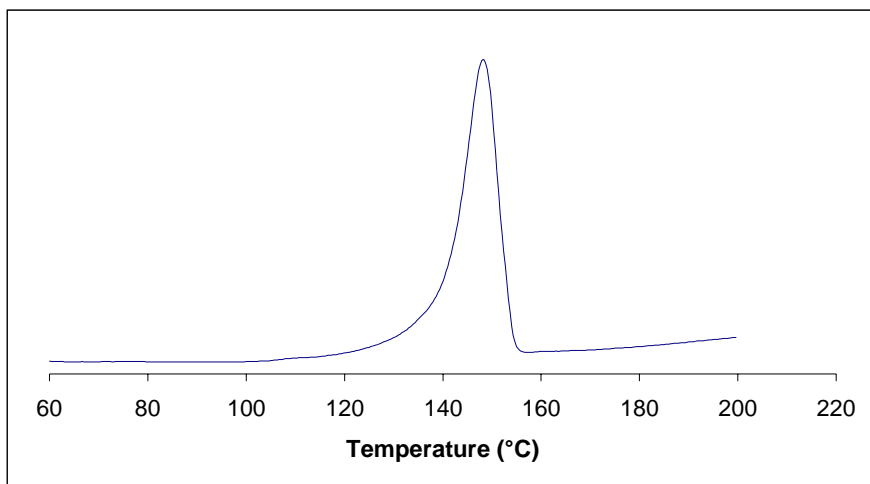


Figure 9. DSC Thermogram of $\text{C}_6\text{F}_{13}\text{-(VDF)}_{20}\text{-I}$.

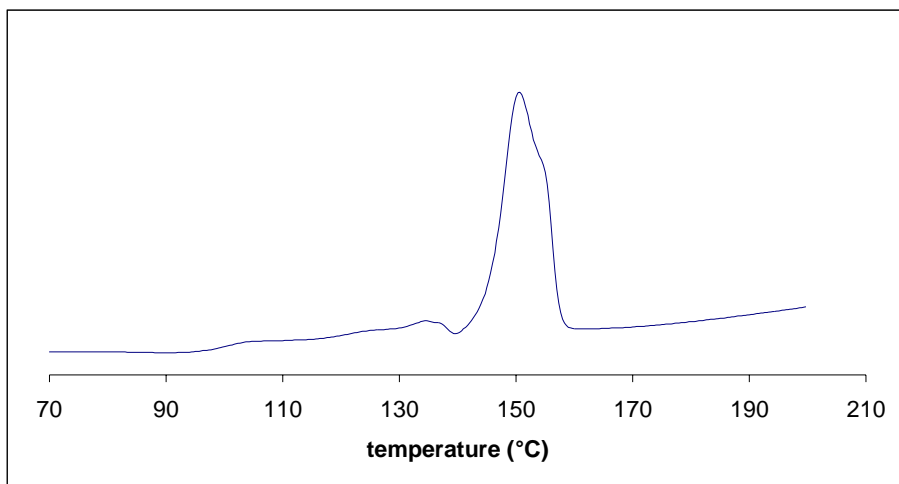


Figure 10. DSC Thermogram of $C_6F_{13}-(VDF)_{20}-(styrene)_{25}-I$ (copo1).

