Journal of Fluorine Chemistry 132 (2011) 956–960

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Fluorinated styrene-based monomers for cyclopolymerizations

Arvind K. Sharma [a,1], Dario Pasini [a,b,1,*]

[a] Department of Chemistry, University of Pavia, Via Taramelli, 10 – 27100 Pavia, Italy
[b] INSTM Research Unit, University of Pavia, Via Taramelli, 10 – 27100 Pavia, Italy

ARTICLE INFO

Article history:
Received 27 April 2011
Received in revised form 19 July 2011
Accepted 19 July 2011
Available online 26 July 2011

Keywords:
Tetrafluorobenzene derivatives
Fluorinated monomers
Fluorinated polymers
Cyclopolymerization

ABSTRACT

The synthesis of versatile fluorine compounds and monomers for conducting polymer research and cyclopolymerizations is presented. Semiprotected 2,3,5,6-tetrafluoroterephthaldehyde **1** could be elaborated through Wittig olefination chemistry, deprotection and reduction to the previously unknown 4-vinyl-2,3,5,6-tetrafluorobenzylalcohol **8** in good yields. Compound **8** can be reacted to form the malonate ester, and then alkylation on the malonate moiety in mild conditions affords difunctional monomer **3**. Through sequential esterifications on the malonate moiety, and subsequent alkylation, compound **4**, a difunctional monomer for cyclopolymerization bearing one styrene and one perfluoroaryl styrene moiety, has been obtained. Preliminary experiments show that it is possible to cyclopolymerize **4** under free radical conditions.

1. Introduction

The control of monomer sequences in synthetic functional polymers is an underdeveloped area of research [1]. This level of control is instead ordinarily achieved in natural biopolymers. In cyclopolymerization processes, two things can be performed at the same time: make polymers efficiently and generate cyclic structures in the polymer backbone, addressing polymer rigidity and stereocontrol [2]. In addition, alternation of monomeric fragments possessing different chemical structures and reactivities towards the propagating free radicals can be achieved during cyclopolymerizations [2d,3]. Polystyrene-like cyclopolymers have to be designed carefully, since both cyclization into large ring repeating units and propagation need to be obtained. Following early work of Wulff [4] and Kakuchi [5], we (monomer **1** in Fig. 1) and others, have demonstrated how, in diluted conditions, difunctional styrenic monomers can efficiently generate homo-cyclopolymers (polymer **2** in Fig. 1) [6,7].

Fluorinated polymers are materials that have attracted significant attention due to a series of favourable properties, such as high thermal stability, hydrophobicity, and good chemical resistance. To the best of our knowledge, only a few aryl fluorinated styrene monomers have been reported, and used in free radical polymerizations. 2,3,4,5,6-Pentafluorostyrene has previously been polymerized through radical polymerization, or copolymerized with styrene; using controlled ATRP polymerizations, block copolymers have also been synthesized [8]. Reports using 4-substituted-2,3,4,5-tetrafluorostyrene derivatives are instead less frequent [9].

Given the different reactivity of aryl perfluorinated styrenes (such as 2,3,4,5,6-pentafluorostyrene) *vs.* styrene in free radical polymerizations [10], we were eager to explore the synthesis and characterization of difunctional monomers such as **3** and **4** (Fig. 1), in order to evaluate their reactivity in cyclopolymerizations, and the potential of monomer **4** for the formation of macromolecules with alternating nonfluorinated/perfluorinated aryl moieties within the rigid polymer backbone.

In this paper, we report the synthesis and the characterization of novel key aryl fluorinated styrene derivatives, their further manipulation for the synthesis of monomers **3** and **4**, and preliminary data for their cyclopolymerization under free radical conditions.

2. Results and discussion

Following our previous work [6b], the insertion of styrene derivatives into the malonate skeleton was approached via the esterification of malonyl chloride with suitably modified 4-vinyl perfluorinated benzyl alcohols. We have shown that dialkylated malonate moieties, in fact, can "orient" the two styrene fragments in **1**, and therefore facilitate cyclization during propagation. 4-Vinyl-2,3,5,6-tetrafluorobenzylalcohol **8** was previously reported, to the best of our knowledge, only in a patent, where its synthesis was not described [11]. Our approach for its synthesis was to develop Wittig olefination chemistry on the monoprotected derivative **5** (Scheme 1) [12]; we had successfully reproduced in

* Corresponding author at: Department of Chemistry, University of Pavia, Via Taramelli, 10 – 27100 Pavia, Italy. Tel.: +39 0382 987835; fax: +39 0382 987323.
E-mail address: dario.pasini@unipv.it (D. Pasini).
[1] Group website: www.unipv.it/labt.

