

Polymer Communication

Synthesis of fluorine-containing block copolymers via ATRP 1. Synthesis and characterization of PSt-PVDF-PSt triblock copolymers

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Abstract

A technique is described for the synthesis of polystyrene-*block*-poly(vinylidene fluoride)-*block*-polystyrene (St-VDF-St) triblock copolymers through a poly(vinylidene fluoride) macroinitiator. The bromine terminated poly(vinylidene fluoride), which was prepared by radical telomerization of vinylidene fluoride with 1,2-dibromotetrafluoroethane, initiated polymerization of styrene in presence of copper(I) bromide and α,α' -bispyridine complexes. It was found that molecular weights increased linearly in styrene conversion and polydispersities were low. The macroinitiator and block copolymers were characterized by g.p.c. and n.m.r. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinylidene fluoride); Styrene; Block copolymer

1. Introduction

During the last decade, poly(vinylidene fluoride) (PVDF) has received much attention because of its extraordinary piezoelectricity, pyroelectricity, processability, and wide practical uses. Physical modification of polymers by blending PVDF with polymethacrylates have also attracted a considerable academic and industrial interest [1]. However, few researchers have reported on the blends of PVDF and polystyrene (PSt). The main reason is that it is not easy to find good compatibilizers. It is well known that the addition of properly designed block or graft copolymers to immiscible polymer blends is an efficient way to improve the phase dispersion, to stabilize the phase morphology, and to improve the interfacial adhesion [2–5]. Unfortunately, it is rather difficult to prepare these well-defined copolymers.

Recently, atom transfer radical polymerization (ATRP), which uses simple alkyl halides as initiators, copper(I)/bispyridine as catalysts, has been successfully used to prepare functional polymers, such as block, graft copolymers etc. [6,7]. This paper reports the synthesis of PSt-PVDF-PSt triblock copolymers by synthesizing a macroinitiator based on PVDF oligomer and subsequent copolymerization with styrene.

2. Experimental

2.1. Materials

Styrene was washed with 5% NaOH and ion-free water, dried over CaCl₂ overnight, and then vacuum distilled from finely powdered CaH₂ before use. CuBr (AR, Shanghai No.1 Chemical Reagent Factory) was purified according to the procedure of Keller and Wycoff [8]. Butyl acetate (BAc) (AR, Shanghai No.1 Chemical Reagent Factory) was washed with saturated Na₂CO₃ and NaCl, respectively, dried over anhydrous MgSO₄ for 24 h, and distilled and purged with nitrogen for 30 min before use. α,α' -Bispyridine (bpy) (AR, Shanghai No. 1 Chemical Reagent Factory) was recrystallized from *n*-hexane. Vinylidene fluoride (VDF), 1,2-dibromotetrafluoroethane (DBTFE) and di-*tert*-butylperoxide (DTBP) were kindly supplied from Shanghai Institute of Organo-fluorine Materials, and used as received.

2.2. Synthesis of macroinitiator bromine-terminated PVDF oligomer

A typical reaction has been carried out in a 25 l stainless steel autoclave under following conditions: DBTFE 2.3 l, DTBP 70 ml, temperature 140°C, reaction time 4.5 h, the pressure of VDF was maintained at 20 kg/cm² during the polymerization process. The product was dissolved in

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acetone and precipitated into *n*-hexane, and then dried in vacuum at 40°C for 24 h. The macroinitiator has been characterized by ¹H n.m.r. using a 400 MHz Bruker instrument. Its molecular weight has been given by vapour pressure osmometry (VPO) and g.p.c., and calculated from n.m.r. and elemental analysis (EA).

2.3. Synthesis of PSt-PVDF-PSt triblock copolymers

Polymerizations were carried out in a three-neck flask equipped with a reflux condenser and a magnetic stir bar. All reagents were added to the reaction flask under nitrogen atmosphere and a positive nitrogen pressure was maintained throughout the reaction. In order to determine the molecular weight and conversion, samples were withdrawn at time intervals and g.p.c. (equipped with Waters 150C, linear 100 Å, 10 000 Å polystyrene standard columns) and GC (102G, Shanghai Anal. Inst. Co.) were performed. The final copolymer was precipitated into methanol and purified by precipitation from tetrahydrofuran solution into methanol. After drying in a vacuum for 48 h, it was characterized by ¹⁹F and ¹H n.m.r. using Bruker instruments.

