Post-modification of poly(pentafluorostyrene): a versatile "click" method to create well-defined multifunctional graft copolymers†

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This *communication* reports a versatile post-modification reaction of poly(pentafluorostyrene) building blocks in order to design multifunctional graft copolymers by taking advantage of the selective replacement of the *para*-fluorine groups.

Significant advances have been made in the field of controlled ('living') radical polymerization,[1] including nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer polymerization (RAFT). Their widespread acceptance and exploitation in polymer synthesis is justified by their seemingly unlimited potential to create a wide range of well-defined macromolecules with accurate control over architecture and functionality. The desire to perfectly copy natural systems gives rise to the tremendous progress in this research area which is also associated with an increased interest in nanotechnology.[2] Complex macromolecular architectures, such as graft copolymers, are known to exhibit good phase separation[3] and are therefore used for a variety of applications, *i.e.* impact-resistant materials, thermoplastic elastomers, compatibilizers and emulsifiers.

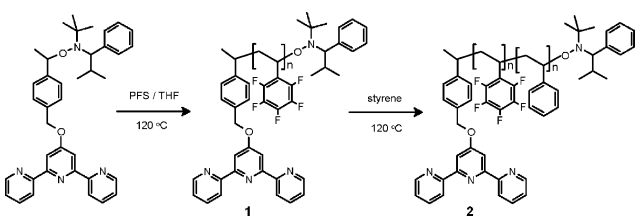
Hawker and co-workers have shown for NMP that the design of the initiator influences the performance of the polymerization to a great extent.[1,4] More importantly, polymers with controlled endgroup functionality are readily available using substituted alkoxyamine initiators since NMP tolerates several functional groups *e.g.* hydroxyl, ester and halide.[5] Our group has used this opportunity to introduce specifically the supramolecular metal-coordinating terpyridine entity as a polymer endgroup which could be exploited for the preparation of reversible supramolecular block copolymers.[6]

The feasibility of performing controlled polymerizations of substituted and unsubstituted styrene monomers using nitroxide mediated polymerization is already reported in the literature.[7] Here, we focus our attention on fluorinated polymers, in particular poly(pentafluorostyrene). Nowadays, fluorinated polymers find applications in microelectronic devices, or as antifouling and antifogging agents due to their specific properties, including high thermal stability, chemical resistance, excellent mechanical properties at extreme temperatures, superior weather durability and low flammability. Wooley *et al.* demonstrated the synthesis of an amphiphilic crosslinked polymer network, consisting of a hyperbranched fluoropolymer and poly(ethylene glycol) for polymer coating purposes by nucleophilic substitution of the *para*-fluorine substituent.[8]

Herein, we report for the first time the powerful strategy of combining nitroxide mediated polymerization and the subsequent microwave-assisted modification reaction of pentafluorophenyl groups using amine-functionalized (macro)molecules. This unique "grafting onto" method leads to the preparation of well-defined multifunctional graft copolymers. Depending on the inserted molecule, subsequent chemical reactions can be carried out. In particular, two examples are presented where the introduced functional groups in the side chain were exploited as initiators for ring opening polymerization and controlled radical polymerization by ATRP, respectively.

A terpyridine-functionalized unimolecular alkoxyamine initiator[6] was used for the nitroxide mediated controlled living radical polymerization of 2,3,4,5,6-pentafluorostyrene (Scheme 1). The polymerization ($[M]/[I] = 70$) was performed up to 50% conversion (5 h, 120 °C) yielding a well-defined polymer with a narrow molecular weight distribution, *i.e.* a polydispersity index below 1.10 (Fig. 1). Furthermore, the composition of the polymer was determined by ^{1}H NMR spectroscopy revealing an experimental degree of polymerization of 30, which corresponds to the theoretical value of 35 at 50% conversion. In addition, well-defined block copolymers were synthesized by using this poly(pentafluorostyrene) as a macroinitiator for the polymerization of styrene (Scheme 1). The unimodal GPC-trace of the block copolymer demonstrates the efficient reinitiation of the macroinitiator and the good control over the polymerization (Fig. 1). The corresponding molecular weight values determined by GPC can be found in Table 1. The respective block ratio of the diblock copolymer was calculated from the ^{1}H NMR spectrum, revealing a degree of polymerization of 73 for the styrene block. In fact, to the best of our knowledge, this is the first literature report on the preparation of well-defined pentafluorostyrene block copolymers by NMP.

It is well-known in organic chemistry that the labile *para*-fluorine of the pentafluorophenyl groups can undergo



Scheme 1 Schematic representation of the synthetic approach for the preparation of well-defined terpyridine-functionalized block copolymers.

