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ORIGINAL ARTICLE

Novel polystyrene bearing highly branched hexafluoropropene trimer pendants

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Abstract A novel styrenic monomer having hexafluoropropene trimer on the benzene ring was prepared. The highly fluorinated monomer was polymerized to yield a white powdery polymer, which was soluble in fluorinated solvents and had resistance to usual organic solvents, good water repellency, and low refractivity. In contrast to common fluoropolymers having linear-fluorinated side-chains, the polymer has a characteristic high glass transition temperature. Thus, the fluorinated polymer and copolymer with styrene are suitable for applications at elevated temperature. The polymers can replace the conventional fluorinated polyacrylates, which are used in large quantity as repellents with potentially generating perfluorooctanoic acid in the environment.

Keywords Fluoropolymers · Polystyrene · Glass transition · PFOA · Fluorinated polymers

Introduction

The long-lived perfluorinated acid notably perfluorooctanoic acid (PFOA), which accumulates in the human body and environment, have raised worldwide environmental concerns. Fluorinated repellents of polyacrylates and polymethacrylates that contain long perfluoroalkyl groups as side-chains appear to be a source of PFOA that forms in the environment when the polymers degrade. Therefore, it is imperative that versatile materials be found in order to replace such conventional fluorinated repellents [1, 2].

Perfluorinated or highly fluorinated polymers with low surface energy show excellent chemical inertness and water- and oil-repellency, however, their processability are often

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poor because of their insolubility in usual organic solvents. Hybrid polymers comprising hydrocarbon and fluorocarbon segments, such as polyacrylates and polymethacrylates with fluorinated side-chains, combine the unique properties of the highly fluorinated polymers and processability of the conventional hydrocarbon-based polymers [3–5].

Although there exists an environmental concern, such polyacrylates and polymethacrylates with linear perfluoroalkyl side-chains are widely used because of their facile monomer synthesis and polymerization.

We recently prepared a styrenic monomer bearing a hexafluoropropene trimer group, a highly branched perfluorinated pendant, and found it fairly polymerizable and copolymerizable with styrene under radical conditions [6]. Whereas the polymer and copolymer retain characteristics of fluoropolymers such as low surface energy, low refractivity, and resistance to usual organic solvents, their glass transition temperatures are somewhat higher than that of polystyrene indicating that the branched perfluorinated pendant is a good choice for the substituent which does not reduce heat-resistance of the polymers. Moreover, the trimer moiety is expected to decompose to hexafluoropropene without forming PFOA when such polymers degrade in the environment.

In this article, a different type of styrene, which had the hexafluoropropene trimer group directly connected to the benzene ring, was synthesized and the properties of the polymer were evaluated.

Experimental

Materials

A hexafluoropropene trimer mixture containing perfluoro(3-ethyl-2,4-dimethyl-2-pentene) (T3, 69% by GC), perfluoro(3-isopropyl-4-methyl-2-pentene) (T2, 29%), and perfluro(2,4-dimethyl-3-heptene) (T1, 2%) was obtained by oligomerization of hexafluoropropene in the presence of cesium fluoride and a crown ether; distillation of the mixture gave a T2-enriched fraction (T2, 81%) [7]. 4-Bromobenzaldehyde diethylacetal and 2,2′-azobis(isobutyronitrile), obtained commercially, were used without further purification; styrene was distilled from calcium hydride. 4-Perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)-oxy-styrene (FOSt) and its polymer were prepared as described in the literature [6].

4-Perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)benzaldehyde diethylacetal

A 1.6 M hexane solution of *n*-butyllithium (16 mL, 26 mmol) was added dropwise to an ethereal solution (40 mL) of 4-bromobenzaldehyde diethylacetal (5.18 g, 20.0 mmol) at 0 °C under an argon atmosphere. To the solution stirred for additional 0.5 h at 0 °C and cooled at –40 °C, a hexafluoropropene trimer mixture (14.1 g) containing T2 (11.4 g, 25.3 mmol) was added dropwise, and the resulting mixture was stirred for additional 3 h at –40 °C. The mixture was washed with water and the organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvents gave a pale yellow liquid, which was purified by column chromatography (silica-gel; eluent: hexane with 2% ethyl acetate) to give the perfluoroalkylated acetal as a colorless liquid (7.67 g, 63% yield).