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.07.021

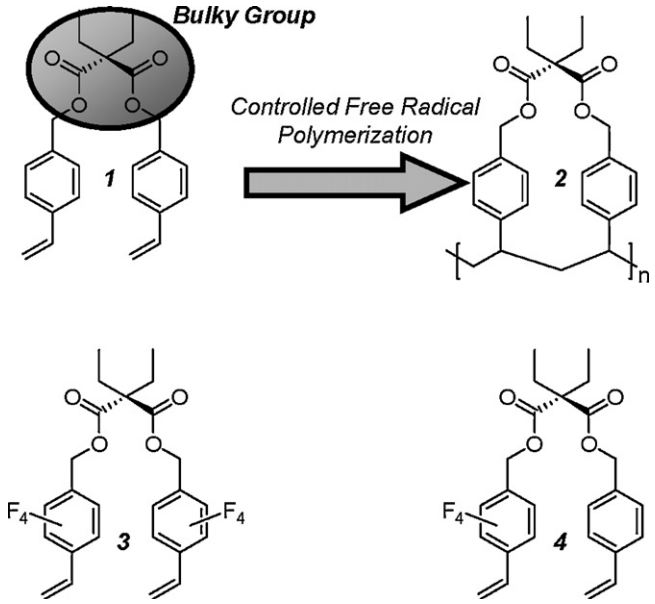
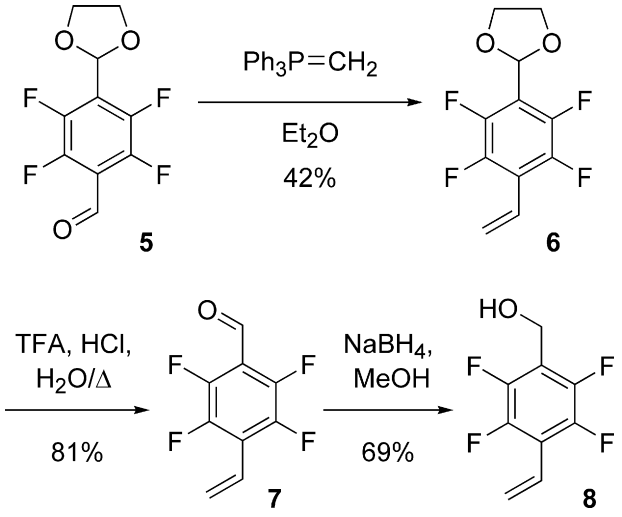


Fig. 1. Difunctional monomers undergoing efficient cyclopolymerization under free radical conditions.



Scheme 1. Synthesis of 4-vinyl-2,3,5,6-tetrafluorobenzylalcohol **8**.

our laboratories the synthesis of **5** in multigram quantities, in the process of making symmetrically 1,4-functionalized-2,3,5,6-tetrafluorobenzene derivatives [13]. Compound **6** was obtained in reasonable yields after purification by column chromatography, and deprotected (TFA, H_2O, HCl) to give compound **7**. The deprotection reaction was conducted following a reported protocol for compound **5** [12], and had to be monitored by ^1H NMR; compound **7** was used in the following step without further purification. Reduction with $NaBH_4$ in classical conditions afforded the key benzylic alcohol **8** (Scheme 1).

