# Notes

## Preparation of Poly(2,3,4,5,6-pentafluorostyrene) and Block Copolymers with Styrene by ATRP

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### Introduction

The introduction of atom transfer radical polymerization (ATRP) in recent years[1] has revitalized the concept of controlled/living polymerization and the immediate implications of this approach. Among many important aspects are the possibilities for hybrid processes with crossover from ionic polymerizations to radical processes.[2] Similarly, there is a multitude of possibilities for the production of macroinitiators[3] and initiation[4] or termination[5] of well-defined polymers with specific functionality. Moreover, the number of functional, polymerizable monomers[5−7] in combination with the much less rigorous experimental conditions opens up new material avenues, not least in the area of block copolymers.[8−11]

Fully or partly fluorinated polymers are a class of materials that attract significant attention due to their high thermal stability, oil and water repellency, and good resistance to chemical and physical treatments. Moreover, thin films of fluorinated polymers with low-loss optical waveguiding properties, low permittivity, or low dielectric constant are of particular interest to the (opto)electronic industry. With such applications in mind, 2,3,4,5,6-pentafluorostyrene has previously been polymerized anionically[12] or under plasma conditions.[13,14] Likewise, radical polymerization[15] or a number of studies of radical copolymerization with styrene,[15] 4-fluorostyrene by vapor deposition,[16] or glycidyl methacrylate[17] have been published. We report here on the polymerization of 2,3,4,5,6-pentafluorostyrene using ATRP, involving both homo- and block copolymerization with styrene, which to our best knowledge has not previously been described.

### Experimental Section

**Materials.** 2,3,4,5,6-Pentafluorostyrene (FS) (Aldrich) was passed through a ready-to-use, disposable prepacked inhibitor−remover column AL-154 (Aldrich). Styrene (St) (Riedel-de Haen) was passed through a column of activated $Al_2O_3$ (Aldrich, neutral, Brockman I, Standard grade, ca. 150 mesh, 58 Å) to remove the inhibitor. Both monomers were stored over $CaH_2$ and then vacuum-distilled before polymerization. CuBr (Aldrich), 1-phenylethyl bromide (PhEBr) (Aldrich), and 2,2′-bipyridine (bipy) (Aldrich) were employed as received. All other chemicals were used after usual drying and/or distillation. Solvents employed for the solubility studies were normal chromatographic or analytical grades as supplied.

**Polymerizations. 1. ATRP of FS and St.** In a characteristic homopolymerization of FS or St by heterogeneous ATRP, a Schlenk tube was charged with 0.070 mL (0.51 mmol) of PhEBr, 0.0740 g (0.51 mmol) of CuBr, and 0.1602 g (1.02 mmol) of bipy. 3.8 mL (27.50 mmol) of FS or 3.2 mL of St was added, and the system was degassed three times by freezing and thawing and then heating to 110 °C under nitrogen. At time intervals an appropriate volume of the mixture was withdrawn with a degassed syringe, diluted with solvent for NMR or SEC, and analyzed for conversion, $\bar{M}_n$ and $\bar{M}_w$. Upon completion of the experiment the polymerization mixture was diluted with THF, and the solution was filtered (to remove catalyst) and precipitated in methanol where PFS appeared as a fluffy, white material that was recovered after vacuum-drying.

**2. Block Copolymers.** In a typical block copolymerization 0.5 g (0.05 mmol) of PFS macroinitiator (PFS−Br) was dissolved in 7 mL of xylene and 7 mL (61 mmol) of St, 0.0072 g (0.05 mmol) of CuBr, and 0.0156 g (0.10 mmol) of bipy were added. After three freeze−thaw cycles, the mixture was heated to 110 °C for 7 h. When employing 0.5 g of PS macroinitiator (PS−Br), the latter was diluted in 5 mL of xylene, and 0.43 mL (3.11 mmol) of FS was added. The molar ratio of PS−Br/CuBr/bipy was kept 1:1:2. The block copolymer solutions were filtered and precipitated in methanol with an appearance similar to that of the homopolymers. Yields of the powdered block copolymers were determined gravimetrically after vacuum-drying.

**Characterization. 1. NMR Spectroscopy.** The macroinitiators and the block copolymers were characterized by $^1H$ NMR, using a Bruker 250 MHz spectrometer and $CDCl_3$ as solvent.

**2. SEC Analyses.** Molecular masses were determined by size exclusion chromatography (SEC) employing a Viscotek 200 instrument equipped with a PL guard and 2 PLgel mixed D columns in series from Polymer Laboratories. Measurements were performed in THF at room temperature with a 1 mL/min flow and RI detection; molecular weights were calculated using PS narrow molecular weight standards in the range $7 \times 10^2 - 4 \times 10^5$ from Polymer Laboratories.