The acetal exists as an equilibrium mixture of two rotation isomers A and B (A/B = 1.8/1 at 25 °C), as confirmed by ^{19}F- and ^{1}H -NMR. The isomers can be separated by HPLC; each isomer reverts in part to the other to give the same equilibrium mixture at room temperature within an hour.

GC–MS (EI, 70 eV, isomers mixture) *m*/*z*: 565 $[M–OC_2H_5]^+$ (relative intensity: 100), 537 $[M–OC_2H_5–C_2H_4]^+$ (69), 469 $[C_9F_{15}C_6H_4]^+$ (10), 419 $[C_8F_{13}C_6H_4]^+$ (11), 399 $[C_8F_{12}C_6H_3]^+$ (11), 331 (11), 300 (22), 299 (20), 297 (14), 281 (22), 250 (16), 232 (13), 231 (12), 201 (16), 200 (11), 182 (41), 151 (14), 133 (13), 103 (46), 75 (58), 69 (59), 47 (89).

^{19}F-NMR (isomer A in $CDCl_3$): –63.1 ppm (sept, 3F, $J = 16.7$ Hz), –69.9 (qm, 6F, $J_q = 16.7$), –71.8 (dm, 6F, $J_d = 39.3$), –151.6 (dm, 1F, $J_d = 10.7$), –157.1 (sept d, 1F, $J_{sept} = 39.3$, $J_d = 10.7$); ^{1}H-NMR (isomer A in $CDCl_3$): 7.5–7.6 ppm (m, 2H), 7.16 (d, 2H, $J = 8.1$ Hz), 5.55 (s, 1H), 3.56 (m, 2H), 1.25 (t, 3H, $J = 7.0$).

^{19}F-NMR (isomer B in $CDCl_3$): –56.0 ppm (dm, 3F, $J_d = 64.1$ Hz), –70.0 (s, 6F), –71.3 (d, 6F, $J = 38.2$), –161.9 (qdm, 1F, $J_q = 64.1$, $J_d = 11.8$), –164.2 (sept dm, 1F, $J_{sept} = 38.2$, $J_d = 11.8$); ^{1}H-NMR (isomer B in $CDCl_3$): 7.5–7.6 ppm (m, 2H), 7.42 (d, 1H, $J = 8.1$ Hz), 7.22 (d, 1H, $J = 8.1$), 5.56 (s, 1H), 3.56 (m, 2H), 1.24 (t, 3H, $J = 7.0$).

IR (neat, isomers mixture): 1059 ($C–O–C_2H_5$); 1308–1119, 980 (C–F) cm^{-1}.

4-Perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)benzaldehyde

A tetrahydrofuran solution (70 mL) of 4-perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)benzaldehyde diethylacetal (7.00 g, 11.5 mmol) and an aqueous solution (6 mL) of *p*-toluenesulfonic acid monohydrate (0.35 g, 1.8 mmol) were mixed and refluxed for 0.5 h. The mixture was diluted with ether, washed with water and aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$. Evaporation of the solvents and purification by column chromatography (silica-gel; hexane with 2% ethyl acetate) gave the perfluoroalkylated benzaldehyde as a colorless liquid (5.39 g, 88% yield).

The aldehyde exists as an equilibrium mixture of two rotation isomers C and D (C/D = 3.8/1 at 25 °C), as confirmed by ^{19}F- and ^{1}H-NMR.

