Semifluorinated ABA Triblock Copolymers: Synthesis, Characterization, and Amphiphilic Properties

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ABSTRACT: In this study a series of novel semifluorinated ABA triblock copolymers with different fluorinated segment lengths and different fluorocarbon side-chain structures were synthesized via atom transfer radical polymerization (ATRP) and macroinitiator techniques. The macroinitiator, telechelic bromine terminated polystyrene, was obtained from bulk ATRP of styrene with α,α'-dibromo-*p*-xylene as the initiator and cuprous bromide/α,α'-bispyridine complex as the catalyst. The polymerization reactions of 2-[(perfluorononenyl)oxy] ethyl methacrylate and ethylene glycol monomethacrylate monoperfluorooctanoate were initiated by the macroinitiator in the presence of additional catalyst. The characterization of the block copolymers was performed by gel permeation chromatography, ^{1}H-NMR spectroscopy, and differential scanning calorimetry. The surface activities of the block copolymers in toluene were investigated with the Wilhelmy plate method. The solid surface energy of the block copolymers was determined by measurement of the contact angles. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2625–2633, 2002

Key words: fluorinated block copolymer; atom transfer radical polymerization; characterization; properties

INTRODUCTION

A polymer that contains fluorine moieties in the chain exhibits superior chemical and thermal stability, biocompatibility, and extremely low surface energy. Because of these unique properties, many research efforts have contributed to exploring the preparation of fluorinated polymers. Of particular interest are block copolymers containing both fluorinated and nonfluorinated segments. The potential applications of fluorinated block copolymers are quite diverse. For example, they can be used to reduce the surface energy of a bulk material,[1] as a solution state viscosity modifier,[2] and as a surfactant containing a "CO_2-philic" segment for reactions in supercritical CO_2.[3]

It is well known that living polymerization methodology is the most efficient tool for synthesis of well-defined block copolymers. However, the need for high-purity monomers and solvents, reactive initiators, and anhydrous conditions have dramatically limited the industrial application of many techniques based on ionic and group transfer polymerization processes. Fortunately, in recent years there has been a significant advance in "living" radical polymerization. The main systems include 2,2,6,6-tetramethyl piperidinyl-1-oxy (TEMPO) mediated radical polymerization,[4] atom

$$P \!-\! X \;+\; M_t^n X / L \;\underset{k_d}{\overset{k_a}{\rightleftharpoons}}\; P\cdot \;+\; M_t^{n+1} X_2 / L$$

$$(+M) \; k_p$$
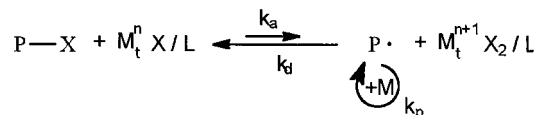
Scheme 1 The method of atom transfer radical polymerization.

transfer radical polymerization (ATRP),[5] and reversible addition fragmentation chain transfer (RAFT) polymerization.[6] Generally, the TEMPO system is only suited for styrene and its derivatives and in the RAFT process dithioesters as chain transfer agents can result in colored polymers or give some odor for low molar mass species. ATRP utilizes a simple organic halide (R-X) as an initiator and a transition metal complex (M_t^nX/L) as a catalyst. After initiation, the polymerization occurs by establishing a fast equilibrium between active species (P•) and dormant species (P-X) based on redox cycles (Scheme 1). ATRP has been applied for the precise control of the polymer architecture of vinyl monomers such as acrylics, styrenics, and dienes.[7]

In this article our work focuses on the synthesis, characterization, and properties of the triblock copolymers composed of styrene and fluorinated methacrylate (MA) segments. The effects of the lengths of the fluorinated segments and the structures of the pendant fluorocarbon side chains on the thermal transition behavior, solution, and solid-state surface properties of the block copolymers were also investigated.

EXPERIMENTAL

Materials

Styrene was washed with 5% NaOH and ion-free water, dried over $CaCl_2$ overnight, and then vacuum distilled from finely powdered CaH_2 before use. α,α'-Dibromo-p-xylene (DPX) was prepared as reported.[8] Cuprous bromide (AR, Shanghai No. 1 Chemical Reagent Factory) was purified according to the procedure of Keller and Wycoff.[9] Benzotrifluoride (99%, Fluka) was used as received. α,α'-Bispyridine (BPY, AR, Shanghai No. 1 Chemical Reagent Factory) was recrystallized from n-hexane. β-Hydroxyethyl MA (HEMA 95%, Fluka) was used as received. Hexafluoropropylene trimer and perfluorooctanic acid were kindly supplied by Shanghai Institute of Organo-Fluorine Materials. 2-[(Perfluorononenyl)oxy] ethyl MA (FNEMA) and ethylene glycol monomethacrylate monoperfluo-

rooctanoate (EGMAFO) were synthesized by the reaction of hexafluoropropylene trimer and perfluorooctanoic acid with HEMA, respectively.[10] Toluene was dried over CaH_2 and distilled. The n-alkanes (octane, decane, docane, and tetradecane; >99%, Fluka) were used as received.