3. Results and discussion

Transition metal-catalysed atom transfer radical addition (ATRA) is an efficient method for carbon–carbon bond formation in organic synthesis [9]. Atom transfer radical polymerization (ATRP) is a novel concept which is based on the ATRA. As early as 1969, Burton and his coworkers

Table 1
Molecular weight and polydispersity of the bromine-terminated PVDF oligomer

Sample	M_n	M_w/M_n	Measurement method
Br-PVDF-Br	3870	1.1	g.p.c.
	2304	—	n.m.r.
	2195	—	VPO
	2240	—	EA ^a

^a Bromine content percent, 7.135%

studied copper(I) chloride-ethanolamine catalysed addition of polyhaloalkanes to 1-octene [10]; they discovered that while CH₂Br₂ gave no addition, CF₂Br-CF₂Br formed the desired adduct in a 77% yield (57% conversion), an indication of the ability of the fluorine atoms to activate the bromine atom toward radical attack (bromine-atom abstraction). On the other hand, C₂F₄Br₂ is known to be an excellent telogen for the radical telomerization of fluorinated olefin, and the corresponding telomeric molecules have quantitative functionality [11]. These facts prompted us to synthesize bromine-terminated PVDF as the macroinitiator for the triblock copolymer of PSt-PVDF-PSt.

3.1. Synthesis and characterization of bromine-terminated PVDF

Bromine-terminated PVDF was prepared by radical telomerization, using di-*tert*-butylperoxide as an initiator, and 1,2-dibromotetrafluoroethane as a telogen. Fig. 1 shows ¹H n.m.r. spectrum for the bromine-terminated PVDF

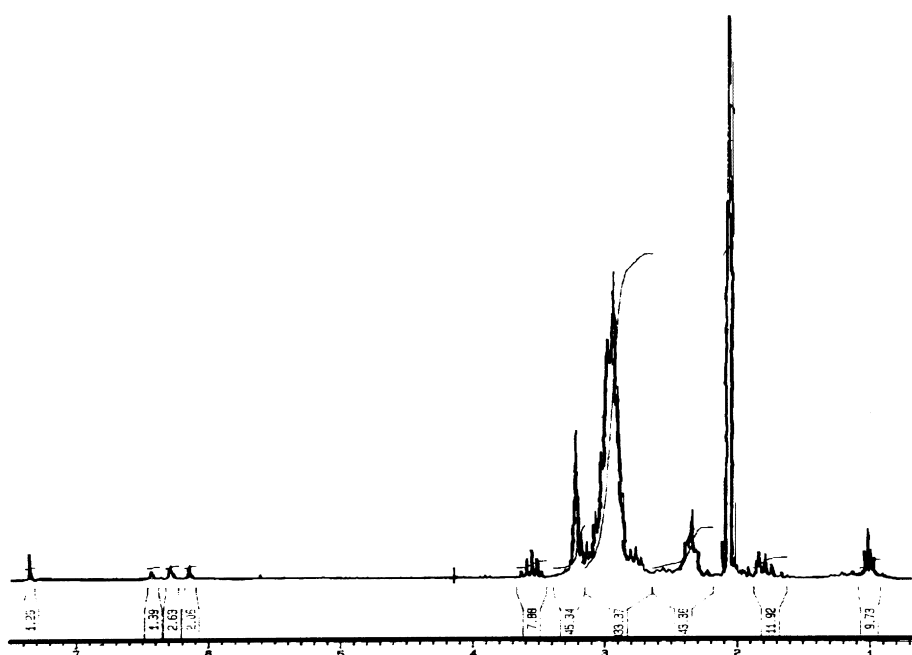
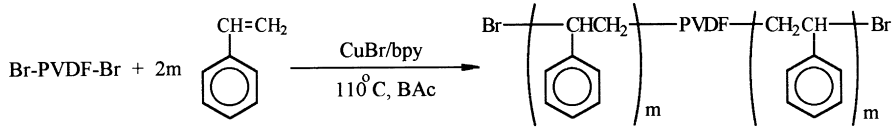


Fig. 1. 400 MHz ¹H n.m.r. spectrum of the difunctional PDVF macroinitiator (d₆-acetone solvent).