GC–MS (EI, 70 eV, isomers mixture) *m*/*z*: 536 M^+ (relative intensity: 58), 535 $[M–H]^+$ (91), 469 $[C_9F_{15}C_6H_4]^+$ (16), 419 $[C_8F_{13}C_6H_4]^+$ (24), 369 $[C_7F_{11}C_6H_4]^+$ (23), 350 (16), 300 (26), 297 (47), 281 (28), 250 (53), 231 (22), 201 (20), 200 (26), 182 (19), 69 (100), 51 (17), 50 (16).

^{19}F-NMR (isomer C in $CDCl_3$): –62.5 ppm (sept, 3F, $J = 16.6$ Hz), –69.8 (m, 6F), –71.7 (dm, 6F, $J_d = 39.6$), –150.6 (dm, 1F, $J_d = 10.2$), –157.2 (sept d, 1F, $J_{sept} = 39.6$, $J_d = 10.2$); ^{1}H-NMR (isomer C in $CDCl_3$): 10.1 ppm (s, 1H), 7.9–8.0 (m, 2H), 7.37 (d, 2H, $J = 8.1$ Hz).

^{19}F-NMR (isomer D in $CDCl_3$): –54.9 ppm (dm, 3F, $J_d = 66.3$ Hz), –69.8 (s, 6F), –71.2 (d, 6F, $J = 37.3$), –162.1 (qdm, 1F, $J_q = 66.3$, $J_d = 11.7$), –164.5 (sept dm, 1F, $J_{sept} = 37.3$, $J_d = 11.7$); ^{1}H-NMR (isomer D in $CDCl_y$): 10.1 ppm (s, 1H), 7.9–8.0 (m, 2H), 7.43 (d, 2H, $J = 7.8$ Hz).

IR (neat, isomers mixture): 1713 (CH=O); 1308–1119, 982 (C–F) cm^{-1}.

4-Perfluoro(2-isopropyl-1,3-dimethyl-1-butenyl)styrene (FSt)

A 1.6 M hexane solution of *n*-butyllithium (9.5 mL, 15 mmol) was added dropwise to an ethereal suspension (27 mL) of methyltriphenylphosphonium bromide (5.40 g, 15.1 mmol) at 0 °C under an argon atmosphere. To the mixture stirred at room temperature for 0.5 h and cooled again in an ice-water bath, 4-perfluoro (2-isopropyl-1,3-dimethyl-1-butenyl)benzaldehyde (2.70 g, 5.04 mmol) was added over 10 min. The resulting mixture was stirred at room temperature for 2 h, poured in water, and extracted twice with ether. The combined ether layers were washed with water and dried with anhydrous $MgSO_4$. Evaporation of the solvents and purification by column chromatography (silica-gel; eluent: hexane) gave the FSt monomer as a colorless liquid (1.31 g, 49% yield).

B.p. 38.5–39 °C/0.03 Torr.

The FSt monomer exists as an equilibrium mixture of two rotation isomers E and F (E/F = 1.8/1 at 25 °C), as confirmed by ^{19}F- and ^{1}H -NMR.

GC–MS (EI, 70 eV, isomers mixture) *m*/*z*: 534 M^+ (relative intensity: 94), 515 $[M–F]^+$ (17), 465 $[M–CF_3]^+$ (95), 396 $[M–C_2F_6]^+$ (100), 327 $[M–C_3F_9]^+$ (53), 307 (17), 296 (26), 276 (25), 227 (60), 208 (29), 177 (35), 69 (57).

^{19}F-NMR (isomer E in $CDCl_3$): –63.2 ppm (sept, 3F, $J = 16.6$ Hz), –69.9 (m, 6F), –71.7 (dm, 6F, $J_d = 39.1$), –151.7 (dm, 1F, $J_d = 11.7$), –157.2 (sept d, 1F, $J_{sept} = 39.1$, $J_d = 11.7$); ^{1}H-NMR (isomer E in $CDCl_3$): 7.4–7.5 ppm (m, 2H), 7.13 (d, 2H, $J = 8.1$ Hz), 6.73 (dd, 1H, $J_{d1} = 17.5$, $J_{d2} = 10.9$), 5.84 (dd, 1H, $J_{d1} = 17.5$, $J_{d2} = 8.2$), 5.37 (dd, 1H, $J_{d1} = 10.9$, $J_{d2} = 8.2$).