**3. Thermal Investigations.** Thermal analyses were performed with a differential scanning calorimeter DSC Q1000 from TA Instruments in a temperature range of −30 to 250 °C at a heating rate of 10 °C $min^{-1}$ under nitrogen. The glass transition temperature ($T_g$) was determined automatically by the instrument from the second heating trace and is reported as the midpoint of the thermal transition. Thermal degradation was investigated by thermogravimetric analysis (TGA) performed with a TGA Q500 from TA Instruments measuring the total weight loss on approximately 8−9 mg samples from 30 to 550 °C at a rate of 5 °C/min in a nitrogen flow of 90 mL/min.

**4. Solubility Examination.** An initial 4−8 mass % of the polymer sample in known masses of the solvent in capped vials was inspected after 24 h with intermittent shaking. A completely transparent solution was the criterion for solubility. Insoluble mixtures and swelled or opaque solutions were inspected after 4 h in an oven at 50 °C. More polymer was added to the transparent solutions, and these were reinspected after 24 h. More solvent was added to the insoluble mixtures,

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**Table 1. Preparation of PFS, PS, and Block Copolymers by ATRP (Polymerization Temperature 110 °C, Initiator:CuBr:bipy = 1:1:2)**

| sample | initiator (g) | monomer (mL) | xylene (mL) | time (min) | yield (%) | $\bar{M}_n^{theo} \times 10^{-3}$ | $\bar{M}_n^{a} \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n^{a}$ | PFS (wt %)$^{b}$ | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| PFS1 | PhEBr, 0.095 | FS, 5.0 | | 100 | 96.0 | 9.7 | 11.4 | 1.21 | 100 | 95.3 |
| PFS1-*b*-PS | PFS1, 0.500 | St, 7.0 | 7 | 260 | 14.3 | 18.8 | 20.8 | 1.32 | 42 | 101.4 |
| PFS2 | PhEBr, 0.068 | FS, 5.0 | | 40 | 47.8 | 9.2 | 10.9 | 1.13 | 100 | 93.5 |
| PFS2-*b*-PS | PFS2, 0.480 | St, 7.0 | 7 | 420 | 11.6 | 16.4 | 16.1 | 1.24 | 48 | 101.3 |
| PS1 | PhEBr, 0.339 | St, 30.0 | | 270 | 59.2 | 9.0 | 10.0 | 1.13 | 0 | 91.2 |
| PS1-*b*-PFS | PS1, 0.500 | FS, 0.4 | 5 | 880 | 86.5 | 15.2 | 14.2 | 1.35 | 51 | 96.5 |
| PS2 | PhEBr, 0.170 | St, 20.0 | | 300 | 43.8 | 13.1 | 16.5 | 1.11 | 0 | 100.0 |
| PS2-*b*-PFS | PS2, 0.500 | FS, 0.6 | 6 | 1140 | 73.4 | 20.9 | 19.4 | 1.16 | 21 | 91.7 |

[a] Determined by SEC using PS calibration. [b] Calculated by $^1$H NMR.

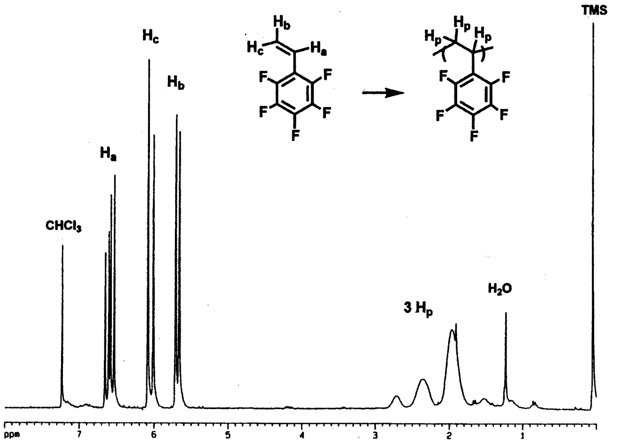

**Figure 1.** $^1$H NMR spectrum of the reaction mixture for calculation of the conversion of FS (presented spectrum corresponds to 42% conversion).