Polymerization Procedure

The catalyst, initiator, and ligand were added to a 50-mL one-necked round bottom flask equipped with a stopcock and a magnetic stirring bar. The reaction flask was tightly sealed with a rubber septum, degased under a vacuum, and charged with nitrogen (3 times). The monomers and solvents were purged with nitrogen just before use and then introduced by syringe. The reaction mixture was immersed in an oil bath heated at a desired temperature. The polymer samples were isolated by precipitation with methanol. Samples for gel permeation chromatography (GPC) measurement were purified via passing them through a column of alumina.

Characterization

The monomer conversion was determined gravimetrically.

The molecular weight (MW) and MW distribution were measured on a Waters 150C gel permeation chromatograph equipped with Ultrastyragel columns of 100 and 10,000 Å porosities using tetrahydrofuran as the eluent. Narrow MW distribution polystyrene (PS) standards were used for calibration.

The copolymer structures were analyzed using a Bruker 500-MHz ^{1}H-NMR spectrometer. $CDCl_3$ was used as the solvent.

The glass-transition temperature (T_g) was determined using a differential scanning calorimetry device (DSC-SP, Rheometric Scientific Co.) equipped with a liquid nitrogen subambient cooling accessory and employing nitrogen as the purge gas. Samples (ca. 10 mg) were pretreated at 140°C for 3 min, quenched rapidly to −50°C, and scanned upward at 10°C/min. The quoted T_g values are the second onset temperature as computed with Rheometric Scientific 6.4.3 software.

The surface tension was measured in toluene at 25°C using the Wilhelmy plate method.[11] The contact angles were measured with the sessile drop method (JY-82 series instrument) at 20°C. Copolymer solutions in tetrahydrofuran (1%) were filtered through 0.45-μm microporous membrane filters. Thin copolymer coatings were pre-
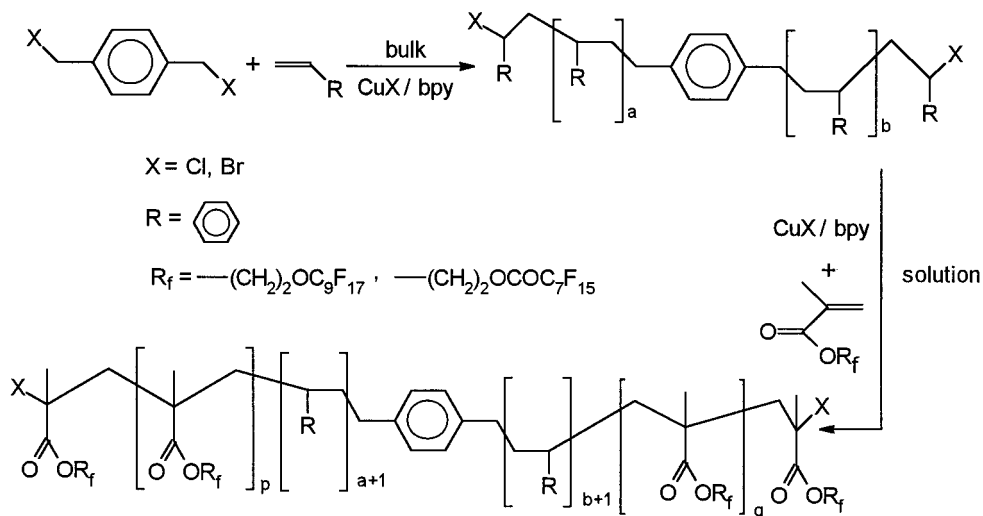
Scheme 2 The synthesis of fluorocarbon/hydrocarbon triblock copolymers by atom transfer radical polymerization.

pared by slow dipping of cleaned microscope glass coverslips (15 × 15 mm). The films were dried under a vacuum at room temperature for 1 day and then heated at 80°C for about 14 h. A homologous series of n-alkanes (octane, decane, docane, tetradecane) was used as the wetting liquids. In each case, five drops on different sites of the surface were analyzed and the contact angle was averaged over five measurements.