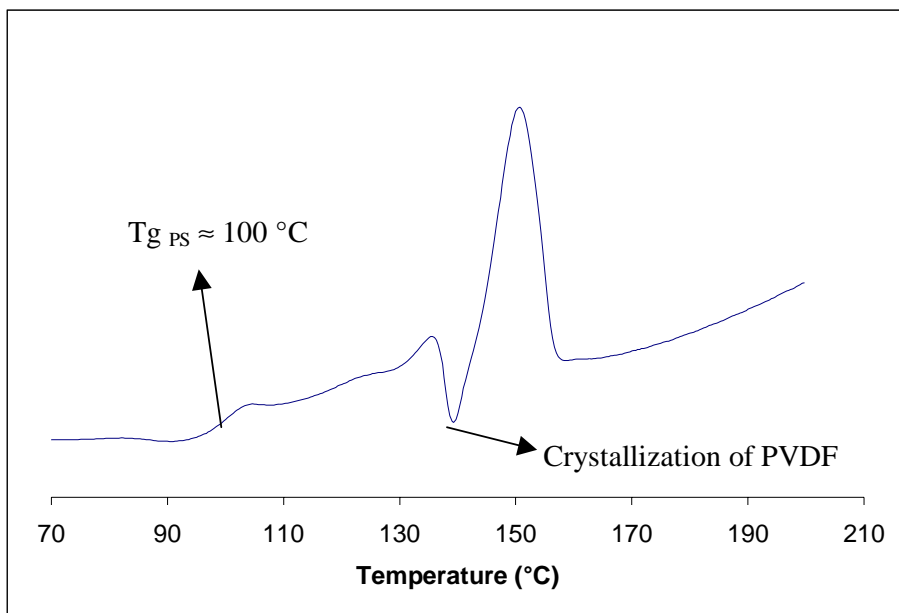


Figure 11. DSC thermogram of $C_6F_{13}-(VDF)_{20}-(styrene)_{65}-I$ (copo 2).

CTA [CTA] ₀ = 0.1M	Initiator [Ini] ₀ = 0.1M	Temp (°C)	Time (hrs)	Conv. (%)	Mn theo/found (g/mol)	PDI	Ref.
None	AIBN	70	6	86	65500	3.7	[1]
	BPO	80	3	97	40500	2.1	[1]
1-PEI	AIBN	70	16	94	6580/7810	1.5	[1]
	AIBN	50	39	92	6500/7830	1.4	[1]
	AIBN	90	2	52	3670/5840	1.5	[1]
	BPO	80	4	83	6570/7280	1.4	[1]
Iodomethane	BPO	80	3	93	7380/34500	2.1	[1]
Diiodomethane	BPO	80	5	91	7250/20140	2.0	[1]
Iodoform	BPO	80	5	80	6360/5120	1.4	[1]
Carbon tetraiodide	BPO	80	5	31	2480/390	1.0	[1]
<i>n</i> -propyl iodide	BPO	80	3	99	7420/34050	2.2	[1]
Isopropyl iodide	BPO	80	3	86	6460/33730	2.0	[1]
<i>Tert</i> -butyl iodide	BPO	80	4	57	4300/25540	2.0	[1]
Perfluorohexyl iodide	BPO	80	4	94	7440/11200	1.5	[2]
Iodobenzene	BPO	80	4	98	8260/29700	2.0	[1]
1,4-diiodobenzene	BPO	80	4	77	6050/33620	2.0	[1]
iodoacetonitrile	BPO	80	4	83	6550/5800	1.4	[1]

Table 1. Use of various alkyl iodides for the bulk polymerization of styrene ([Sty]₀=1M).

PDI, AIBN, BPO and 1-PEI stand for polydispersity index, azobisisobutyronitrile and dibenzoyl peroxide, 1-phenyl ethyl iodide, respectively.

Runs	M_n of PVDF block (g mol ⁻¹)	M_n of PS block (g mol ⁻¹)	T_m (°C)	Enthalpy (J g ⁻¹)	T_g (°C)
21	1,020	-	150	66	-
22	1,020	2,500	149	58	90
23	1,020	3,300	149	30	92
24	1,020	5,100	147	25	94
25	1,020	6,900	145	13	94

Table 2. Summary of the thermal properties of PVDF-b-PS block copolymers.

References:

1. Gaynor, S.G.; Wang J.-S.; Matyjaszewski K. *Macromolecules* **1995**, 28, 8051-8056.
2. Lansalot, M.; Farcet, C.; Charleux, B.; Vairon J.-P.; Pirri R. *Macromolecules* **1999**, 32, 7354-7360