^{19}F-NMR (isomer F in $CDCl_3$): –56.2 ppm (dm, 3F, $J_d = 64.4$ Hz), –70.0 (s, 6F), –71.3 (d, 6F, $J = 39.2$), –161.9 (qdm, 1F, $J_q = 64.4$, $J_d = 11.7$), –164.3 (sept dm, 1F, $J_{sept} = 39.2$, $J_d = 11.7$); ^{1}H-NMR (isomer F in $CDCl_3$): 7.4–7.5 ppm (m, 2H), 7.18 (d, 2H, $J = 8.1$ Hz), 6.72 (dd, 1H, $J_{d1} = 17.7$, $J_{d2} = 11.1$), 5.84 (dd, 1H, $J_{d1} = 17.7$, $J_{d2} = 8.2$), 5.37 (dd, 1H, $J_{d1} = 11.1$, $J_{d2} = 8.2$).

IR (neat, isomers mixture): 1609, 1508 (benzene); 1404, 918 (vinyl); 1308–1121, 980 (C–F) cm^{-1}.

Bulk polymerization

The FSt monomer and 2,2′-azobis(isobutyronitrile) as the radical initiator were placed in an ampoule, and the mixture was degassed by successive freeze–thaw cycles. The polymerization was done at 60 °C in vacuo, after which the mixture was diluted with hexafluorobenzene and poured into methanol. The polymer that precipitated was collected and dried in vacuo then purified twice by reprecipitation from methanol.

Found: C, 36.62%; H, 1.61%; F, 60.43%. Calcd. for $C_{17}H_7F_{17}$: C, 38.22%; H, 1.32%; F, 60.46%.

IR (KBr): 1611, 1508 (benzene); 1310–1119, 980 (C–F) cm^{-1}.

Copolymerization of FSt and styrene was done by a method similar to that described above. The copolymers formed were dissolved in hexafluorobenzene (or tetrahydrofuran), precipitated in methanol, and purified by reprecipitation.

Instruments

IR spectra were obtained with a Shimadzu FTIR-8600PC spectrophotometer. Mass spectra were taken with a Shimadzu QP-5000 instrument at 70 eV. ^{1}H-NMR (300.0 MHz) and ^{19}F-NMR (282.2 MHz) measurements were recorded on a Varian UNITY INOVA-300, the chemical shifts being defined as δ values relative to TMS and $CFCl_3$, respectively. GPC was performed with a couple of TOSOH GMH6 columns and chloroform as the eluent, or with a Polymer Laboratories PLgel MIXED-C column and $CF_3CF_2CHCl_2/CClF_2CF_2CHClF$ (1/1). Glass transition temperatures and thermal decomposition temperatures of polymers were measured with a Shimadzu DSC-50 differential scanning calorimeter and a TG-50 thermogravimeter. Contact angles of water droplets to polymer film surfaces were measured with an Erma G-1 goniometer.

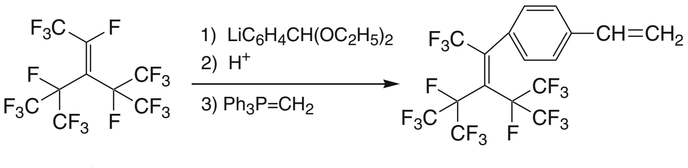
Results and discussion

Monomer preparation

A novel styrenic monomer, FSt, was prepared as shown in Scheme 1. The phenyllithium reacted with a hexafluoropropene trimer T2 to give the monomer precursor, in which the trimer group is directly bonded to the benzene ring. The vinyl group was introduced by the Wittig reaction.