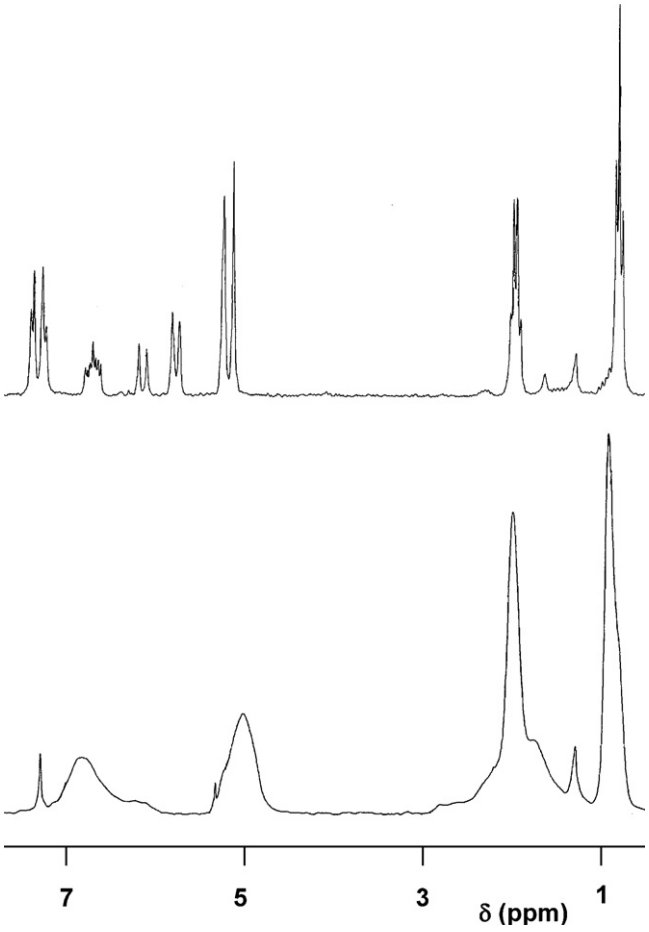


Fig. 2. ^1H NMR spectra of monomer 4 (top) and polymer 13 (bottom) after purification.

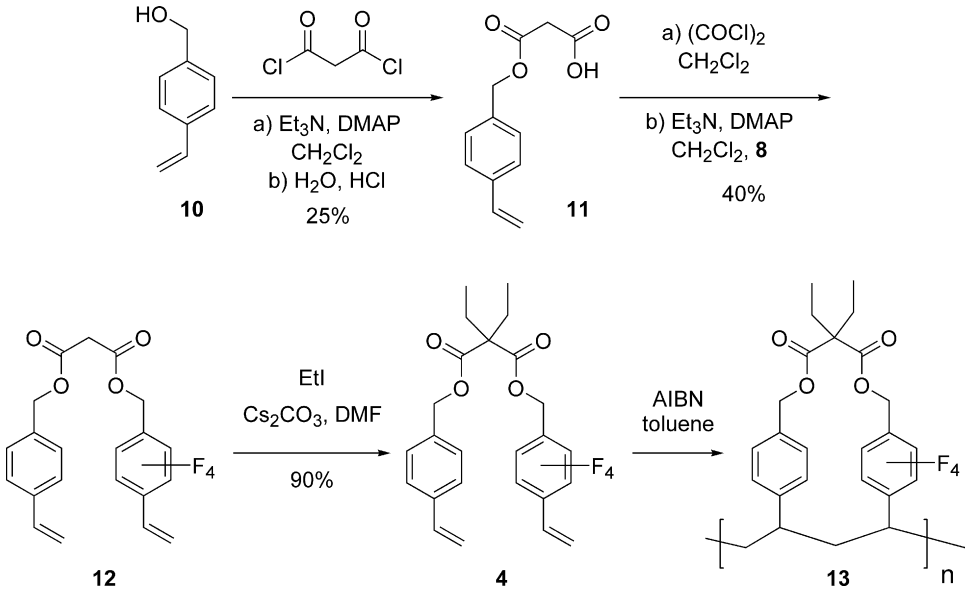
Esterification of **8** using malonyl chloride, following conditions developed for the synthesis of monomer **1**, gave malonate ester **9** in moderate yields, after purification by column chromatography. Its subsequent alkylation gave monomer **3** in 72% yields (Scheme 2). All novel compounds were characterized by NMR (^1H and ^{13}C), and elemental analysis.

A statistical approach for the synthesis of monomer **4** (that is, the reaction of malonyl chloride with one equivalent each of 4-vinylbenzyl chloride **10** and the fluorinated analogue **8**) did not yield the target compound in reasonable yield. The synthesis of **4**,

Table 1
Cyclopolymerization of monomers **1**, **3** and **4** under free radical conditions.