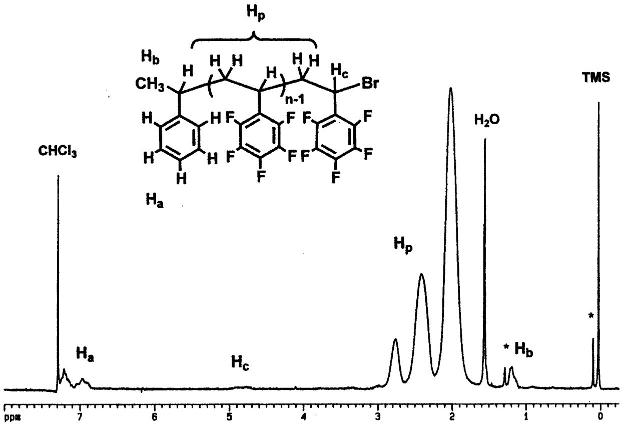

**Figure 2.** $^1$H NMR spectrum of PFS1 for calculation of the $\bar{M}_n$ (* unidentified impurities).

and these were likewise reinspected. The solubility examinations were stopped when a total of 12 mL solvent had been used.

## Results and Discussion

**Homopolymerizations.** FS polymerizes rapidly in bulk at 110 °C under ATRP conditions. The rate of reaction depends on the conditions, for example, with a $[M]_0$:$[PhEBr]_0$ ratio of 55:1 around 90% conversion is obtained in 90 min, and almost complete conversion (96%) is achieved in 100 min with PhEBr initiation and the catalytic system CuBr/bipy (Table 1). Table 1 also lists the results of the preparation of another PFS and some PS prepared in the same manner. The highest previously reported conversion for polymerization of FS appears to be 43.5% obtained after 7 days at 60 °C in THF initiated by $n$-$C_4H_9Li$ in sealed ampules,[12] whereas the highest reported conversion for a radical-initiated polymerization is 34.4%.[15]

An ATRP kinetic study under bulk conditions was performed over a period of 90 min. Samples were withdrawn with time intervals in order to investigate the nature of the FS polymerization by NMR and SEC analyses. However, the viscosity of the medium increased rapidly, and that caused problems in the withdrawal of samples at high conversions. The conversion of FS monomer in the withdrawn samples was calculated from the $^1$H NMR spectra (Figure 1) by use of the normalized area for the olefinic $-CH{=}CH_2$ (6.65 ppm) and $-CH{=}CH_2$ (5.85 and 6.19 ppm) protons for FS as compared to the sum of the aliphatic $-CH-CH_2$ protons (1.7−3.0 ppm) for PFS. Therefore, the NMR results employed in the kinetic curve only consist of samples up to 50% conversion based on unprecipitated samples containing unreacted monomer.

Samples with higher than 48% conversion were analyzed after precipitation. The molecular masses were determined by use of the PS calibration. Similar figures for the molecular masses of PFS were obtained employing NMR. Because of the relatively high molecular weight of PFS, it is difficult to exploit the area of the ⟩CHBr terminal group that appears in PS at 4.50 ppm[18] and at around 4.9 ppm in the case of PFS. However, the presence of the signals from the five aromatic protons from the initiator permitted calculation of the degree of polymerization and thus the molecular weight of PFS (from Figure 2).[19]

The number-average molecular weight ($\bar{M}_n$ obtained by SEC) as a function of conversion is plotted in Figure 3, which also contains the corresponding polydispersities ($\bar{M}_w/\bar{M}_n$). The theoretical solid line was calculated from the monomer-to-initiator ratio taking the obtained conversion into consideration and assuming the absence of termination or side reactions such as elimination.

The relatively good agreement between the experimental points and the theoretical line indicates almost 100% initiating efficiency. The relatively low polydispersities ($\bar{M}_w/\bar{M}_n \leq 1.2$) during the entire conversion range should also be noted. Thus, both the linear $\bar{M}_n$ vs monomer conversion plot and the corresponding narrow polydispersities imply the living ATRP character of FS. Further support is gained from the first-order plot of the bulk polymerization of FS in Figure 4.

The kinetic analysis reveals the polymerization to be first order with respect to monomer up to almost 48% monomer conversion, after which some deviation from linearity is observed. Thus, the concentration of growing radicals is constant over a fairly large conversion range.

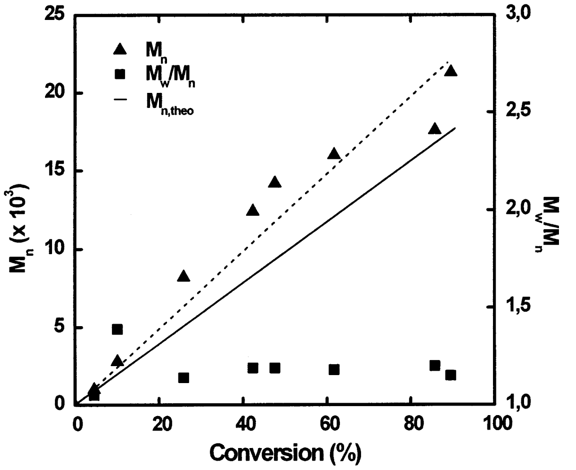

**Figure 3.** Molecular weights and polydispersities of PFS by SEC as a function of conversion for ATRP at 110 °C. $[M]_0$:$[PhEBr]_0$:$[CuBr]_0$:$[bipy]_0$ = 100:1:1:2.