As shown in Fig. 1, ^{19}F-NMR revealed the FSt monomer to exist as a mixture of rotation isomers at room temperature [8]. The population of the isomers indicates comparable steric hindrance of the benzene ring and trifluoromethyl group at the same carbon of the double bond with respect to the conformation of the gear-meshed heptafluoroisopropyl groups at the other carbon of the double bond. Although the isomers can be separated by HPLC, the each isomer reverts in part to the other thus affording the equilibrium mixture within an hour at ambient temperature. The slow isomerization due to the barrier to rotation of the heptafluoropropyl groups indicates the rotation about the C–C bond between the benzene ring and the trimer group is restricted as well.

In contrast to the FSt monomer, FOSt having the trimer group attached to the benzene ring with the ether linkage can be easily prepared from hexafluoropropene trimer and hydroxystyrene (Fig. 1). Rotation isomers of FOSt are not found at room temperature.



Scheme 1 FSt monomer preparation

Polymerization and polymer properties

Homopolymerization of FSt and copolymerization with styrene were done in bulk with 2,2′-azobis(isobutyronitrile) as the radical initiator. As shown in Table 1, the FSt homopolymer was obtained although the radical homopolymerization rate of FSt in bulk was significantly slow with the small degree of polymerization, compared with those for St and FOSt.

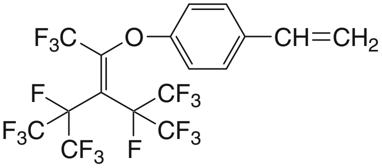
The FSt homopolymer was insoluble in the non-fluorinated organic solvents tested but soluble in hexafluorobenzene, *m*- and *p*-bis(trifluoromethyl)benzene, 1,1,2-trichlorotrifluoroethane, and a mixed solvent of $CF_3CF_2CHCl_2/CClF_2CF_2CHClF$ (1/1).

The molecular weight of polyFSt determined by GPC is sufficiently high to give a self-supporting film. The film formed by casting the hexafluoro-benzene solution of the polymer on a glass surface and evaporation of the solvent has good water repellency with the contact angle of 112°, comparable to that of poly(tetrafluoroethylene) (108°) [9]. The low surface energy of the polymer is attributed to the trifluoromethyl groups in its highly branched perfluorinated moieties [10]. Due to its high fluorine content, the polymer film has a significantly low refractive index.

The copolymerization gave poly(St-*co*-FSt)s with good solubility in the usual organic solvents such as chloroform, toluene, and tetrahydrofuran (e.g., copolymers with 2.2, 18.5, and 30.3% FSt). The copolymers with 18.5 and 30.3% FSt are partly soluble in fluorinated solvents as well. ^{19}F-NMR spectra of the FSt monomer and its copolymer show that the perfluoroalkenyl moiety of FSt was intact throughout the polymerization (Fig. 2). The molecular weights of the copolymers are in the range of ca. 5×10^4–1×10^5, which are somewhat low compared with that of polySt prepared under the similar condition.

The monomer reactivity ratios were determined based on the copolymerization data in Table 1 by means of the Mayo-Lewis integrated equation and the Kelen–Tüdős linear least-squares procedure [11] giving $r_{FSt} = 0.90$ and $r_{St} = 0.36$. The calculated composition curve for the copolymerization and plots of the experimental data are shown in Fig. 3. The reactivity of FSt as a monomer is higher than that of styrene and FOSt ($r_{FOSt} = 0.73$ and $r_{St} = 0.62$ [6]) in the radical copolymerizations, although the polymerization rate is markedly reduced by FSt, which indicates the significantly low reactivity of the FSt radical of the propagating chain end. The reduced reactivity would be attributed to the hindered structure of the FSt radical.

