Preparation and Surfactancy of Branched Copolymers from Poly(oxyalkylene)-amine and Trichlorotriazine Coupling

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ABSTRACT: A family of branched and block copolymers consisting of poly(oxyalkylene) segments was prepared by using 2,4,6-trichloro-1,3,5-triazine as the amine coupling agent. The copolymers were characterized to have a high molecular weight of up to 22,600 g/mol (Mn) and be thermally stable due to the presence of triazine cores and reactive chloride functionalities. Using the trifunctional poly(oxypropylene)-block amines as the starting material and a two-step coupling process, the prepared copolymers are star-shape or branched, multiple-block copolymers, with a versatile solubility in water or organic solvents. Further variation in amine structures of hydrophobic poly(oxypropylene) (POP-) and hydrophilic poly(oxyethylene) (POE-) blocks may allow the prepared copolymers to be amphiphilic. As an example, the triazine/POP T-5000/POE ED-2001 copolymer behaves as a surfactant and exhibits the capability of reducing toluene/water interfacial tension until 1.3 mN/m at critical association concentration as low as 0.001 wt %. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 29–36, 2005

Key words: triazine; block copolymers; poly(oxyalkylene)-amine; amphiphilic; hyperbranched

INTRODUCTION

Block copolymers consisting of hydrophilic poly(oxyethylene) segments including polyethyleneglycol functionality may have a self-assembling nature and versatile applications as surfactants.[1–3] The presence of the -(OCH_2CH_2)- chemical group often offers the copolymers properties such as metal chelation,[4] hydrophilicity,[5] crystallinity,[6] surface activity,[7] and so on. In combining poly(oxypropylene) (POP) and poly(oxyethylene) (POE) blocks, suitable hydrophilic/hydrophobic balance may render the copolymer surfactant properties. While there is a demand for POE–POP block copolymers in industrial applications, the synthetic methods for making such copolymers have been limited due to the process difficulty.[2] The commercially available products are limited to the EO/PO block copolymers such as PLURONIC.[8] Previously, we have explored the utilization of poly(oxyalkylene)-amines as the starting material to construct EO/PO copolymers with different functionalities for various applications such as antistatics[9–11] and surface active agents.[6] The derivation is performed by taking advantage of the high amine reactivity toward carboxylic acid, ester, anhydride, and isocyanate functionalities.

Recently, we developed the use of 2,4,6-trichloro-1,3,5-triazine as the coupling agent to selectively react with hydrophilic POE- and hydrophobic POP-amines to form linear block copolymers.[12] In using the highly selective nature of trichlorotriazine coupling, a series of high-molecular-weight and linear POE/POP copolymers was prepared from poly(oxyalkylene)-diamines. With respect to the important applications of hyperbranched block copolymers in the areas of ionic transfer,[13] electronic delocalization,[14] virus inhibition,[15] gelation,[16] and others,[17–21] we extend the triazine-coupling reaction to prepare a series of branched copolymers and also investigate their fundamental surfactant behaviors.

EXPERIMENTAL

Materials

A family of poly(oxyalkylene)amines including poly(oxyethylene)- and poly(oxypropylene)-amine of different molecular weights, trade name Jeffamine Amines, were obtained from Huntsman Chemical Co. or Aldrich Chemical Co. Their chemical structures are shown in Figure 1, including poly(oxypropylene) bis(2-propylamine) of ~2000 Mw (i.e., Jeffamine D-2000, amine content 0.98 meq/g), poly(oxypropylene-oxyethylene-oxypropylene) bis(2-propylamine) of ~2000 Mw (i.e., Jeffamine ED-2001, white waxy solid, m.p. 35°C, amine content 0.95 meq/g), methoxy-poly(oxyethylene-oxypropylene)-2-propylamine of ~2000 Mw (i.e., Jeffam-
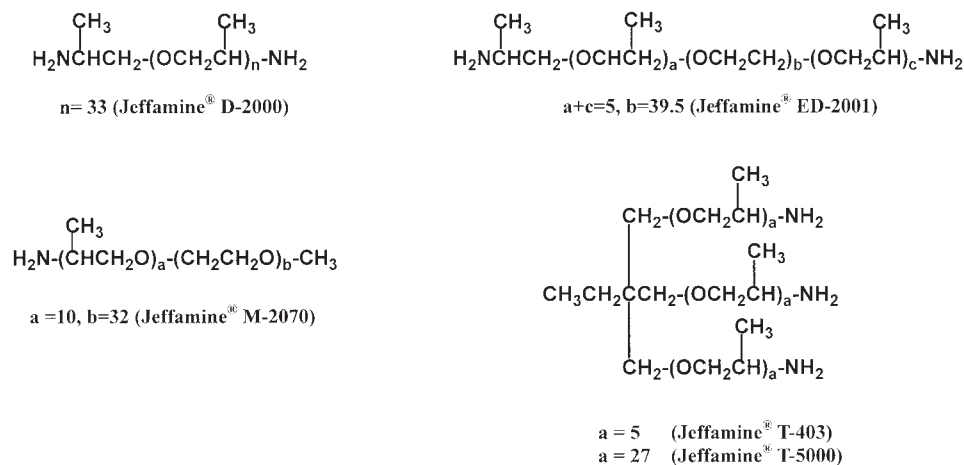
Figure 1   Chemical structures of poly(oxyethylene)- and poly(oxypropylene)-amines.