RESULTS AND DISCUSSION

In the past decade a wide range of block copolymers have been prepared. Most systems in academic research consist only of common monomers. The goal of our research is based on the idea to present a new strategy for the controlled and simultaneous formation of fluorine-containing block copolymers. These block copolymers should exhibit distinct differences in their micelle formation, solubilization behavior, and air–polymer interface energy to create a macroscopic system with properties and abilities superior to common polymers.

Synthesis and Characterization

The ATRP of styrene was performed at 110°C with DPX as the difunctional initiator and CuBr/BPY complex as the catalyst. This process produces telechelic bromine terminated polystyrene ($M_{n,\text{GPC}} = 6242$; $M_w/M_n = 1.37$). In order to elucidate the relationship between the properties

of the fluorinated block copolymers and the length of the fluorinated segments, as well as the structure of the pendent fluorocarbon side chains, two MAs containing branched perfluorononenyl (FNEMA) and linear perfluorooctyl (EGMAFO) were synthesized and then polymerized at 100°C in benzotrifluoride using telechelic bromine terminated PS as the macroinitiator and CuBr/BPY as the catalyst, respectively (Scheme 2).

The typical ^{1}H-NMR spectrum of the resulting copolymer is shown in Figure 1. The signals at 4.13 ppm correspond to the two methylenes of the ester group of FNEMA, and the peaks at 6.6–7.1 ppm can be assigned to the aromatic protons in the styrene unit.

Figure 2 gives the GPC traces of the copolymers and the macroinitiator. The monomodal shape of the GPC trace of the obtained copolymer suggests the formation of block copolymer without homopolymerization. No observable peak of the macroinitiator from the size exclusion chromatography trace of the block copolymer indicates the complete initiation of the macroinitiator. However, an interesting phenomenon was found: a high MW shoulder appeared in the GPC trace of the block copolymer containing an EG-MAFO segment. This may be responsible for the coupling reaction between the block copolymer active chains, which would lead to doubling of the MW and to decreasing the number of chains in the polymerization system. Unlike EGMAFO, there is a bulky branched fluoroalkyl group linking to the ester moiety in the molecular structure of FNEMA. The steric effect reduces the reactiv-
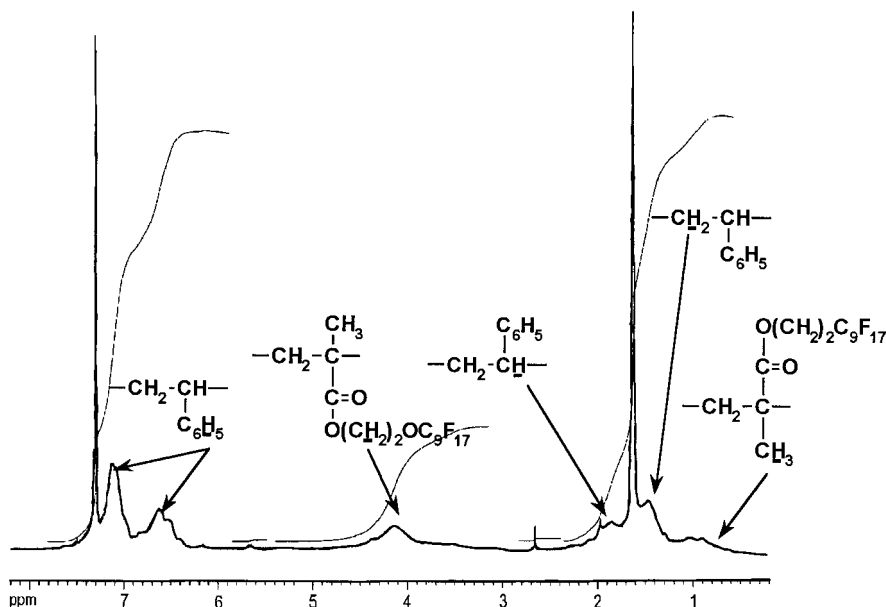
Figure 1   A 500-MHz ^{1}H-NMR spectrum of PFNEMA-*b*-PS-*b*-PFNEMA prepared by ATRP with CDCl$_3$ as the solvent.

ity of propagating species in the course of polymerization. As a result, the block copolymerization of PS with FNEMA exhibits better control

PEGMAFO-PSt-PEGMAFO

PFNEMA-PSt-PFNEMA

Figure 2   GPC traces of the (—) semifluorinated triblock copolymers and (- - -) macroinitiator.