Scheme 1. Synthesis of PSt-PVDF-PSt triblock copolymers.

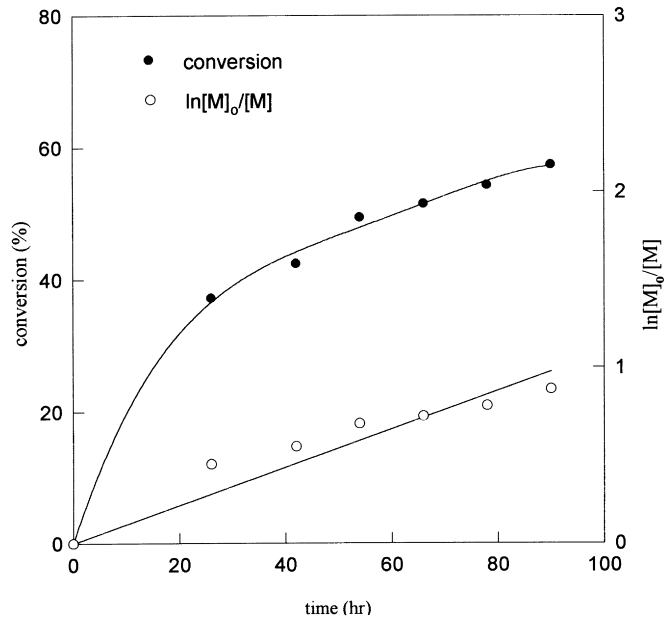


Fig. 2. Kinetic plot for the ATRP of styrene in butyl acetate using difunctional PVDF as macroinitiator. $[\text{St}]_0 = 6.25 \text{ M}$, $[\text{Br-PVDF-Br}]_0 = 1.85 \times 10^{-2} \text{ M}$, $[\text{CuBr}]_0 = 0.15 \text{ M}$, $[\text{bpy}]_0 = 0.45 \text{ M}$, temp. = 110°C .

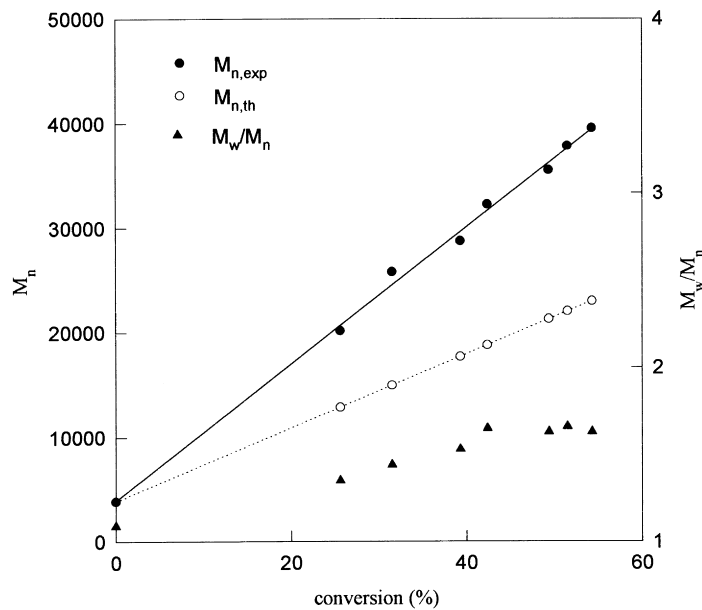


Fig. 3. M_n and polydispersity dependence on conversion for the ATRP for styrene with difunctional PVDF macroinitiator.