ine M-2070), and poly(oxyalkylene) triamine of ~400 and 5000 Mw (i.e., Jeffamine T-403 and Jeffamine T-5000, respectively). These polyetheramines can be classified into water-soluble and water-insoluble amines. The low-molecular-weight (<400 g/mol) or the high-molecular-weight POE-backboned amines are generally highly hydrophilic and water soluble. The ED-2001 diamine, consisting of oxyethylene-rich triblock backbone with an average 39.5/5 EO/PO unit ratio, and M-2070 mono-amine of EO/PO ratio of 32/10 are water-soluble. The PO backboned amines, triamine T-5000 with an average 27 PO units and diamine D-2000, are hydrophobic amines.

The linking agent, 2,4,6-trichloro-1,3,5-triazine (m.p. 145.5–148.5°C), was obtained from Aldrich Chemical Co. This reagent was purified by recrystallization from methanol.

Measurement

The average molecular weight was estimated using gel permeation chromatography (Waters GPC, 515 HPLC pump, 717 autosampler, 2410 refractive index detector), calibrated with polystyrene standards. Elutions were performed using degassed THF at a flow rate of 1.0 mL min^{-1} at 40°C. A thermal gravimetric analyzer (TGA, Perkin–Elmer Pyris 1) measured the thermal stability by ramping the temperature from room temperature to 500°C at a rate of 10°C/min. Interfacial tension was measured by Wilhelmy method using a Kruss-K10 digital tensiometer equipped with a spherical ring.