behavior than that with EGMAFO. Similar results were obtained from ATR homopolymerization of FNEMA and EGMAFO.[12]

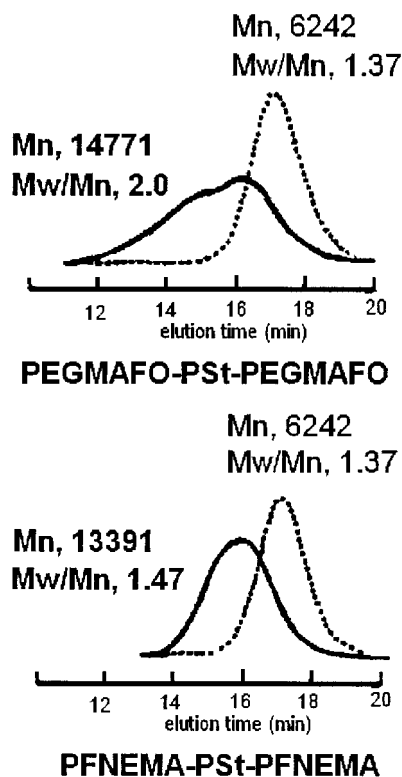The number-average molecular weights (M_n) and polydispersities (M_w/M_n) of the block copolymers are summarized in Table I. As shown in Table I, the molecular weights of the block copolymers determined by GPC increase with the initial concentration of fluorinated monomers and are close to their calculated values ($M_{n,\text{th}} = [M]_0/[I]_0 \times$ MW $\times$ convn. $+ M_I$). The data of the MW obtained from ^{1}H-NMR gives comparable results. Moreover, the polydispersities of the block copolymers are low except for the 1 : 3.5 PEGMAFO-PS-PEGMAFO sample (2.0).

The transition temperatures of the block copolymers determined by DSC are listed in Table II. Typical DSC traces are shown in Figure 3. In order to eliminate the effect of thermal history on sample transitions, all samples were heated to 140°C, held there for 3 min before quenching to −50°C, and then heated at a rate of 10°C/min. The tabulated DSC data are collected from the second run. As shown in Table II, all block copolymers have two glass-transition temperatures T_{g_1} and T_{g_2}. Obviously, the block copolymer phase separates into two different phases because of the incompatibility of the PS and the fluorinated block. The lower glass-transition temperature corresponds to the fluorinated segment while the higher temperature is assigned to the PS moiety.

Table I   Results of Block Copolymerization of Fluoroalkyl Methacrylates with Telechelic Bromine Terminated Polystyrene

Sample (PS/EGMAFO or FNEMA, g/g)	$M_{n,\mathrm{GPC}}$	$M_{n,\mathrm{NMR}}$ [a]	$M_{n,\mathrm{th}}$	M_w/M_n	Yield[b] (%)
PEGMAFO-PS-PEGMAFO (1 : 0.8)	9233	9398	7237	1.38	64.8
PEGMAFO-PS-PEGMAFO (1 : 2.4)	12311	17814	11575	1.66	55.0
PEGMAFO-PS-PEGMAFO (1 : 3.5)	14771	33068	17977	2.0	64.3
PFNEMA-PS-PFNEMA (1 : 0.8)	8612	9602	7191	1.34	64.3
PFNEMA-PS-PFNEMA (1 : 2.4)	10950	12962	10724	1.41	50.9
PFNEMA-PS-PFNEMA (1 : 3.5)	13391	16882	16530	1.47	59.0

Solution polymerization conditions: $[\mathrm{EGMAFO}]_0 = 9.81 \times 10^{-2}$, 2.77×10^{-1}, and 3.87×10^{-1} M; $[\mathrm{FNEMA}]_0 = 9.22 \times 10^{-2}$, 2.60×10^{-1}, and 3.63×10^{-1} M; $[\mathrm{Br\text{-}PS\text{-}Br}]_0 = (9.3\text{–}10.3) \times 10^{-3}$ M; $[\mathrm{Br\text{-}PS\text{-}Br}]_0/[\mathrm{CuBr}]_0/[\mathrm{BPY}]_0 = 1 : 5 : 14$; and 100°C reaction temperature.

[a] Determined from ^{1}H-NMR and the M_n of the macroinitiator.
[b] The yield of the block copolymer equals the weight of the obtained copolymer divided by the total weight of added monomer and macroinitiator.