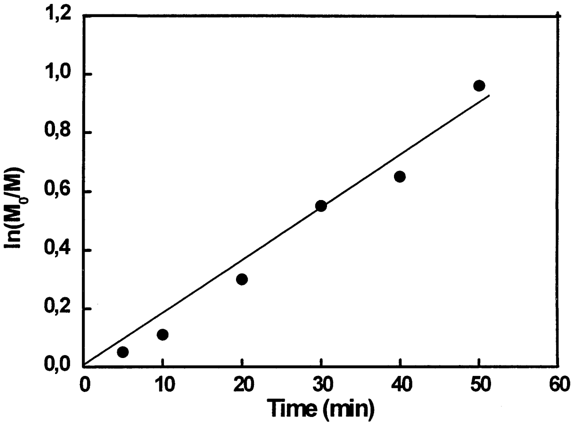

**Figure 4.** First-order plot for ATRP of FS at 110 °C. $[M]_0$:$[PhEBr]_0$:$[CuBr]_0$:$[bipy]_0$ = 100:1:1:2.

An apparent rate coefficient ($k_p^{app} = -d(\ln[M]/dt)$) of 3.0 × $10^{-4}$ $s^{-1}$ is calculated from the slope of this kinetic plot. Apparent rate coefficients of ATRP of a number of 4- or 3-substituted styrenes (110 °C in diphenyl ether, otherwise conditions quite similar) have previously[7] been reported in the range (0.10−1.44) × $10^{-4}$ $s^{-1}$ (e.g., 3-$CF_3$: 1.44 × $10^{-4}$ $s^{-1}$; 4-$CF_3$: 1.25 × $10^{-4}$ $s^{-1}$; and 4-F: 0.39 × $10^{-4}$ $s^{-1}$). Despite the small difference in experimental conditions, the present result seems to strongly support the former conclusion[7] that electron-withdrawing substituents on styrenes (here five F) provide better polymerization control and faster polymerization as compared to electron-donating substituents. The deviations from linearity in the first-order plot at high conversions of the bulk polymerization were probably due to the increased viscosity that would alter the polymerization of PFS from a kinetic- to a diffusion-controlled process. Careful inspection of the narrow and monomodal SEC traces of these samples revealed no evidence of permanent termination from recombination, since no high molecular weight shoulders could be observed (Figure 5).

**Block Copolymerizations.** The diblock copolymers were synthesized by ATRP in xylene solution employing either PFS or PS as the macroinitiator. The molecular weights of the macroinitiators, their block copolymers, and block copolymer compositions were determined by SEC and NMR; the SEC characteristics are listed in Table 1. SEC traces of PFS1 macroinitiator and the resulting diblock copolymer with PS obtained in xylene solution are presented in Figure 6. The SEC traces show that PFS1-*b*-PS is formed, since the entire elution curve is shifted toward higher molecular weight. This indicates the involvement of essentially all macroinitiator chains in initiating the ATRP of styrene. The PFS content in the diblock copolymers was determined by ratio analysis of the areas of aliphatic protons (from both PFS and PS main chains) and the areas of the aromatic protons (from only PS).

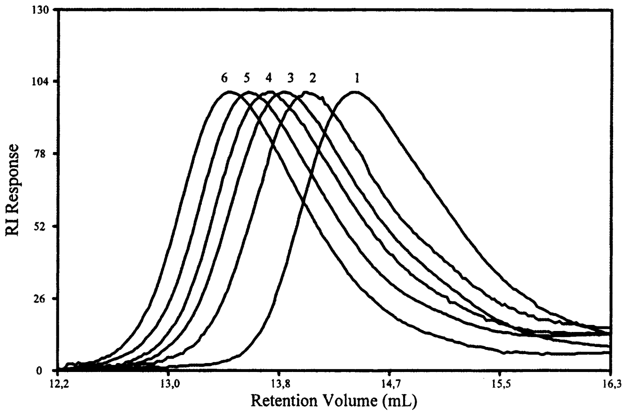

**Figure 5.** SEC traces of PFS as a function of increasing conversion (%). **1**: 26%, $\bar{M}_n$ 8200, $\bar{M}_w/\bar{M}_n$ 1.14; **2**: 42% $\bar{M}_n$ 12 400, $\bar{M}_w/\bar{M}_n$ 1.19; **3**: 48% $\bar{M}_n$ 14 200, $\bar{M}_w/\bar{M}_n$ 1.19; **4**: 62% $\bar{M}_n$ 16 000, $\bar{M}_w/\bar{M}_n$ 1.18; **5**: 86% $\bar{M}_n$ 17 600, $\bar{M}_w/\bar{M}_n$ 1.20; **6**: 90% $\bar{M}_n$ 21 300, $\bar{M}_w/\bar{M}_n$ 1.15. Integration values 12.2 mL ~ $\bar{M}_n$ 79 000 and 16 mL ~ $\bar{M}_n$ 2600.