Tough copolymer films were also obtained by casting the chloroform solutions on glass surfaces. As the fluorine content of the copolymer increased, the contact angle of water to the copolymer surface also increased (Table 2). The copolymer



FOSt

Fig. 1 FOSt molecular structure

Table 1 Bulk copolymerization of FSt and styrene with 0.10 mol.% AIBN at 60 °C in vacuo

Run	Feed		Time (h)	Yield (g(%))	Polymer		
	FSt (g)	St (g)			FSt (mol.%[a])	M_n[b] (10^4)	M_w/M_n
1	1.00	–	96	0.170 (17)	–	7.6	2.2
2	0.855	0.0417	72	0.186 (21)	80.9	9.2	2.2
3	0.641	0.0833	72	0.156 (22)	65.4	6.8	2.3
4	0.427	0.125	72	0.153 (28)	50.2	6.0	2.4
5	0.427	0.333	48	0.270 (36)	30.3	4.7	2.5
6	0.534	0.937	24	0.412 (28)	18.5	6.1	2.0
7	0.054	1.03	12	0.286 (26)	2.2	9.9	1.9
8	–	1.04	12	0.290 (28)	–	10.8	1.9
9	FOSt						
	5.00	–	5	2.15 (43)	–	23.6	2.2

[a] Determined by elemental analysis (F%)

[b] Determined by GPC correlating to standard poly(dimethylsiloxane)s in $CF_3CF_2CHCl_2/CClF_2CF_2CHClF$ for runs 1–5, 9 and standard polystyrenes in $CHCl_3$ for runs 6–8

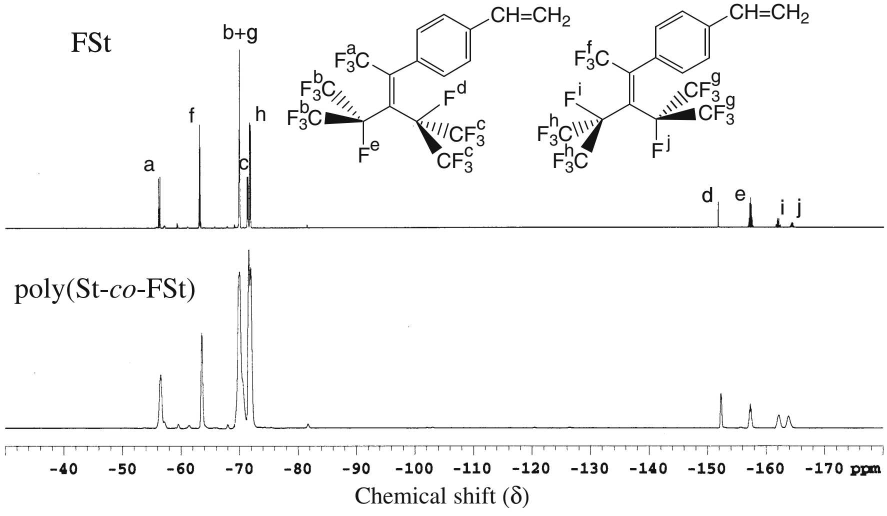


Fig. 2 ^{19}F-NMR spectra of FSt monomer and poly[St-*co*-FSt (18.5%)] in $CDCl_3$; the chemical shift defined with $CFCl_3$ as the reference

containing 18.5% FSt combines good solubility in most organic solvents and marked water repellency comparable to that of the homopolymer.

Glass transition

DSC curves of the polymers are shown in Fig. 4. The glass transition of polyFSt occurs at a higher temperature than that of polySt, which is attributable to the bulky,

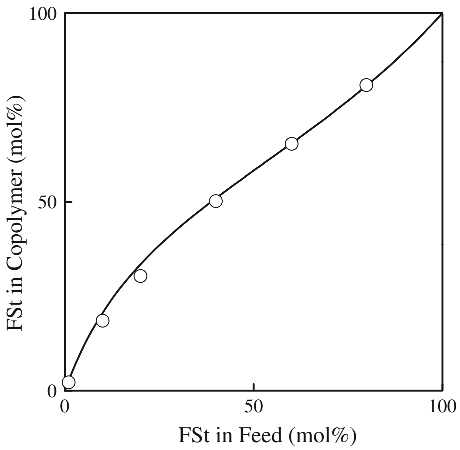


Fig. 3 Calculated composition curve for copolymerization of FSt with styrene; *plots* indicate the experimental data