The thermal curve of the block copolymer with EGMAFO segments shows a pronounced melting endotherm at $[T_m(\max)]$ 27.4°C and an enthalpy of fusion (ΔH) of 9.0 J/g (Fig. 3). As the weight fraction of EGMAFO in the block copolymer increases, the enthalpy of fusion grows from 9.0 to 17.3 J/g (Table II). Because the block copolymers are formed under atactic ATRP conditions and PFNEMA-PS-PFNEMA triblock copolymers do not crystallize, the crystallinity of PEGMAFO-PS-PEGMAFO triblock copolymers is assumed to occur as a result of linear fluoroalkyl side-chain packing and to not involve the backbone.

Solution Properties

For amphiphilic polymers, surface activity has to be added as a key property. The property is attributed to the intramolecular formation of hydrophobic domains, often referred to as "polymeric micelles," analogous with micelles formed from standard surfactants.

The curves of the surface tension versus the polymer concentration for the series with perfluorooctyl and perfluorononenyl are given in Figures 4 and 5, respectively. All block copolymers show a declining surface tension with increasing copolymer concentration. At the same copolymer concentration, the higher the fraction of fluorine that the copolymer contains, the more quickly the surface tension decreases. Although the surface tension value of the block copolymer with a linear fluorocarbon side chain is lower than that with a branched fluorocarbon side chain, the latter seems to have a steeper descent.

The surface activity of fluorine-containing block copolymers is intensely dependent on the effective and efficient use of fluorine. The former refers to the amount that the addition of fluorine lowers the surface tension relative to the parent material, and the latter refers to the minimum concentration of fluorine necessary to reach the minimum surface tension. These effects can be estimated quantitatively by the Gibbs adsorption equation[13]:

Table II   Results of Differential Scanning Calorimetry Analysis for Semifluorinated Triblock Copolymers

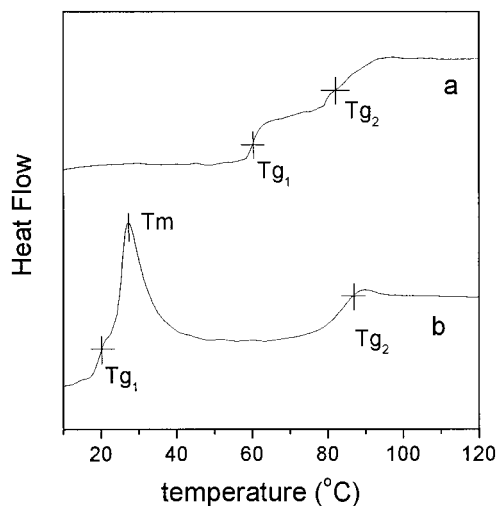| Sample (PS/EGMAFO or FNEMA, g/g)	T_{g_1} (°C)	T_{g_2} (°C)	T_m (°C)	ΔH (J/g)
PEGMAFO-PS-PEGMAFO (1 : 0.8)	34.3	86.7	ND	ND
PEGMAFO-PS-PEGMAFO (1 : 2.4)	22.8	90.8	27.4	9.0
PEGMAFO-PS-PEGMAFO (1 : 3.5)	22.8	89.4	28.6	17.3
PFNEMA-PS-PFNEMA (1 : 0.8)	50.1	88.0	ND	ND
PFNEMA-PS-PFNEMA (1 : 2.4)	60.2	84.4	ND	ND
PFNEMA-PS-PFNEMA (1 : 3.5)	60.3	82.8	ND	ND

ND, not detected.

Figure 3 A DSC plot (second heating) of the semifluorinated triblock copolymers (a) PFNEMA-PS-PFNEMA (1 : 3.5) and (b) PEGMAFO-PS-PEGMAFO (1 : 3.5).