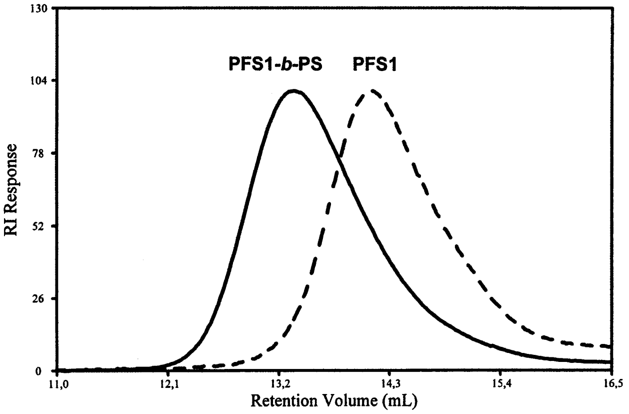

**Figure 6.** SEC traces of macroinitiator PFS1 and the block copolymer PFS1-*b*-PS.

Table 1 also summarizes the results of the ATRP of block copolymers. It can be seen that block copolymers with varying PFS content and molecular weights were prepared. Furthermore, the copolymers almost retain the relatively low polydispersity from the macroinitiator with only a small further increase in polydispersity regardless of which macroinitiator is used. These findings substantiate the ability of FS to be employed in a controlled manner by ATRP.

**Thermal Stability.** The thermal stability in $N_2$ of the FS-containing polymers was investigated by thermogravimetry. Figure 7 depicts representative TGA curves of the total weight loss of PFS1 and one of the block copolymers (PFS1-*b*-PS) compared to both a PS macroinitiator (PS2) and a physical blend of PFS1 and PS2. The degradation plot of the fully phenyl-fluorinated polystyrene (PFS1) has the same shape as PS with comparable molecular weight, however, with an almost 50−60 °C higher thermal stability. This is a result of

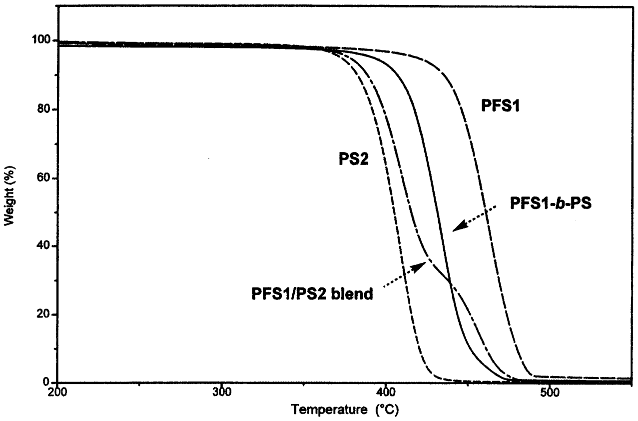

**Figure 7.** Thermal stability of PFS1 (– –), PFS1-*b*-PS (—), PS2 (- - -), and a blend of PFS1 and PS2 (– -) measured by TGA.

**Table 2. Influence of Poly(2,3,4,5,6-pentafluorostyrene) Content in the Polymers on the Thermal Degradation[a] in a Nitrogen Atmosphere**

| polymer | PFS (wt %) | temp (°C) 10% wt loss | 50% wt loss | 90% wt loss |
|---|---|---|---|---|
| PFS1 | 100 | 436 | 461 | 480 |
| PFS-therm[20] | 100 | 396 | 447 | 472 |
| PFS-AiBN[20] | 100 | 423 | 447 | 465 |
| PFS1-*b*-PS | 42 | 409 | 432 | 452 |
| 44% PFS1 56% PS2 blend | 44 | 388 | 415 | 461 |
| PFS-*co*-PS[20] | 47 | 411 | 432 | 448 |
| PS1-*b*-PFS | 51 | 400 | 423 | 448 |
| PS2-*b*-PFS | 21 | 390 | 419 | 436 |
| PS1 | 0 | 379 | 404 | 421 |
| PS2 | 0 | 383 | 405 | 421 |
| PS PSS[20] | 0 | 384 | 406 | 422 |
| PS-AiBN[20] | 0 | 371 | 401 | 419 |
| PS N 2000[20] | 0 | 374 | 402 | 416 |

[a] Heating at 5 °C/min.