Table 2 FSt Polymer properties

Polymer	CA[a] (deg.)	n_D^{20}	T_g^b (°C)
PolyFSt	112	1.410	158
Poly[St-*co*-FSt (65.4%)]	–	–	145
Poly[St-*co*-FSt (18.5%)]	105	–	115
Poly[St-*co*-FSt (2.2%)]	99	–	102
PolySt	92	–	102
PolyFOSt	111	1.415	124

[a] Contact angle of water at 25 °C

[b] Glass transition temperature determined by DSC in the 2nd heating (10 °C/min)

highly branched perfluorinated trimer moieties that restrict motion of the polymer backbones. The hindered rotation about the carbon–carbon bond between the benzene ring and the trimer group in polyFSt would make the polymer backbone stiffer than that of polyFOSt resulting in the glass transition at higher temperature. This enhanced T_g of polyFSt contrasts well with the lowered T_gs of polystyrenes that have linear polyfluoroalkyl groups [12–14], in which the plasticizing effects of the side-chains are thought to have a role in their glass transitions. For instance, the T_gs of polystyrenes with p-$CF(CF_3)_2$ [15], p-C_7F_{15} [16], p-$CH_2OCH_2CH_2C_4F_9$, p-$CH_2OCH_2CH_2C_6F_{13}$, and p-$CH_2OCH_2CH_2C_8F_{17}$ [14] are 108, 47, 15, 19, and 55 °C (melting peak 82 °C), respectively.

PolyFSt and polyFOSt began to degrade at lower temperatures than polySt and decomposed more rapidly as shown in Fig. 5. Steric repulsion between the repeating units in the polymers would be the cause for the thermal instability, although the difference in the decomposition behavior of polyFSt and polyFOSt is not marked.

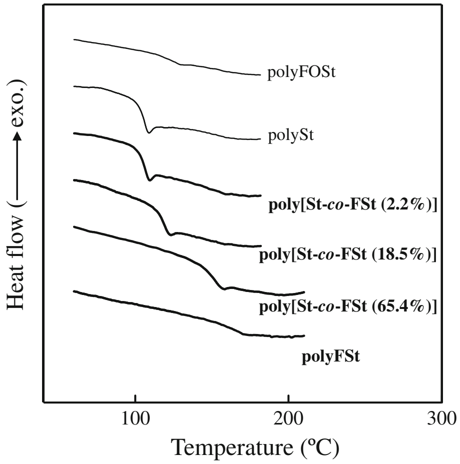


Fig. 4 Glass transition traces of polyFSt and poly(St-*co*-FSt)s recorded by DSC in the 2nd heating (10 °C/min)

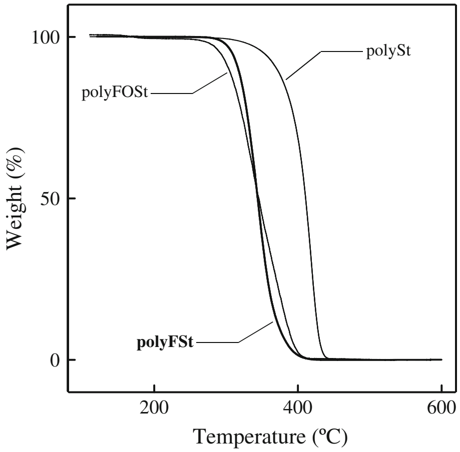


Fig. 5 Thermal weight loss curves recorded by TG at 10 °C/min under inert atmosphere

Conclusion

Polystyrene having hexafluoropropene trimer pendants directly connected to the benzene rings was prepared. The highly fluorinated polymer has an enhanced glass transition temperature in contrast to polymers having linear fluorinated side-chains. Whereas the polymerization rate was reduced by the fluorinated monomer, the copolymers with styrene having good processability, water repellency, and high glass transition temperatures were attained.

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