Synthetic procedures

Typical reaction procedures for the amine substitution of trichlorotriazine were reported previously.[12] Three different chlorides can be reacted and substituted dis-
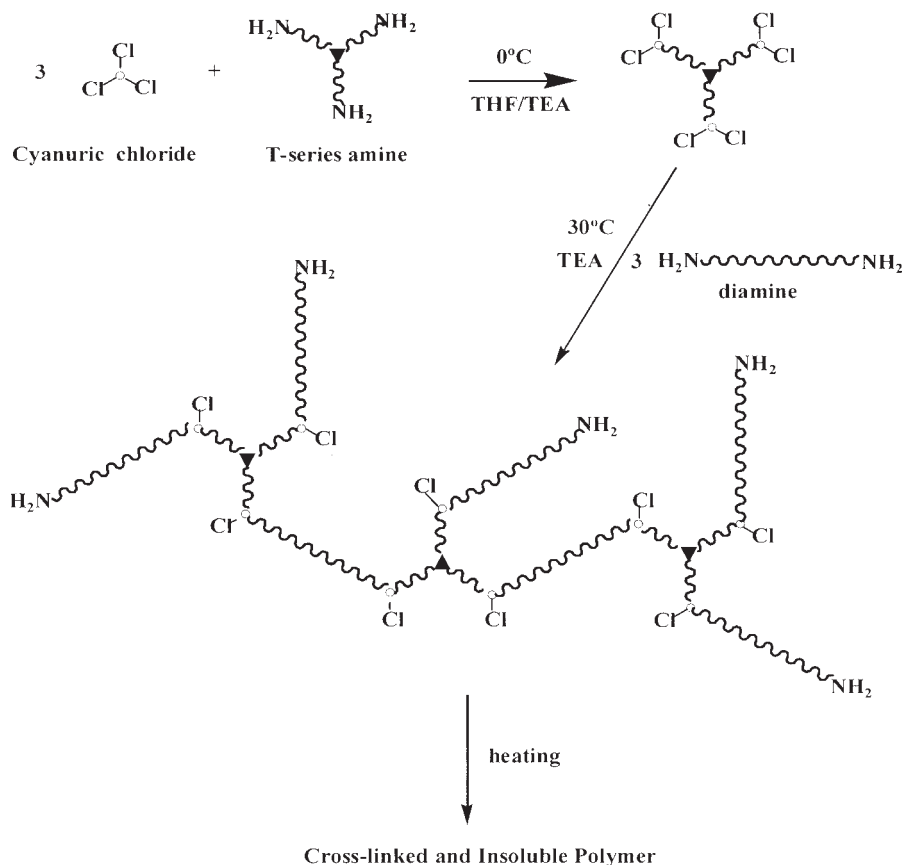
tinctively in a controllable manner, mainly by varying the reaction temperature. By taking advantage of this phenomenon, we have developed typical reaction procedures as described below. To a three-neck, round-bottom flask, equipped with a magnetic stirrer, nitrogen inlet–outlet lines, and a thermometer was charged with poly(oxypropylene)triamine of ~400 Mw (i.e., Jeffamine T-403, 2.0 g, 5 mmol) and THF (70 mL). The mixture was stirred while cooled to near 0 ± 5°C under nitrogen atmosphere. Powder cyanuric chloride (2.8 g, 15 mmol) was then added to the mixture in one portion. With continuous agitation at 0 ± 5°C, triethylamine (1.5 g, 15 mmol) was added. During the reaction, the quaternary ammonium salt precipitated out from the reaction solution. After 3 h, the reactor was allowed to warm up to 30 ± 5°C. The second amine, a hydrophilic monoamine of ~2000 Mw (i.e., Jeffamine M-2070, 30 g, 15 mmol), and triethylamine (1.5 g, 15 mmol) was added. The reaction was prolonged for 24 h at ambient temperature. The reaction product was filtered through filter paper (Whatman No.5) using a Buchner funnel attached to an aspirator. The filtrate was concentrated in a rotary evaporator below 30°C under reduced pressure. The viscous liquid or semisolid product was analyzed for its molecular weight using GPC and its thermal properties by TGA.

RESULTS AND DISCUSSION

Preparation of branched poly(oxyalkylene) block copolymers

The trichloride–triazine linking agent was allowed to react with different poly(oxyalkylene)-amines (POA-amines) in a sequential process. In the first step of triazine substitution, a trifunctional amine is used to form the star-shape core followed by a second POA-amine substitution. As a result, two distinctly different

Scheme 1 Two-step synthesis of triazine/T-series/monoamine copolymers via the trifunctional triazine intermediate.

POA-amines could be coupled in the same copolymer molecule. These POA-amines are commercial products[22,23] and are produced via ammonia amination of the corresponding EO/PO polyol precursors. The available products include M-series monoamines, D-series diamines, T-series triamines, and ED-series ethylene oxide diamines. To form the desired branched copolymers, a trifunctional T-series amine such as T-403 or T-5000 is required for the triazine coupling.

Since trichlorotriazine is highly selective for the amine addition at 0°C for the primary, 25°C for the secondary, and 130°C for the tertiary chloride substitution, the linking agent can be considered to have three distinct reactive sites.[12] Hence, by taking advantage of the selective primary chloride reaction, the stepwise process is developed and an intermediate is prepared from the reaction of trichlorotriazine and T-series amine at 3:1 M ratio at $0 \pm 5°C$. With trifunctional amines such as T-403 (400 g/mol) or T-5000 (5000 g/mol), the intermediates are synthesized (Scheme 1). Each triazine/T-5000 and triazine/T-403 intermediate consists of three triazine cores with three secondary and three tertiary triazine chlorides. These intermediates are soluble in common organic solvents such as THF, toluene, chloroform, and ethanol. In the second step, the addition of 3 eq of monoamines at $30 \pm 5°C$ afforded a star-shape copolymer of multiple EO/PO blocks. The sequential reaction scheme is illustrated in Scheme 1. This second-stage coupling reaction was generally performed using THF solvent and triethylamine as the HCl scavenger and with a 24-h reaction period at $30 \pm 5°C$ (Fig. 2). The overall sequential coupling of triazine/T-series/monoamine at a 3:1:3 M ratio produced the star-shape copolymers with a molecular weight of 12,000 Mn on the basis of