$$\gamma = f^{\sigma} - \sum_i \Gamma_i \mu_i^{\sigma} \tag{1}$$

where γ is the surface tension, Γ_i is the surface excess of the ith component in moles per unit area of the surface σ, μ_i^{σ} is the surface chemical potential of the ith component, and f^{σ} is the Helm-
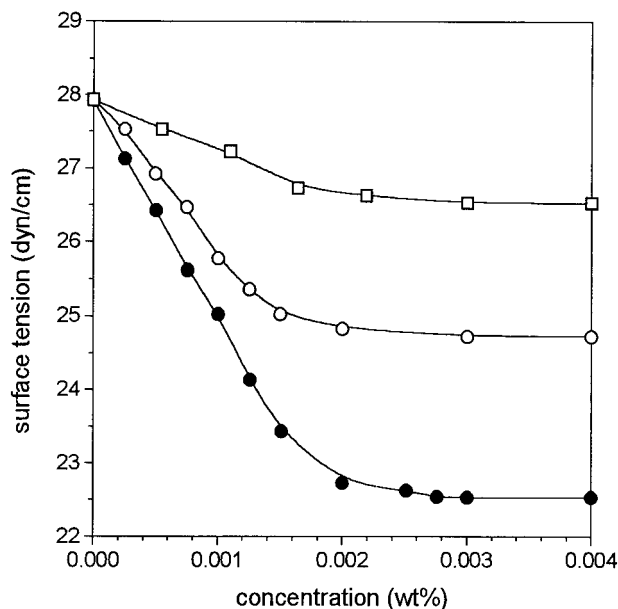
Figure 4 The surface tension as a function of the polymer concentration for the PEGMAFO-PS-PEGMAFO triblock copolymers with EGMAFO segments of (□) 1 : 0.8, (○) 1 : 2.4, and (●) 1 : 3.5 as measured in toluene.
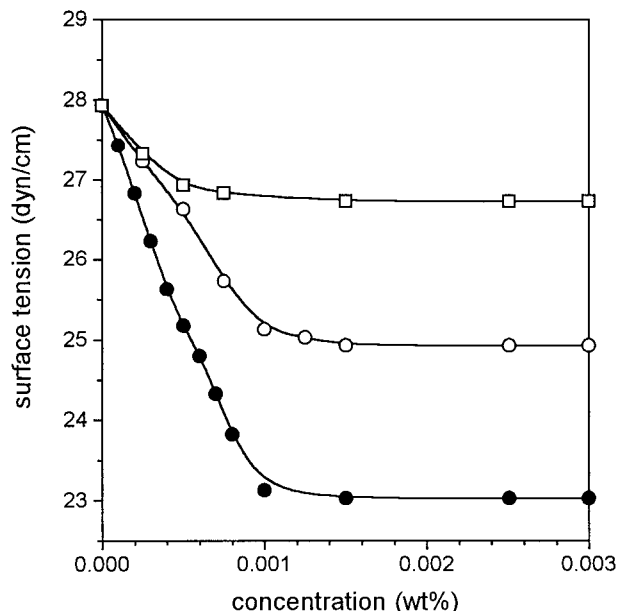

Figure 5 The surface tension as a function of the polymer concentration for the PFNEMA-PS-PFNEMA triblock copolymers with FNEMA segments of (□) 1 : 0.8, (○) 1 : 2.4, and (●) 1 : 3.5 as measured in toluene.

holtz free energy per unit area of surface σ. For a two-component system at constant temperature, eq. (1) is expressed below[14]:

$$d\gamma = -\Gamma_1 d\mu_1^{\sigma} - \Gamma_2 d\mu_2^{\sigma} \tag{2}$$

Rearrangement of the Gibbs adsorption equation produces an expression that relates the surface excess and surface tension:

$$\Gamma_1 = -\frac{1}{RT}\frac{d\gamma}{d\ln C} \tag{3}$$

in which C is the concentration of component 1, R is the ideal gas constant, and T is the temperature. It can be seen from eq. (3) that if the item $d\gamma/d\ln C < 0$, then there will be a surface excess of component 1. Namely, if component 1 has a lower surface tension than component 2, there will be an enthalpic driving force for surface segregation of 1 to the air–liquid interface. According to eq. (3) and using a $\gamma \ln C$ plot, the Γ and the occupied surface area of one molecule A (Å^2) can be obtained and are given by eq. (4).

$$A = \frac{10^{20}}{N_A \Gamma} \tag{4}$$

where N_A is the Avogadro number.

Table III   Air–Liquid and Air–Solid Interface Properties of Semifluorinated Triblock Copolymers

Sample (PS/EGMAFO or FNEMA, g/g)	γ_C (dyn/cm)	γ_s^D (dyn/cm)	Γ (μmol/m^2)	A (Å^2)
PEGMAFO-PS-PEGMAFO (1 : 0.8)	17.3	16.3	0.60	275
PEGMAFO-PS-PEGMAFO (1 : 2.4)	15.7	14.2	0.29	560
PEGMAFO-PS-PEGMAFO (1 : 3.5)	14.6	13.2	0.17	970
PFNEMA-PS-PFNEMA (1 : 0.8)	18.4	18.1	1.08	154
PFNEMA-PS-PFNEMA (1 : 2.4)	17.5	17.4	0.27	603
PFNEMA-PS-PFNEMA (1 : 3.5)	17.2	16.6	0.21	793

The A values shown in Table III are rather large and can be further converted to the surface area per fluorinated MA repeating unit via dividing by the polymerization degree of the fluorinated block. The calculated values of 19–50 Å^2 are in good agreement with reported values (24–46 Å^2) for low MW fluoroalkylated species.[15,16] These results are an intense implication that perfluoroalkyl chains are adsorbed at the air–liquid interface.