Entry[a]	Monomer	[M]/[%AIBN][b]	M_n[c]	PDI[c]	DP[d]	Yield%[e]	Polymer
1[f]	**1**	0.2/5	6980	2.0	18	60	**2**
2[g]	**3**	0.2/5	–	–	–	–	–
3	**4**	0.2/5	14920	2.8	32	30	**13**

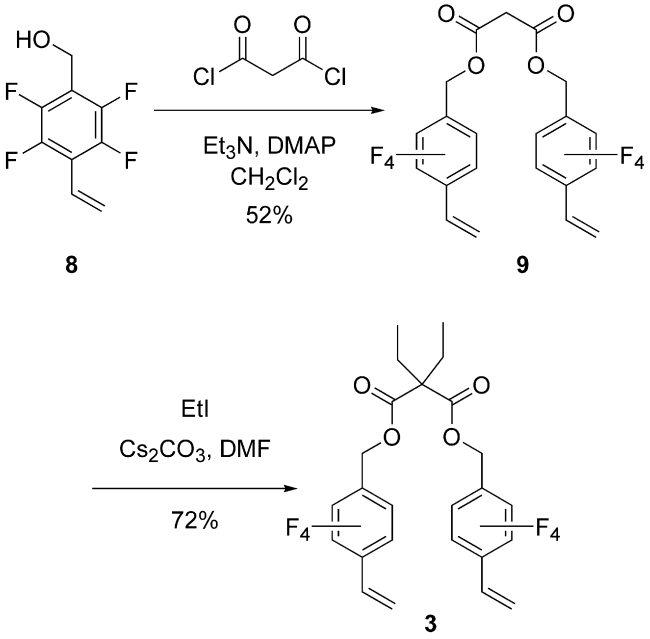
[a] Polymerizations were run at 70 °C in toluene for 48 h (entry 1) or 90 °C in toluene for 60 h (entry 2 and 3).
[b] [M] refers to the monomer concentration in toluene, and [%AIBN] is the molar percentage of initiator with respect to monomer.
[c] As determined by GPC relative to polystyrene standards. PDI = polydispersity index.
[d] Degree of polymerization; calculated on the basis of M_n.
[e] Yield determined on the basis of the molecular weight of monomer after purification by filtration of eventual crosslinked material and precipitation in the nonsolvent (MeOH).
[f] Data taken from Ref. [6b].
[g] Oligomeric material was obtained, which could not be purified further by precipitation in a nonsolvent.



Scheme 3. Synthesis of fluorinated monomer **4** and its cyclopolymerization.

therefore, was approached through a sequential, stepwise functionalization protocol. The malonate monoester **11** could be obtained by reaction of malonyl dichloride with compound **10** (one equivalent each), and subsequent hydrolysis of the remaining acid chloride functionality Scheme 3). The structure of **11** could be confirmed by ^{1}H NMR spectroscopy. Regeneration of the acid chloride, and esterification with compound **8**, using the previously applied conditions, afforded compound **12**, which could be purified by chromatography. Finally, alkylation under mild basic conditions as before afforded the functionalized monomer **4**.

Preliminary experiments for the cyclopolymerization of **3** and **4** were conducted using AIBN as the free radical initiator, as reported in Table 1. Using the optimized conditions for monomer **1**, monomer **3** did not afford polymeric materials, but rather oligomeric species, difficult to further purify and characterize; with monomer **4**, instead, cyclopolymer **13** could be obtained and characterized. Comparing entry 1 and entry 3 in Table 1, the aryl fluorinated difunctional monomer **4** gives a slightly higher degree of polymerization, but also lower isolated yields and higher poyldispersities, with respect to **1**. The ^{1}H NMR of the purified, precipitated polymer (Fig. 2), when compared with that of the starting monomer **4**, shows that efficient cyclization and propagation had occurred, as there are no pendant vinyl resonances present in the ^{1}H NMR spectra, typical of efficient cyclopolymerization processes.



Scheme 2. Synthesis of fluorinated monomer **3**.

3. Conclusions

We have presented a synthetic approach to styrene and perfluoroarylstyrene difunctional monomers for cyclopolymerization. The unknown precursor 4-vinyl-2,3,5,6-tetrafluorobenzylalcohol **8** can be synthesized in good yields and multigram quantities. We have identified good synthetic strategies for the synthesis of symmetrical asymmetrical difunctional styrenic monomers **3** and **4**. These versatile fluorinated monomers have the potential to be used to replace their styrene counterparts in other molecules and polymers. We have studied and characterized in a preliminar way their ability to undergo cyclopolymerization. We aim, in further studies, to optimize the cyclopolymerization conditions for monomers **3** and **4**, and to study, in combination with other difunctional monomers with styrene moieties with differing reactivities, the propensity of alternation of these molecular systems, under free radical or controlled free radical cyclopolymerization conditions.