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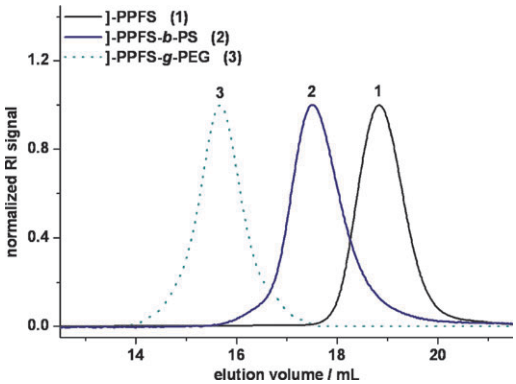


Fig. 1 Normalized GPC-chromatograms of polymers **1**, **2** and **3**. Eluent: *N*,*N*-dimethyl acetamide (DMA) with LiCl (2.1 g L^{-1}).

Table 1 Molecular weight determination of polymers **1** to **8** by ^{1}H NMR spectroscopy and GPC

Polymer		M_n [^{1}H NMR]	M_n (PDI)[a] [GPC]
1	PPFS	6400	4500 (1.09)
2	PPFS-PS	14 000	9 900 (1.22)
3	PPFS-*g*-PEG	40 200	27 700 (1.12)
4	PPFS-*g*-AP	7200	5800 (1.13)
5	PPFS-*g*-AP-PLA	21 600	27 200 (1.12)
6	PPFS-PS-*g*-AP	14 700	13 400 (1.18)
7	PPFS-PS-*g*-AP-Br	15 900	12 600 (1.19)
8	PPFS-PS-*g*-AP-OEGMA	49 100	27 700 (1.15)

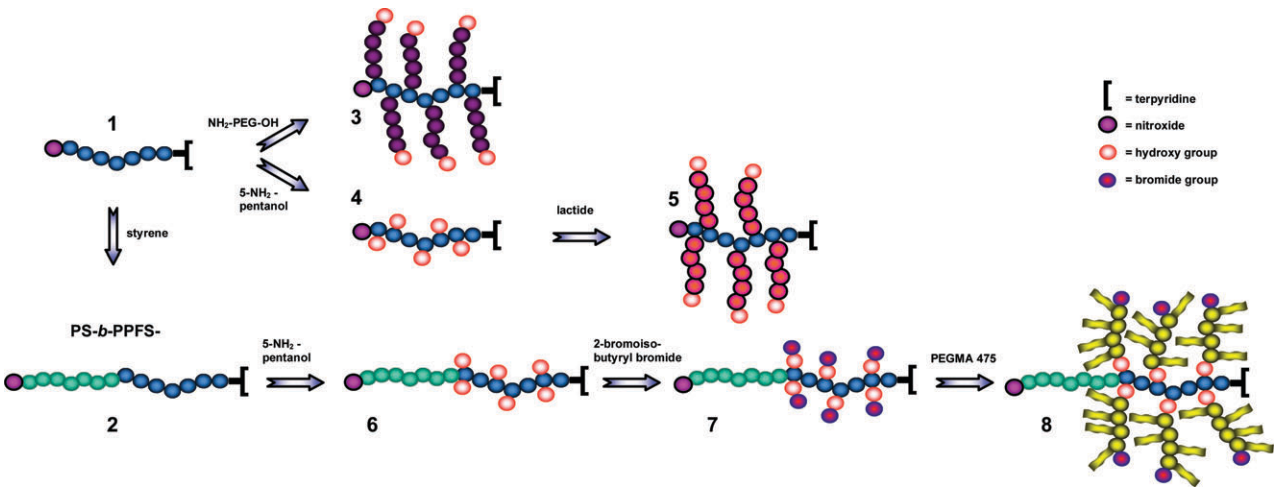
[a] GPC in DMA with LiCl (2.1 g L^{-1}), polystyrene calibration.

nucleophilic substitution by primary amino groups.[9] This synthetic route is, *e.g.*, frequently employed in porphyrin chemistry.

Surprisingly, this strategy has not yet been applied as versatile tool to synthesize graft copolymers. Therefore, homopolymer **1** was reacted with amino-functionalized poly(ethylene glycol) (M_w = 3400 g mol^{-1}) to prepare the amphiphilic graft copolymer **3** (Scheme 2). The substitution reactions of **1** were performed in *N*-methylpyrrolidone in a capped microwave vial for 20 min at 95 °C under microwave irradiation based on a recent publication.[10] After purification of the graft copolymer by precipitation and preparative SEC to remove unreacted PEG, the GPC-curve shows a clear chain extension indicating the successful insertion of several PEG macromolecules (Fig. 1). The number of attached PEG chains was determined by ^{1}H NMR spectroscopy revealing 10 grafted side chains per pentafluorostyrene backbone.