Solid Surface Properties

The critical surface energies of (co) polymers can be determined by an n-alkane wetting experiment. Thus, thin films of the obtained block copolymers were cast from tetrahydrofuran solutions (1% of the copolymers) and then dried under a vacuum at room temperature for 1 day. In order to bring the fluorinated side chains to the copolymer surface, the films were heated at 80°C for about 14 h. The wettability of the copolymer films with octane, decane, docane, and tetradecane was determined by measuring the contact angles (θ). According to the following empirical wetting equation presented by Zisman,[17]

$$\cos \theta = 1 + m(\gamma_L - \gamma_C) \tag{5}$$

The cosine of the contact angle ($\cos \theta$) is plotted versus the surface tension of the wetting liquid (γ_L), which gives a straight line with the slope m. The critical surface tension (γ_C) is obtained followed by extrapolating to the condition of complete wetting of the copolymer surface ($\cos \theta = 1$).

Figures 6 and 7 are Zisman plots for PEGMAFO-PS-PEGMAFO and PFNEMA-PS-PFNEMA triblock copolymers, respectively. The extrapolated values for the γ_C of the block copolymers are summarized in Table III. Moreover, from the above wettability data, the dispersion force component of the surface energy (γ_s^D) is also obtained by means of the Girifalco–Good–Fowkes–Young equation[18,19]:

$$\cos \theta = -1 + 2(\gamma_s^D)^{1/2}(\gamma_L)^{-1/2} \tag{6}$$

The plot of $\cos \theta$ versus $\gamma_L^{-1/2}$ should be a straight line with the intercept -1. An equality ($\gamma_s^D = \gamma_L$) exists at the point of intersection between the straight line and the horizontal line ($\cos \theta = 1$). Figures 8 and 9 show Girifalco–Good–Fowkers–Young plots for PEGMAFO-PS-PEGMAFO and PFNEMA-PS-PFNEMA triblock copolymers, respectively. The obtained γ_s^D data are also listed in Table III. As shown in Table III, the γ_s^D values of the triblock copolymers are very close to γ_C values, indicating that dispersion forces are the predominant component in the interaction of the block copolymers with wetting liquids.
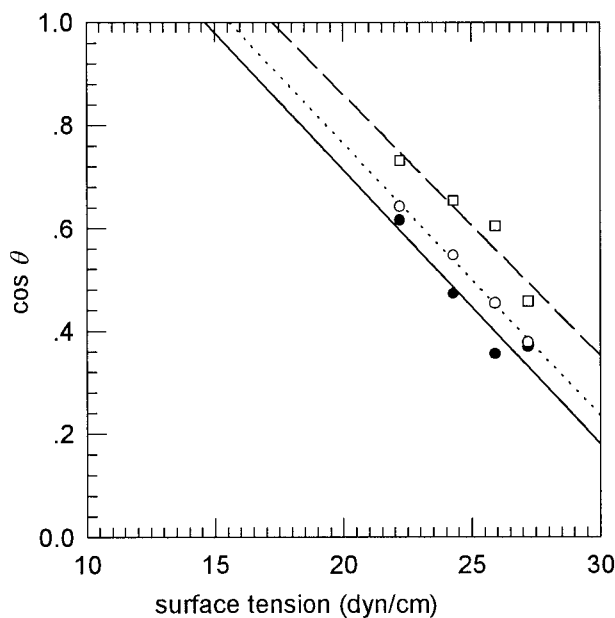