4. Experimental

4.1. General

All commercially available reagents and solvents were used as received. THF and diethyl ether (Na, benzophenone) and CH_2Cl_2 (CaH_2) were dried and distilled before use. Compounds **5** [12], and **10** [14], were obtained following previously published procedures. Flash chromatography was carried out using silica gel (Merck 60). ^{1}H and ^{13}C-NMR spectra were recorded from solutions in $CDCl_3$ on Bruker 200 or AMX300 with the solvent residual proton signal or tetramethylsilane (TMS) as a standard. Size-exclusion chromatography was carried out on a Waters system equipped with a DRI

detector. Low polydispersity polystyrene standards were used for the calibration curve, and the mobile phase was tetrahydrofuran (1 mL/min, 40 °C). A bank of two columns (Styragel 4E and 5E) in series was used. Elemental analyses were done on a Carlo Erba 1106 elemental analyzer.

Compound **6**: to a suspension of methyl triphenylphosphonium bromide (9.4 g, 0.026 mol) in dry ether (80 mL) at −20 °C under nitrogen, *n*-BuLi (11.6 mL, 2.5 M) was added dropwise. The resulting pink coloured solution was stirred at 0 °C for 2 h. After this time, this solution was transferred to a solution of compound **5** (6 g, 0.024 mol) in dry ether (40 mL), prepared in a separate flask under N_2 atmosphere. The resulting red coloured reaction mixture was stirred overnight at room temperature, followed by the addition of H_2O. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4), the solvent removed under reduced pressure and the residue purified by column chromatography over silica gel (hexanes/AcOEt 99.8/0.02) affording pure compound **6** (2.5 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.05–4.20 (m, 4H; –OC$\underline{H}_2$C$\underline{H}_2$O–), 5.75 (1H, d, J = 11.7; CH=C$\underline{H}_2$), 6.15 (1H, d, J = 11.7; CH=C$\underline{H}_2$), 6.24 (1H, s; acetal CH–), 6.69 (1H, m; C$\underline{H}$=CH$_2$). Anal. calcd. for $C_{11}H_8F_4O_2$: C 53.2%, H 3.2%; found: C 52.9%; H 3.0%.

Compound **7**: compound **6** (1.5 g, 6.05 mmol) was slowly added with stirring to trifluoroacetic acid (5 mL, excess), followed by addition of H_2O (5 mL) and HCl 37% (2 mL). After 3 h stirring at 60 °C, the mixture was cooled to room temperature. The solution was extracted with CH_2Cl_2, the organic phase was washed with H_2O (10 mL) and the solvent was removed under reduced pressure to afford desired compound **7** (1 g, 81%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.77 (d, 1H, J = 11.7; CH = C$\underline{H}_2$), 6.14 (d, 1H, J = 11.7; CH = C$\underline{H}_2$), 6.71 (m, 1H; C$\underline{H}$ = CH$_2$), 10.03 (s, 1H; –C$\underline{H}$O).

Compound **8**: a solution of compound **7** (1 g, 4.9 mmol) in MeOH (20 mL) was cooled to 0 °C in an ice bath and $NaBH_4$ (0.3 g, 7.9 mmol) added portionwise. The reaction was then stirred at room temperature for 4 h. MeOH was removed from reaction mixture under reduced pressure, the residue was taken in H_2O, extracted with CH_2Cl_2, and the combined organic layers were dried (Na_2SO_4) and concentrated to dryness. The residue was purified by column chromatography (SiO_2: hexanes/AcOEt 8/2) to afford pure compound **8** (0.7 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (bs, 1H; –CH$_2$O$\underline{H}$), 4.83 (s, 2 H; –C$\underline{H}_2$OH), 5.74 (d, 1H, J = 11.8; CH=C$\underline{H}_2$), 6.15 (d, 1H, J = 18.2; CH=C$\underline{H}_2$), 6.70 (dd, 1H, J = 18.2, 11.8; C$\underline{H}$=CH$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 52.7, 105.8 (t, J = 22.5), 116.8 (t, J = 18), 122.2, 123.8 (t, J = 7.5), 144.3 (dm, J = 249), 144.8 (dm, J = 248). Anal. calcd. for $C_9H_6F_4O$: C 52.4%, H 2.9%; found: C 52.7%; H 3.0%.