The scope of this synthetic concept was extended by reacting poly(pentafluorostyrene) **1** with 5-aminopentanol which leads to the introduction of several hydroxy groups (Scheme 2). These functional groups allow the direct access to a wide variety of chemical modifications including concepts and strategies from organic and polymer chemistry while the terpyridine is still available for supramolecular self-assembly processes and the nitroxide moiety for further radical reactions. In order to obtain the desired graft copolymer, a ring opening polymerization of L-lactide was performed at 100 °C for 5 h with polymer **4** as co-initiator in the presence of stannous octoate as catalyst and some drops of dry toluene to ensure sufficient solubility of the polymer. The polymerization was monitored in time by GPC revealing an increase of the molecular weight in time with narrow molecular weight distributions, as is expected for a controlled polymerization process. Fig. 2 displays the GPC-traces of all involved polymers: homopolymer **1**, poly(pentafluorostyrene) substituted with 5-aminopentanol (AP) **4** and polymer **5** with grafted polylactide (PLA) arms. The polymers **4** and **5** were also characterized by ^{1}H NMR spectroscopy demonstrating that, on average, nine aminopentanol units were attached per polymer chain and that all hydroxy groups initiated a PLA graft. A degree of polymerization of approximately 11 per graft was determined by ^{1}H NMR spectroscopy.

The full potential of the here presented methodology is demonstrated by the subsequent combination of a nitroxide mediated block copolymerization and ATRP of a macromonomer resulting in a block "graft-on-graft" architecture (Scheme 2). For this purpose, the terpyridine-functionalized block copolymer **2** was reacted with 5-aminopentanol, in the same way as polymer **4**, to yield polymer **6**. The ^{1}H NMR spectrum after precipitation into methanol revealed an average of eight inserted aminopentanol groups per chain by integration over the corresponding signals. In a subsequent reaction, the hydroxy groups were reacted with 2-bromoisobutyryl bromide in the presence of triethylamine. This quantitative



Scheme 2 Schematic representation of the synthesized graft copolymers.

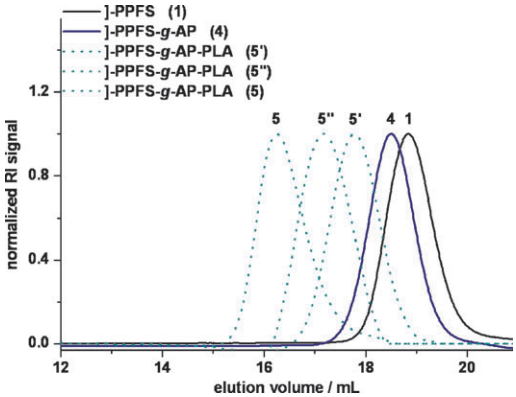


Fig. 2 Normalized GPC-traces of the polymers **1**, **4** and **5** (**5′** and **5″** correspond to intermediate samples obtained after 1 h and 3 h polymerization time, respectively) showing successful chain extensions after each reaction. Eluent: DMA with LiCl (2.1 g L^{-1}).

esterification reaction incorporates a bromo-functionality into polymer **7**, as demonstrated by ^{1}H NMR spectroscopy, which can be used to initiate a subsequent ATRP. The slightly lower retention time in the GPC after esterification (Fig. 3) is most likely due to the decreased solubility (decreased hydrodynamic volume) of the grafts in DMA. In the next step, the controlled radical polymerization of oligo(ethylene oxide) methacrylate (OEGMA 475) was carried out in toluene at 75 °C for 5 h with *N*,*N*,*N′*,*N″*,*N‴*-pentamethyldiethylenetriamine (PMDETA) and CuBr as catalytic system. The unimodal GPC-trace (Fig. 3) indicates that the polymerization proceeded in a controlled fashion. Due to the fact that the terpyridine group is still linked to the polymer (which can form complexes with any kind of transition metal ion in low oxidation states) a loss of control during the ATRP might be expected. Therefore, the ATRP was performed using a large excess of copper ions so that sufficient free copper was available after all terpyridine moieties are complexed. After removing the copper from polymer **8** by treating the polymer solution with the strong chelating ligand hydroxyethyl ethylenediaminetriacetic acid (HEEDTA), the polymer was precipitated twice into ice-cold hexane. A subsequent ^{1}H NMR measurement revealed the incorporation of 70 OEGMA units into the polymer: Approximately 9 OEGMA units were "grafted-from" each arm assuming an uniform distribution. Table 1 summarizes the