Figure 6 A Zisman plot for PEGMAFO-PS-PEGMAFO triblock copolymers with EGMAFO segments of (□) 1 : 0.8, (○) 1 : 2.4, and (●) 1 : 3.5.
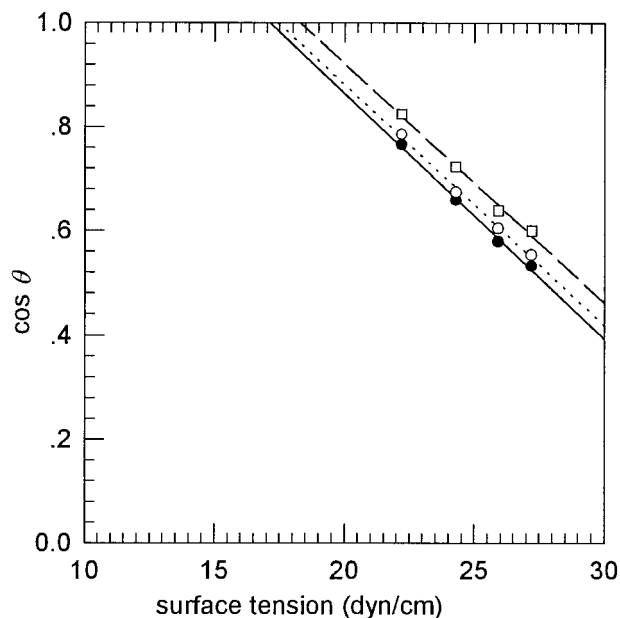
Figure 7 A Zisman plot for PFNEMA-PS-PFNEMA triblock copolymers with FNEMA segments of (□) 1 : 0.8, (○) 1 : 2.4, and (●) 1 : 3.5.

CONCLUSIONS

A series of semifluorinated triblock copolymers with different fluorinated segment lengths and structures of pendent fluorocarbon side chains
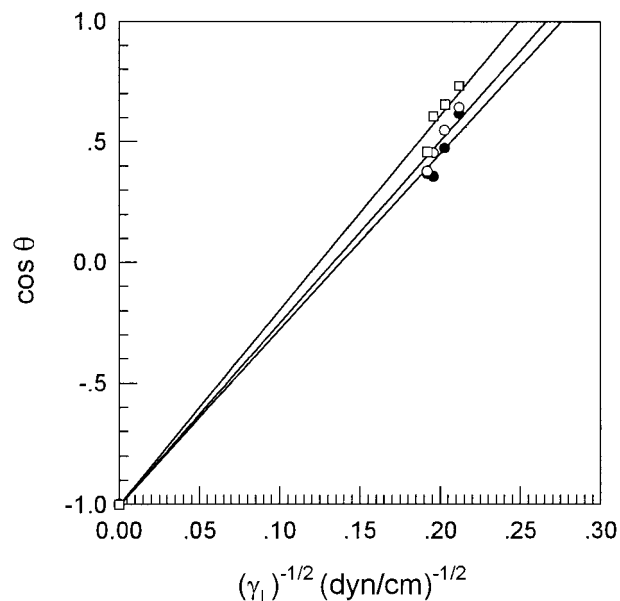

Figure 8 A Girifalco–Good–Fowkes–Young plot for PEGMAFO-PS-PEGMAFO triblock copolymers with EGMAFO segments of (□) 1 : 0.8, (○) 1 : 2.4, and (●) 1 : 3.5.
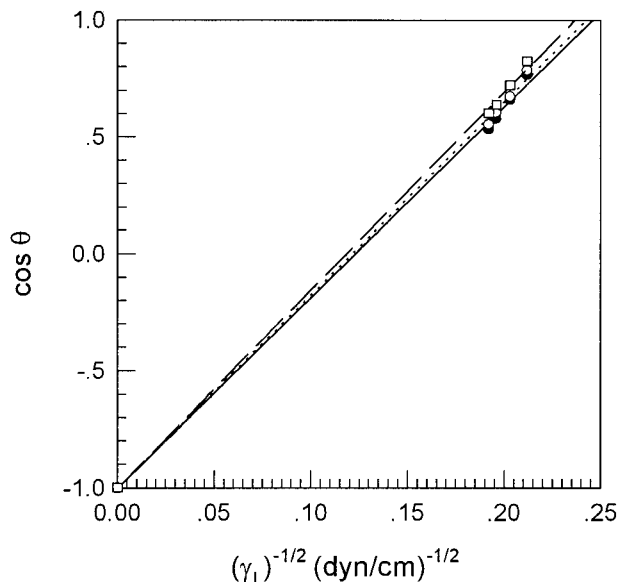

Figure 9 A Girifalco–Good–Fowkes–Young plot for PEGMAFO-PS-PEGMAFO triblock copolymer with EGMAFO segments of (□) 1 : 0.8, (○) 1 : 2.4, and (●) 1 : 3.5.

were successfully synthesized by ATRP. The investigation of the thermal transition behavior of the block copolymers reveals that the block copolymers have two glass-transition temperatures and that the block copolymers with EGMAFO segments exhibit the crystallinity of side chains. The surface activities in toluene and solid surface properties of the triblock copolymers were also explored. The experimental results show that these block copolymers have high surface activity in organic solvents and low solid surface energy, implying that they can be applied as potential highly effective and efficient surfactants, as well as low surface energy materials.

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