GPC using polystyrene as the standard. Besides the monofunctional M-2070, the POA-diamines such as the hydrophilic ED-2001 and hydrophobic D-2000 (both 2000 Mn) can also be coupled into high-molecular-weight block copolymers. With these diamines, the triazine/T-series/diamine at 3:1:3 M ratio coupling can reach the number-average molecular weights of 22,600 and 20,400 g/mol, respectively. It is noted that, by using diamines as the second coupling amine, the hyperbranched copolymers are obtained as structurally described in Scheme 2. The structure consists of multiple secondary triazine chlorides and terminating amines. Their chemical compositions and

Figure 2 Gel permeation chromatography peaks of (a) T-403 starting material, (b) triazine/T-403 (1:3) intermediate, and (c) triazine/T-403/M-2070 (3:1:3) at 30°C.

Scheme 2 Conceptual representation of hyperbranched block copolymers from the triazine/triamine/diamine sequence.

GPC analysis are illustrated in Table I. It is noteworthy that the synthesis is straightforward because it requires one reaction vessel and only mild temperatures of 0 ± 5 and 30 ± 5°C for the two-step synthesis. The star-shape copolymers are produced by adopting the highly selective mode for the primary and secondary chlorides in the triazine core. The coupling involves only the first two chlorides in the triazine ring. The tertiary chloride in the copolymer chain remained reactive for further coupling at 130 ± 5°C with a 2-h

reaction period. Under high temperature conditions, the tertiary chloride was found to be reactive for the residual amine termini. The copolymer formed a crosslink structure by simply heating to high temperature (~130°C), at which point it became insoluble in common organic solvents. The crosslinked copolymers can swell in solvents as summarized in Figure 3. The crosslink structure of triazine/T-5000/ED-2001, for example, can absorb toluene up to 4.5 g, compared to 11.6 g of chloroform per gram of the sample.

TABLE I
Properties of Star-Shape Copolymers by T-Series Amine/Triazine Coupling

Composition	Molar ratio	Theoretical[a] (g/mol)	GPC Mn (g/mol)	Mw/Mn[b]	Yield (%)
Triazine/T-403/D-2000	3:1:3	6500	13300	1.70	97
Triazine/T-403/ED-2001	3:1:3	6500	11100	1.45	90
Triazine/T-403/M-2070	3:1:3	6500	9200	1.12	97
Triazine/T-5000/D-2000	3:1:3	11700	20400	1.59	95
Triazine/T-5000/ED-2001	3:1:3	11700	22600	1.71	91
Triazine/T-5000/M-2070	3:1:3	11700	12000	1.37	96

[a] Theoretical molecular-weight based on the idealized structures.
[b] Polydispersity.
[c] All are soluble in toluene; triazine/T-403/ED-2001 and triazine/T-403/M-2070 are soluble in water.
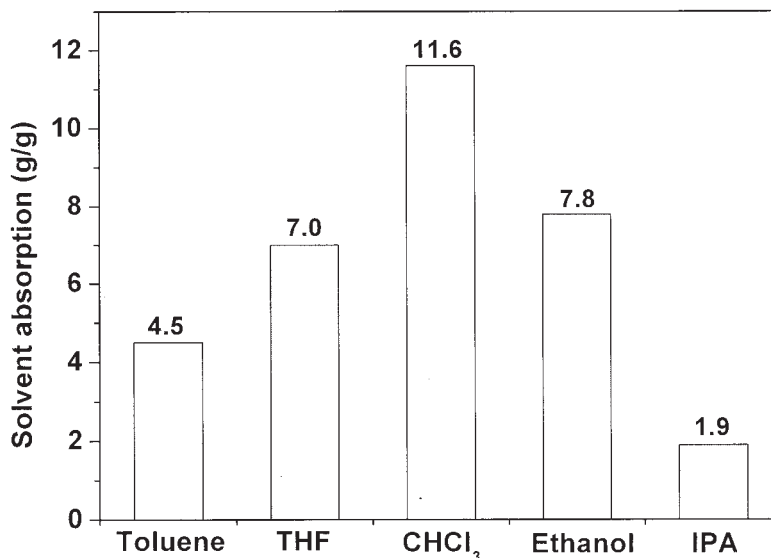
Figure 3   Solvent affinity of triazine/T-5000/ED-2001 (crosslinked copolymer).