Compound **9**: a solution of alcohol **4** (0.5 g, 2.4 mmol), DMAP (5 mg), dry Et_3N (0.67 mL, 4.8 mmol) in dry CH_2Cl_2 (20 mL) was cooled to 0 °C with an ice bath. Malonyl dichloride (0.2 mL, 1.2 mmol) was added dropwise over a 10 min period. The solution was left stirring at 0 °C for 1 h, overnight at room temperature and at reflux for 4 h. After cooling, H_2O (40 mL) was added, the organic phase separated, dried (Na_2SO_4) and the residue purified by column chromatography (SiO_2: hexanes/AcOEt 95/5) to yield **9** as a colourless oil (0.30 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.47 (s, 2H; –OOCC$\underline{H}_2$COO–), 5.29 (s, 4H; ArC$\underline{H}_2$O–), 5.78 (d, 2H, J = 11.9; CH=C$\underline{H}_2$), 6.18 (d, 2H, J = 18; CH=C$\underline{H}_2$), 6.71 (dd, 2H, J = 18, 11.9; C$\underline{H}$=CH$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 40.7, 54.4, 111.7 (t, J = 17.3), 117.9 (t, J = 12.8), 122.1, 124.4 (t, J = 7.5), 144.3 (dm, J = 248), 145.2 (dm, J = 255), 165.2.

Compound **3**: a solution of compound **9** (0.13 g, 0.3 mmol), Cs_2CO_3 (150 mg, 0.46 mmol) and ethyl iodide (0.1 g, 0.62 mmol) in DMF (2 mL) was stirred overnight at room temperature. Then H_2O (10 mL) was added to reaction mixture and extraction was done with Et_2O. Combined extracts were dried (Na_2SO_4), concentrated under reduced pressure and product purified by column chromatography (SiO_2: hexanes/AcOEt 98/2) to afford pure compound **3** (0.10 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, 3H, J = 7.6; CH$_2$C$\underline{H}_3$), 1.94 (q, 2H, J = 7.6; C$\underline{H}_2$CH$_3$), 5.22 (s, 4H; ArC$\underline{H}_2$O–), 5.78 (d, 2H, J = 11.9; CH=C$\underline{H}_2$), 6.15 (d, 2H, J = 18; CH=C$\underline{H}_2$), 6.71 (dd, 2H, J = 18, 11.9; C$\underline{H}$=CH$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 8.0, 24.6, 54.3, 58.4, 112.0 (t, J = 17.3), 117.7 (t, J = 13.35), 122.9, 124.3 (t, J = 7.5), 144.2 (dm, J = 240), 145.1 (dm, J = 248), 170.6. Anal. calcd. for $C_{25}H_{20}F_8O_4$: C 59.7%, H 3.7%; found: C 59.9%; H 3.6%.

Compound **11**: malonyl dichloride (0.7 g, 5 mmol) was dissolved in CH_2Cl_2 (30 mL) and solution cooled to 0 °C in ice-bath followed by addition of Et_3N (0.75 mL, 0.54 mmol) and DMAP (5 mg). A solution of compound **10** (0.75 g, 5 mmol) in CH_2Cl_2 (15 mL) was added dropwise over 2 h. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with solution of Na_2CO_3, aqueous layer separated, acidified with 1N HCl and extracted with CH_2Cl_2. Combined CH_2Cl_2 extracts were dried (Na_2SO_4) and concentrated under reduced pressure to afford compound **11** which was used as such without further purification (0.27 g, 25%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.49 (s, 2H; –OOCC$\underline{H}_2$COO–), 5.20 (s, 2H; ArC$\underline{H}_2$O–), 5–28 (d, 1H, J = 11; CH=C$\underline{H}_2$), 5.77 (d, 1H, J = 17.6; CH=C$\underline{H}_2$), 6.73 (dd, 1H, J = 17.6, 11; C$\underline{H}$=CH$_2$), 7.28–7.45 (m, 4H; –C$_6\underline{H}_4$–), 8.12 (bs, 1H; –COOH).