**Table 3. Glass Transition Temperature, $T_g$, of PFS[a] as a Function of Molecular Weight**

| $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ | $T_g$ (°C) | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ | $T_g$ (°C) |
|---|---|---|---|---|---|
| 4000 | 1.08 | 76.9 | 11400[b] | 1.21 | 95.3 |
| 8100 | 1.24 | 91.8 | 16000 | 1.18 | 97.7 |
| 9200 | 1.21 | 92.4 | 17600 | 1.20 | 100.8 |
| 10100 | 1.24 | 92.5 | 21300 | 1.15 | 100.5 |
| 10900[b] | 1.13 | 93.5 | 52000[20] | 1.50 | 101.2 |

[a] Prepared by ATRP unless otherwise noted. [b] Samples from Table 1: PFS1 and PFS2.

the significant improvement in thermal stability of polystyrene due to the fluorine substitution on the phenyl rings. In an attempt to compare the thermal stability of different samples, the calculated temperatures for 10%, 50%, and 90% weight loss are listed in Table 2.

The thermal stability of the PFS prepared by ATRP is also higher than that of PFS produced thermally (PFS-therm) or by conventional radical polymerization (PFS-AiBN). As seen in Table 2, all comparable weight losses appear from 8 to 40 °C higher for PFS1 than for any of the other samples. Thus, it seems that the more regular chains resulting from the controlled polymerization ensure higher thermal stability than that of polymers produced by conventional radical polymerization where significant amounts of structural defects resulting from radical–radical termination can occur. On the other hand, molecular mass seems to be of less importance since PFS1 with a $\bar{M}_n$ of 11 400 still has higher stability than PFS-therm and PFS-AiBN with $\bar{M}_n$ of 150 000 and 52 000, respectively. Moreover, this strongly implies that the terminal bromine group in PFS1 does neither decrease nor affect the thermal stability of the PFS chain. Support for this implication is also obtained from the recorded weight losses of the PS series included in Table 2. PS1 and PS2 produced by ATRP in this work have thermal stabilities that are very similar to a PS prepared by anionic polymerization with a similarly low molecular weight. On the other hand, the recorded weight losses of both PS-AiBN and a commercial PS, with higher molecular weights in all cases, start at lower temperatures, and thus these polymers exhibit lower thermal stability. On the basis of these facts, we conclude that regular main chains impart higher thermal stability for both PFS and PS. Furthermore, the terminal benzylic bromine originating from the ATRP initiator does not seem to affect the thermal stability. This is in strong contrast to earlier findings by Ellzey and Novak,[21] who observed an almost 50 °C lower onset decomposition temperature for 10% weight loss for a PS prepared by ATRP with 1-chloro-1-phenylethane and thus containing the benzylic chloride end group. The thermal stability of poly(meth)-acrylates prepared by ATRP has also been addressed by several groups.[22,23] A triazolinyl end group on PMMA has been shown to cause reduced thermal stability as compared to conventional radically polymerized PMMA.[24] In general, one important point and strong recommendation in order to maintain good thermal stability is the careful removal of catalyst residues (copper) from the recovered ATRP polymer.[22,25]

The thermal stability of the block copolymer, PFS1-*b*-PS, with 42 wt % PFS is lowered by approximately 30 °C compared to that of PFS1. A statistical copolymer with 47 wt % PFS but with a considerably higher molecular mass and polydispersity ($\bar{M}_n$ = 154 000, $\bar{M}_w/\bar{M}_n$ = 2.8) also shows this behavior. Other block copolymers with varying, but smaller, amounts of PFS also exhibit degradation "waves" between those of PFS1 and PS2. However, the "waves" are shifted toward the PS "wave" in such a manner that the "wave" position somehow correlates with the PFS content. Nevertheless, a PFS block imparts higher stability to the adjoining PS block. Even a relatively small amount of PFS such as 21 wt % improves the thermal stability of a PS block copolymer by up to 15 °C compared to PS (see Table 2). The degradation temperatures for the characteristic weight losses of all the discussed copolymer samples are summarized in Table 2. On the other hand, the physical blend of PFS and PS demonstrates the expected classical two "waves" behavior.[26] PFS in random copolymers with glycidyl methacrylate has been shown to increase the thermal stability of the copolymers by approximately 50 °C when the FS content is increased by 60 mol %.[17]

**Glass Transition.** Table 3 lists $T_g$ of a range of PFS with varying but increasing molecular masses. The $T_g$ of PFS increases from 77 °C for the sample with $\bar{M}_n$ of 4000 to 92 °C for $\bar{M}_n$ 8100 and levels off at $\bar{M}_n$ = 17 000 to approximately 101 °C. In fact, when $T_g$ is plotted against $1/\bar{M}_n$ (Figure 8), an almost linear relationship is demonstrated. At higher molecular weights no further increase of $T_g$ is observed. This is in contrast to an earlier study[27] in which a $T_g$ of 105 °C was reported but without any specification of the molecular weight influence. We have observed a similar molecular weight/$T_g$ dependence for low molecular weight PS starting at 71