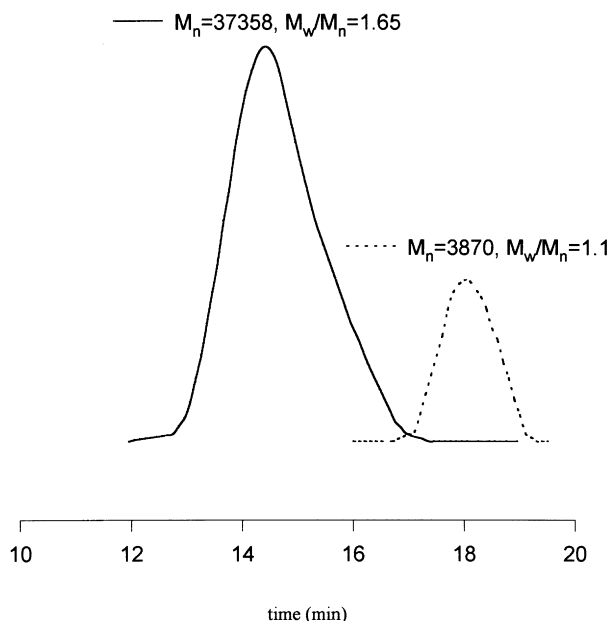


Fig. 4. G.p.c. traces of the difunctional PVDF macroinitiator (---) and the produced polymer (—) after 90 h.

oligomer. The peaks (δ , 3.0~3.5 ppm) are associated with the normal head-to-tail (h-t) structures, $-\text{CF}_2-\text{CH}_2^*-\text{CF}_2-$, or $-\text{CF}_2-\text{CH}_2^*-\text{CF}_2\text{Br}$. The signals (δ , 2.4 ppm) correspond to the $-\text{CH}_2^*$ resonances in the head-to-head (h-h) or tail-to-tail (t-t) structures, $-\text{CH}_2^*\text{CH}_2^*\text{CF}_2$ or $-\text{CH}_2^*\text{CH}_2^*\text{CF}_2\text{Br}$. The peaks (δ , 1.77 and 6.28 ppm) can be assigned to $-\text{CH}_3^*$ and CF_2H^* groups, respectively, which have a relatively small contribution. Molecular weight of the oligomer was estimated from EA, n.m.r., VPO and g.p.c. The various methods gave comparable

results listed in Table 1. Bromine end-group elemental analysis reveals that the functionality of the oligomer is very close to 2.

3.2. Synthesis and characterization of triblock copolymer

By using the bromine-terminated PVDF as the macroinitiator for the atom transfer radical copolymerization of styrene, PSt-PVDF-PSt triblock copolymer could be obtained (Scheme 1).

The kinetic plot of the copolymerization is shown in Fig. 2. The linear semilogarithmic plot of $\ln([M]_0/[M])$ versus time indicates that polymerization is nearly first-order with respect to monomer and that the concentration of active centres remains almost constant throughout the copolymerization. As shown in Fig. 3, the number-average molecular weight (M_n) increases gradually with monomer conversion, the polydispersity increases slightly at initial stage (<40% conversion) and then remains nearly constant. However, some deviation of the $M_{n,\text{exp}}$ (from g.p.c. calibrated using PSt standards) from the $M_{n,\text{th}}$ (calculated from $M_{n,\text{th}} = ([M]_0/[I]) \times M_{\text{St}} \times \text{conv.} + M_1$) was observed. It might be owing to instrument deviation for fluorine-containing polymer.

Fig. 4 displays the g.p.c. trace of the copolymer. It shows no additional peak, confirming that triblock copolymer has been formed. ^1H and ^{19}F n.m.r. spectra of the copolymer (Figs 5 and 6) further verify that the copolymer has PVDF segments. Moreover, the triblock copolymer composition can be calculated from the peak area of ^1H n.m.r. spectrum. The molar ratio of VDF and styrene units in the copolymer is 14.3:85.7.