Relative thermal stability of the starting materials and the star-shape copolymers

All of these prepared star-shape copolymers consist of triazine cores and POE or POP backbones. Several representative copolymers in this study and their starting amine were analyzed using TGA in nitrogen (Table II and Fig. 4). The structural difference between the POE and POP blocks is the major factor influencing their thermal stability. The following trend is observed with respect to the 50% weight loss in the TGA curve: triazine/T-403/ED-2001 (3:1:3) > triazine/T-403/M-2070 (3:1:3) > ED-2001 > triazine/T-403/D-2000 (3:1:3) > M-2070 > D-2000 > T-403. More specifically, triazine/T-403/ED-2001 (3:1:3) was 15°C more stable than of triazine/T-403/D-2000 (3:1:3). This is due to the structural difference between the oxypro-

pylene of D-2000 and the oxyethylene of ED-2001. The same is also observed for the D-2000 starting material with a POP backbone, which is less stable than the starting materials ED-2001 or M-2070, which consist of POE-rich blocks. The presence of a tertiary carbon ($-CH_2C^*H(CH_3)O-$) in the POP backbone is considered the more accessible position for the free radical formation compared to the secondary carbon ($-CH_2CH_2O-$) in the POE structure.[12,24] Furthermore, the triazine functionalities in the polymer structure can contribute to the backbone stability. For example, the triazine/T-403/ED-2001 (3:1:3) has a 50% retention temperature at 407°C, which is much higher than 395°C for the starting amines (ED-2001 or T-403) under the same conditions. Furthermore, the triazine/T-403/D-2000 (3:1:3) is more thermally stable than the starting

TABLE II
Thermal Gravimetric Decomposition Pattern in Nitrogen

Composition[a]	Temperature (°C)[b]				Char yield (%)[c]
	95%	75%	50%	25%	500°C
D-2000	316	352	368	382	0.2
ED-2001	340	377	395	410	1.8
M-2070	327	366	383	394	0.0
T-403	204	252	279	304	1.9
T-5000	320	355	372	386	0.3
Triazine/T-403/D-2000	312	373	392	405	1.5
Triazine/T-403/ED-2001	319	386	407	421	4.6
Triazine/T-403/M-2070	285	371	402	419	4.7
Triazine/T-5000/D-2000	351	383	396	408	1.5
Triazine/T-5000/ED-2001	322	380	399	412	2.8
Triazine/T-5000/M-2070	337	382	399	411	2.0

[a] Triazine/T-series amine/POA amine molar ratio = 3:1:3.
[b] Weight loss temperature.
[c] Residual weight retention.
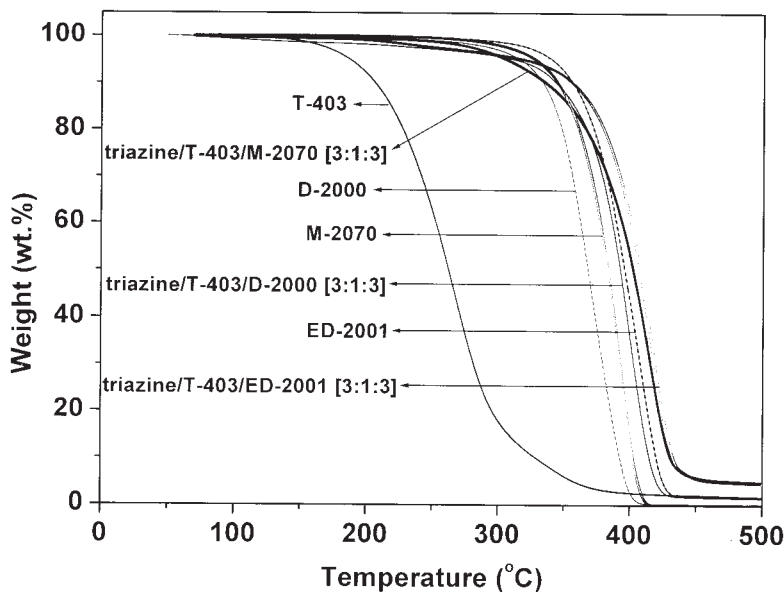
Figure 4   Relative thermal stability of the starting amines and the prepared copolymers in nitrogen.

amines, T-403 or D-2000. The built-in triazine cores in the copolymer structure have enhanced the copolymer stability. Their trend of thermal stability is further analyzed in terms of the thermo-oxidative stability. When measuring by TGA in air (Table III and Fig. 5), the relative oxidative stability is more significantly differentiated by different copolymer structures. Again, the presence of triazine rings renders the copolymer highly stable even under the oxidative condition. In contrast, the starting amines from the D-2000 to the T-5000 series decompose easily compared to those of triazine-coupled copolymers. The presence of the terminal amine also plays a role of radical scavenger.[25] However, the trend of relative stability in air is similar to that in nitrogen: triazine/T-403/ED-2001

> triazine/T-403/M-2070 > triazine/T-403/D-2000 > ED-2001 > M-2070 > D-2000 > T-403.