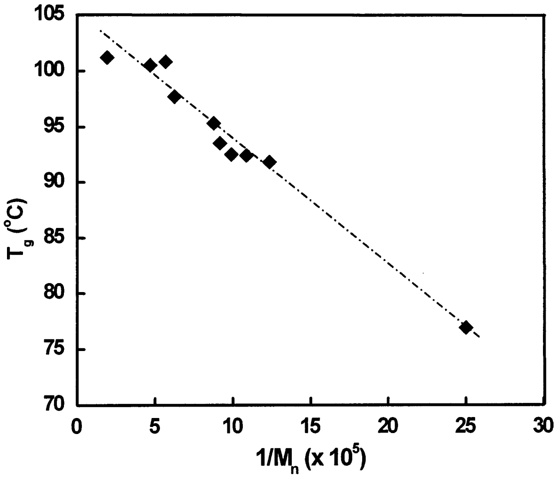

**Figure 8.** Relationship between $T_g$ of PFS and the corresponding 1/$\bar{M}_n$.

°C for $\bar{M}_n = 2300$ and leveling off at approximately 100 °C for $\bar{M}_n = 16\,500$. Most frequently PS $T_g$'s are reported in the 90−100 °C range[28] or even in the 80−110 °C range.[29]

$T_g$ values for the prepared block copolymers are reported in Table 1. As the copolymers are composed of segments of quite similar $T_g$, only one $T_g$ was detected for all the block copolymers, and thus no potential phase separation could be observed. Some influence of block length on $T_g$ was experienced. With low PFS content (PS2-*b*-PFS) or low block copolymer molecular weight (PS1-*b*-PFS) $T_g$'s of 91.7 and 96.5 °C were recorded, respectively. However, with either more than 21 wt % PFS or a block copolymer $\bar{M}_n$ of more than 16 000 a $T_g$ of around 101 °C was determined. Thus, the pentafluoro substituents on the phenyl rings seem to have an almost negligible influence on the $T_g$ of PFS. However, molecular weight is a governing factor in all cases inasmuch as PFS, PS, and block copolymers reach the final achievable $T_g$ value above $\bar{M}_n$ in the 16 000−17 000 range.

**Solubility.** Polymer materials intended for surface coating or thin film applications are often administered from solution by spin-coating or solution casting. Naturally, solubility contrasts chemical resistance to a solvent. Consequently, we addressed these important technological aspects through a thorough investigation of solubility of PFS and some of the block copolymers. The primary criteria for solvent choice, however, were representative solvents that all dissolve >0.5 g of relatively high molecular mass PS in 1 g of solvent.[30] In addition, some other potentially interesting solvents (e.g., highly halogenated) were selected for study.

Table 4 summarizes the solvents that were investigated and reports on the detected solubility at room temperature. In general, the solubilities of the PFS homopolymer and the two copolymers were much lower than that of PS at room temperature with fluorobenzene as an outstanding exception. First, fluorobenzene dissolves 0.413 g of PFS per gram and therefore is a very good solvent for PFS; second, the solubility of the PFS block copolymers in fluorobenzene decreases with increasing PS content, in contrast to any other solvent investigated. Otherwise, the best solubility of PFS was observed in (decreasing order) methyl ethyl ketone, THF, xylene, methyl isobutyl ketone, ethyl acetate, and chloroform, covering a range from 0.143 to 0.027 g of PFS per gram of solvent, whereas dimethoxyethane that dissolves 0.006 g of PFS per gram is considered a marginal solvent. The highly halogenated solvents (hexafluorobenzene and carbon tetrachloride), *o*-dichlorobenzene, acetone, and toluene were poor solvents that dissolve <0.006 g per gram of solvent. Hexachloroacetone and hexafluoro-2-propanol dissolved even less PFS at room temperature (not reported in Table 4). The PS content of the copolymers in many cases significantly improves the solubility (e.g., chloroform, methylene chloride); however, also decreased solubility was observed as for ethyl acetate. It is also noted that heating to 50 °C often only slightly improves the solubility. Our findings on PFS are in agreement with those of Pryor and Huang,[15] except for chloroform which they reported as a nonsolvent. One explanation could be differences in molecular weight. These authors[15] did not specify this, but it was probably relatively high, whereas in the present case PFS is of relatively low molecular weight with narrow polydispersity.