Compound **12**: compound **10** (0.27 g, 1.2 mmol) was dissolved in CH_2Cl_2 followed by the addition of oxalyl chloride (1 mL, excess). Resulting solution was stirred overnight at room temperature and concentrated to dryness under reduced pressure. Meanwhile, a separate solution of alcohol **8** (0.2 g, 0.88 mmol), Et_3N (0.17 mL, 1.2 mmol) and DMAP (5 mg) in CH_2Cl_2 was cooled to 0 °C and a solution of compound **10** was added to it dropwise. After stirring reaction overnight 1N HCl was added and aqueous layer extracted with CH_2Cl_2. Combined CH_2Cl_2 extracts were dried (Na_2SO_4) and concentrated under reduced pressure to afford crude material which was purified by column chromatography (SiO_2: hexanes/AcOEt 98/2) to afford compound **12** (0.14 g, 40%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.48 (s, 2H; –OOCC$\underline{H}_2$COO–), 5.17 (s, 2H; ArC$\underline{H}_2$O–), 5.26 (s, 2H; ArC$\underline{H}_2$O–), 5.77 (d, 2H; CH=C$\underline{H}_2$), 6.15 (d, 2H; CH=C$\underline{H}_2$), 6.61–6.71 (m, 2H; C$\underline{H}$=CH$_2$), 7.28–7.42 (m, 4H; –C$_6\underline{H}_4$–).

Compound **4**: a solution of compound **12** (0.065 g, 0.16 mmol), Cs_2CO_3 (0.06 g, 0.2 mmol) and ethyl iodide (0.06 g, 0.32 mmol) in DMF (2 mL) was stirred overnight at room temperature. H_2O (10 mL) was added to reaction mixture and extraction was done with diethyl ether. Combined extracts were dried (Na_2SO_4), and purified by column chromatography (SiO_2: hexanes/AcOEt 98/2) to give pure compound **4** (0.065 g, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (t, 3H; CH$_2$C$\underline{H}_3$), 1.96 (q, 2H; C$\underline{H}_2$CH$_3$), 5.11 (s, 2H; ArC$\underline{H}_2$O–), 5.22 (s, 2H; ArC$\underline{H}_2$O–), 5.76 (d, 2H; CH=C$\underline{H}_2$), 6.14 (d, 2H; CH=C$\underline{H}_2$), 6.60–6.72 (m, 2H; C$\underline{H}$=CH$_2$), 7.21–7.39 (m, 4H; –C$_6\underline{H}_4$–). Anal. calcd. for $C_{25}H_{24}F_4O_4$: C 69.8%, H 5.1%; found: C 69.5%; H 5.4%.

Polymer **13**: monomer **4** (80 mg) and the initiator (AIBN, 5 mol% *vs.* monomer) were dissolved in toluene (at a monomer concentration of 0.5 M). The solution was deoxygenated by bubbling N_2 for 30 min and then heated under magnetic stirring at 90 °C in a temperature-controlled oil bath. The solvent was then removed under reduced pressure, the remaining solid was dissolved in a minimum amount of CH_2Cl_2, filtered from insoluble material and the solution was added dropwise to MeOH (20 times its cosolvent volume). The purified, precipitated polymer sample was filtered and dried (24 mg, 30%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (bs; CH$_2$C$\underline{H}_3$), 1.97 (bs; C$\underline{H}_2$CH$_3$), 5.01 (bs; ArC$\underline{H}_2$O–), 5.90–7.10 (bs; –C$_6\underline{H}_4$–). Anal. calcd. for $(C_{25}H_{24}F_4O_4)_n$: C 69.8%, H 5.1%; found: C 70.1%; H 4.8%.

References

[1] (a) B.V.K.J. Schmidt, N. Fechler, J. Falkenhagen, J.-F. Lutz, Nat. Chem. 3 (2011) 234–238;
(a) N. Badi, J.-F. Lutz, Chem. Soc. Rev. 38 (2009) 3383–3390;
(b) R.M. Stayshich, T.Y. Meyer, J. Am. Chem. Soc. 132 (2010) 10920–10934.