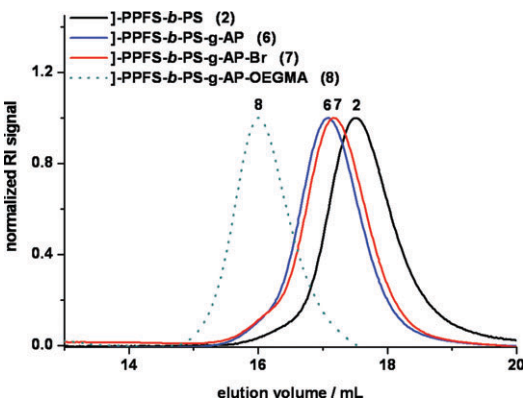


Fig. 3 Normalized GPC-chromatograms of the polymers **2**, **6**, **7** and **8**. Eluent: DMA with LiCl (2.1 g L^{-1}).

characteristics for all eight polymers determined by ^{1}H NMR spectroscopy and GPC, whereby it should be noted that all these polymers still bear the terpyridine at one chain end and the nitroxide at the other.

In summary, the *para*-fluoride of pentafluorophenyl groups reacts readily with primary amines and hence provides a new "graft-onto" approach for the preparation of well-defined multifunctional graft copolymers when combined with NMP of pentafluorostyrene. This reaction type could also be considered as a kind of "click" reaction.[11] The versatility of this approach was demonstrated by directly grafting α-amino-ω-hydroxy-PEG as well as 5-aminopentanol followed by a controlled ring opening polymerization of L-lactide. The resulting well-defined graft copolymers contain a number of functional groups: the nitroxide moiety and the terpyridine ligand as a supramolecular binding motif at the pentafluorostyrene chain ends as well as the hydroxy groups at the graft chain ends, that could be exploited for further functionalization steps. Furthermore, a poly(pentafluorostyrene-*b*-styrene) block copolymer was functionalized with 5-aminopentanol followed by reaction with isobutyryl bromide and ATRP of OEGMA yielding well-defined amphiphilic block "graft-on-graft" copolymers bearing the nitroxide and the terpyridine units as well as bromide endgroups on the graft. Future work will include the exploitation of all functional groups involved in the system and the incorporation of other functionalities.

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Notes and references

1. K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921; M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 2001, **101**, 3689; C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, **101**, 3661; H. Fischer, *Chem. Rev.*, 2001, **101**, 3581; G. Moad, E. Rizzardo and S. H. Thang, *Polymer*, 2008, **49**, 1079.
2. I. W. Hamley, *Angew. Chem., Int. Ed.*, 2003, **42**, 1692.
3. A. V. Dobrynin and I. Y. Erukhimovich, *Macromolecules*, 1993, **26**, 276; H. Shinoda, P. J. Miller and K. Matyjaszewski, *Macromolecules*, 2001, **34**, 3186.
4. C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao and W. Devonport, *Macromolecules*, 1996, **29**, 5245.
5. D. Benoit, V. Chaplinski, R. Braslau and C. J. Hawker, *J. Am. Chem. Soc.*, 1999, **121**, 3904.
6. B. G. G. Lohmeijer and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 1413; B. G. G. Lohmeijer and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4016; B. G. G. Lohmeijer and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 6331; C. Ott, B. G. G. Lohmeijer and U. S. Schubert, *Macromol. Chem. Phys.*, 2006, **207**, 1439.
7. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier and G. K. Hamer, *Macromolecules*, 1993, **26**, 2987.
8. D. Gan, A. Mueller and K. L. Wooley, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3531; C. S. Gudipati, C. M. Greenlief, J. A. Johnson, P. Prayongpan and K. L. Wooley, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 6193.
9. R. D. Chambers, D. Close and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1980, 778; K. M. Kadish, C. Araullo-McAdams, B. C. Han and M. M. Franzen, *J. Am. Chem. Soc.*, 1990, **112**, 8364; P. Battioni, O. Brigaud, H. Desvaux, D. Mansuy and T. G. Taylor, *Tetrahedron Lett.*, 1991, **32**, 2893.
10. D. Samaroo, C. E. Soll, L. J. Todaro and C. M. Drain, *Org. Lett.*, 2006, **8**, 4985.
11. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; D. Fournier, R. Hoogenboom and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1369.