**Table 4. Solubility of Poly(pentafluorostyrene), Copolymers with Styrene, and PS (in g of Polymer/1 g of Solvent at Room Temperature)**

| solvent | PFS | PFS-*b*-PS[a] | PS-*b*-PFS[b] | PS |
|---|---|---|---|---|
| chloroform | 0.027 | 0.062 | 0.118 | >0.7[c] |
| methylene chloride | 0.009 | 0.069 | 0.109 | >0.9[c] |
| carbon tetrachloride | <0.002 | <0.004 | 0.071 | >0.5[c] |
| *o*-dichlorobenzene | <0.002 | <0.002 | <0.002 | >0.5[c] |
| methyl ethyl ketone | 0.143 | 0.226 | 0.349 | >0.9[c] |
| methyl isobutyl ketone | 0.100 | 0.232 | 0.319 | >1.0[c] |
| tetrahydrofuran | 0.125 | 0.146 | 0.159 | >0.9[c] |
| ethyl acetate | 0.089 | 0.034 | 0.017 | >0.9[c] |
| dimethoxyethane | 0.006 | 0.002 | 0.002 | 0.011[d] |
| toluene | <0.002 | <0.008 | 0.008 | >0.9[c] |
| xylene | 0.113 | 0.118 | 0.123 | >1.3[d] |
| fluorobenzene | 0.417 | 0.245 | 0.175 | 0.106[d] |
| hexafluorobenzene | 0.002 | <0.016 | 0.024 | <0.003[d] |

[a] PFS content 55 wt %. [b] PFS content 30 wt %. [c] Reference 30. [d] Solubility investigation performed on PS2.

## Conclusions

Poly(2,3,4,5,6-pentafluorostyrene) can be prepared in high yield at 110 °C under ATRP conditions. The conversion is relatively fast which probably reflects the electron-withdrawing character of the fluorines on the phenyl ring. Furthermore, the polymerization occurs in a controlled manner since the apparent polymerization rate is first order with respect to monomer conversion. In addition, the molecular weight increases linearly with monomer conversion. Finally, the determined molecular weights fit the theoretical values with relatively low polydispersities ($\bar{M}_w/\bar{M}_n \leq 1.2$). The Br-terminated PFS prepared by ATRP can function as a macroinitiator for synthesis of PS containing block copolymers with relatively narrow polydispersities. FS-containing block copolymers can likewise be prepared from a similar PS macroinitiator. FS homo- and block copolymers gain higher thermal stability compared to PS; the extent of the thermal stability is reflecting the relative size of the FS block. The $T_g$ values for PFS and FS block copolymers with styrene depend on the molecular weight up to approximately 16 000 where a final value at around 101 °C is reached. Although the solubility of FS-containing polymers, especially the homopolymer, is much lower than that of PS, the materials can still be handled as solutions. Fluorobenzene is a specially good solvent for PFS and shows reduced solubility for the block copolymers and PS itself. Such solutions may provide opportunities for creation of new low energy, low friction, or higher thermal resistance surfaces cast or spin-coated onto other polymer surfaces. Investigation of these possibilities is under way in our laboratory.

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(19) By use of the relation $\bar{M}_n = (A_{alif}/3)/(A_{ar}/5) \times M_M + M_I$, where $A_{alif}$ and $A_{ar}$ are the areas of the aliphatic (1.8−3.3 ppm) and the aromatic (6.7−7.4 ppm) protons, respectively; $M_M$ and $M_I$ are molecular masses of monomer and initiator, and the molecular mass of PFS could be determined.

(20) PFS-therm is produced by heating FS to 110 °C for 1.5 h without any additives. PFS-AiBN (1.5 h), PFS-*co*-PS (2.5 h), and PS-AiBN (3.5 h) are all prepared with 1 wt % azobis(isobutyronitrile) (AiBN) at 70 °C and recovered after the times indicated in parantheses; the comonomers were in a 1:1 mixture. PS PSS from Polymer Standards Service is prepared by anionic polymerization. PS N 2000 is a sample from SHELL. PFS-therm: $\bar{M}_n = 150\,000$ and $\bar{M}_w/\bar{M}_n = 1.6$. PFS-AiBN: $\bar{M}_n = 52\,000$ and $\bar{M}_w/\bar{M}_n = 1.5$. PFS-*co*-PS: $\bar{M}_n = 154\,000$ and $\bar{M}_w/\bar{M}_n = 2.8$. PS-AiBN: $\bar{M}_n = 34\,200$ and $\bar{M}_w/\bar{M}_n = 1.78$. PS PSS: $\bar{M}_n = 13\,200$ and $\bar{M}_w/\bar{M}_n = 1.03$. PS N 2000: $\bar{M}_n = 85\,000$ and $\bar{M}_w/\bar{M}_n = 3.2$.

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