[2] (a) L.J. Mathias, Trends Polym. Sci. 10 (1996) 330–336;
(b) R.P. Meagley, D. Pasini, L.Y. Park, J.M.J. Fréchet, Chem. Commun. (1999) 1587–1588;
(c) D. Pasini, E. Low, J.M.J. Fréchet, Adv. Mater. 12 (2000) 347–351;
(d) D. Pasini, J.M. Klopp, J.M.J. Fréchet, Chem. Mater. 13 (2001) 4136–4146;
(e) E. Cagnoni, D. Pasini, A. Galbiati, M. Ricci, P.P. Righetti, Macromolecules 36 (2003) 8894–8897;
(f) C. Coluccini, P. Metrangolo, M. Parachini, D. Pasini, G. Resnati, P. Righetti, J. Polym. Sci. Pol. Chem. 46 (2008) 5202–5213;
(g) S. Erkoc, A.E. Acar, Macromolecules 39 (2006) 8936–8942;
(h) B. Ochiai, Y. Ootani, T. Endo, J. Am. Chem. Soc. 130 (2008) 10832–10833;
(i) S. Erkoc, A.E. Acar, Macromolecules 41 (2008) 9019–9024;
(l) Y. Assem, H. Chaffey-Millar, C. Barner-Kowollik, G. Wegner, S. Agarwal, Macromolecules 40 (2007) 3907–3913;
(m) Y. Assem, A. Greiner, S. Agarwal, Macromol. Rapid Commun. 28 (2007) 1923–1928.
[3] B. Yamada, O. Kosonu, Polym. Bull. 41 (1998) 545–552.
[4] (a) G. Wulff, S. Gladow, S. Krieger, Macromolecules 28 (1995) 7434–7440;
(b) G. Wulff, B. Kuehneweg, J. Org. Chem. 62 (1997) 5785–5792.
[5] (a) A. Narumi, R. Sakai, S. Ishido, M. Sone, T. Satoh, H. Kaga, H. Nakade, T. Kakuchi, Macromolecules 40 (2007) 9272–9278;
(b) T. Kakuchi, M. Obata, Macromol. Rapid Commun. 23 (2002) 395–406.
[6] (a) S. Edizer, B. Veronesi, O. Karahan, V. Aviyente, I. Değirmenci, A. Galbiati, D. Pasini, Macromolecules 42 (2009) 1860–1866;
(b) A.K. Sharma, C. Cornaggia, D. Pasini, Macromol. Chem. Phys. 211 (2010) 2254–2259.
[7] (a) T.H. Kim, P. Dokolas, N. Feeder, M. Giles, A.B. Holmes, M. Walther, Chem. Commun. (2000) 2419–2420;
(b) T.H. Kim, M. Giles, A.B. Holmes, Chem. Commun. (2000) 2421–2422;
(c) A.I. Costa, P.D. Barata, J.V. Prata, React. Funct. Polym. 66 (2006) 465–470.
[8] K. Jankova, S. Hvilsted, Macromolecules 36 (2003) 1753–1758.
[9] (a) S. Borkar, K. Jankova, H.W. Siesler, S. Hvilsted, Macromolecules 37 (2004) 788–794;
(b) H. Cinar, O. Kretschmann, H. Ritter, Macromolecules 38 (2005) 5078–5082;
(c) J. Ma, C. Cheng, K.L. Wooley, Aust. J. Chem. 62 (2009) 1507–1519;
(d) S. Kubowicz, J.F. Baussard, J.F. Lutz, A.F. Thunemann, H. von Berlepsch, A. Laschewsky, Angew. Chem. Int. Ed. 44 (2005) 5262–5265;
(e) K. Nilles, P. Theato, J. Polym. Sci. Pol. Chem. 47 (2009) 1696–1705;
(f) P. Theato, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 6677–6687;
(g) K. Nilles, P. Theato, Eur. Polym. J. 43 (2007) 2901–2912.
[10] W.A. Pryor, T.-L. Huang, Macromolecules 2 (1969) 70–77.
[11] K. Iwakura, H. Souda, T. Takagaki, Y. Yamada, Yoshimi, U.S. Patent Appl. 2002/52525 A1, 2002.
[12] F.C. Krebs, T. Jensen, J. Fluorine Chem. 120 (2003) 77–84.
[13] M. Montanari, A. Bugana, A.K. Sharma, D. Pasini, Org. Biomol. Chem. 9 doi:10.1039/C1OB05319, in press.
[14] This compound was synthesized from p-vinylbenzyl chloride by hydrolysis in mild basic conditions following a procedure reported in R.B. Grubbs, C.J. Hawker, J. Dao, J.M.J. Fréchet, Angew. Chem. Int. Ed. Engl. 36 (1997) 270–273.