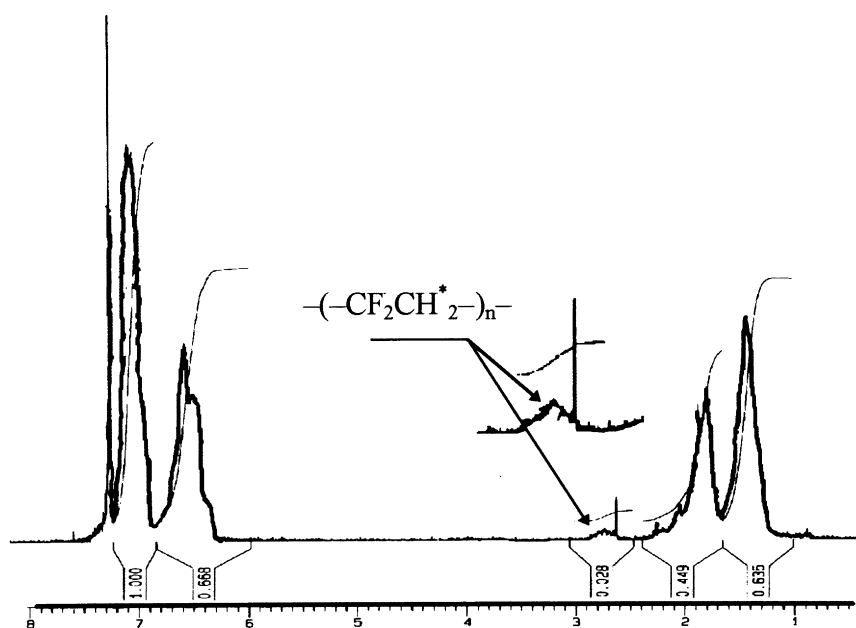


Fig. 5. 300 MHz ^1H n.m.r. spectrum of PSt-PVDF-PSt block copolymer prepared by ATRP (CDCl_3).

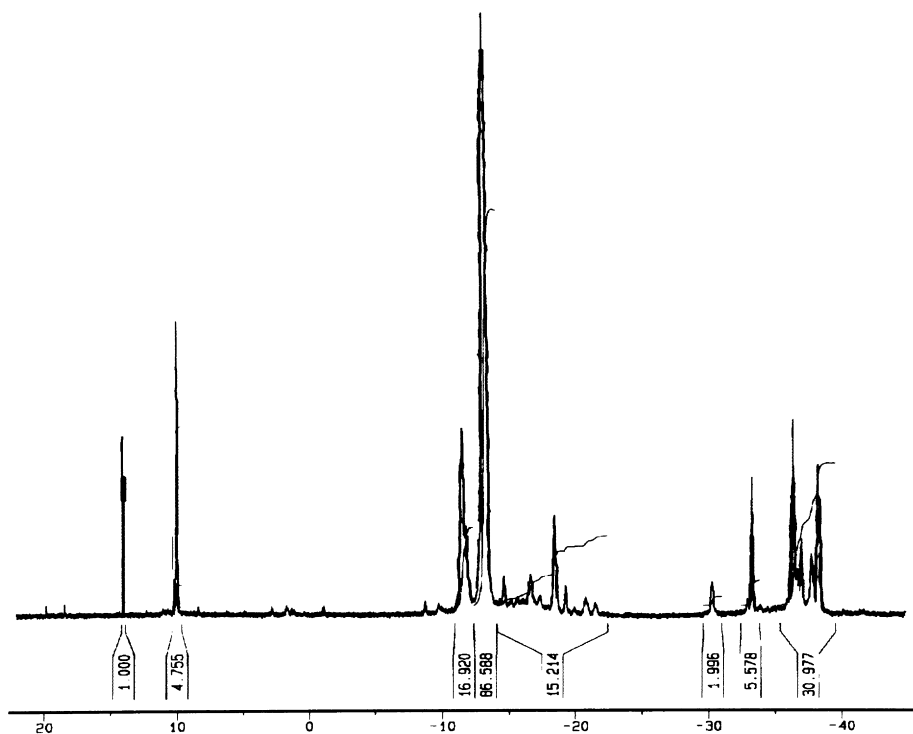


Fig. 6. 376.4 MHz ^{19}F n.m.r. spectrum of PSt-PVDF-PSt block copolymer prepared by ATRP in CDCl_3 (CF_3COOH as external standard).

4. Conclusion

PSt-PVDF-PSt triblock copolymers were successfully synthesized by ATRP technique. Investigation of a kinetics plot of copolymerization using the bromine-terminated PVDF telomer as a macroinitiator showed a linear increase in styrene conversion and molecular weight during copolymerization, indicating a 'living' polymerization mechanism. Other novel block copolymers appeared to be promising for using as compatibilizers for hydrocarbon-fluorocarbon polymer blends and are currently being studied and will be reported in the near future.

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