Surfactancy and self-associating property in the toluene/water interface

The star-shape POE/POP copolymers including triazine/T-5000/ED-2001, triazine/T-5000/M-2070, and triazine/T-403/D-2000 were investigated with respect to their surfactant behaviors in the toluene/water interface. In the presence of hydrophilic POE and hydrophobic POP blocks, the copolymers are amphiphilic. Dissolved in toluene, the self-associating copolymer is capable of reducing the toluene/water interfacial tension effectively (Fig. 6). Additionally, the

TABLE III
Thermal Gravimetric Decomposition Pattern in Air

Composition[a]	Temperature (°C)[b]				Char yield (%)[c]
	95%	75%	50%	25%	500°C
D-2000	213	255	274	288	0.6
ED-2001	244	299	329	352	2.2
M-2070	222	269	292	307	0.6
T-403	183	227	254	313	4.0
T-5000	206	235	254	267	0.2
Triazine/T-403/D-2000	294	361	380	396	4.5
Triazine/T-403/ED-2001	313	373	402	422	7.9
Triazine/T-403/M-2070	269	339	387	416	7.8
Triazine/T-5000/D-2000	240	346	377	394	3.7
Triazine/T-5000/ED-2001	281	369	393	414	5.3
Triazine/T-5000/M-2070	224	297	340	384	4.5

[a] Triazine/T-series amine/POA amine molar ratio = 3:1:3.
[b] Weight loss temperature.
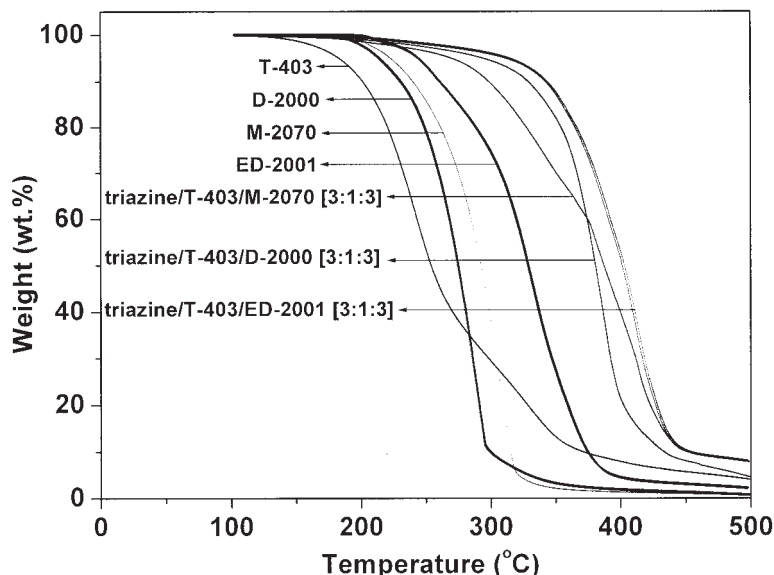[c] Residual weight retention.

Figure 5 Relative thermal stability of the starting amines and the prepared copolymers in air.

triazine/T-5000/ED-2001 (3:1:3) copolymer exhibits a significant reduction of the interfacial tension as low as 1.3 mN/m at the critical association concentration (CAC) of 0.001 wt %.[17] The extremely low interfacial tension and CAC indicate the high efficacy of the surface activity. It implies that the copolymers self-align in the toluene/water interface with a broad coverage of surface area per molecule. From the viewpoint of bonding forces, there are two forces of noncovalent bonding involved for each copolymer molecule. The first is the POE block interaction with water by hydrogen bonding, and the other is the hy-drophobic alkyl effect between the POP block and toluene solvent. Since the starting materials including T-5000, ED-2001, M-2070, and T-403 are either too hydrophobic or hydrophilic, they fail to show any surface-active ability. In the case of triazine/T-403/D-2000, the amphiphilic balance is derived from the hydrophobic D-2000 and the hydrophilic T-403. Although T-403 consists of a POP backbone, the amine is actually soluble in water and hydrophilic in nature due to the presence of trifunctional amine. The proper hydrophilic/hydrophobic balance is hence determined by the length of POP or POE segments. Pre-
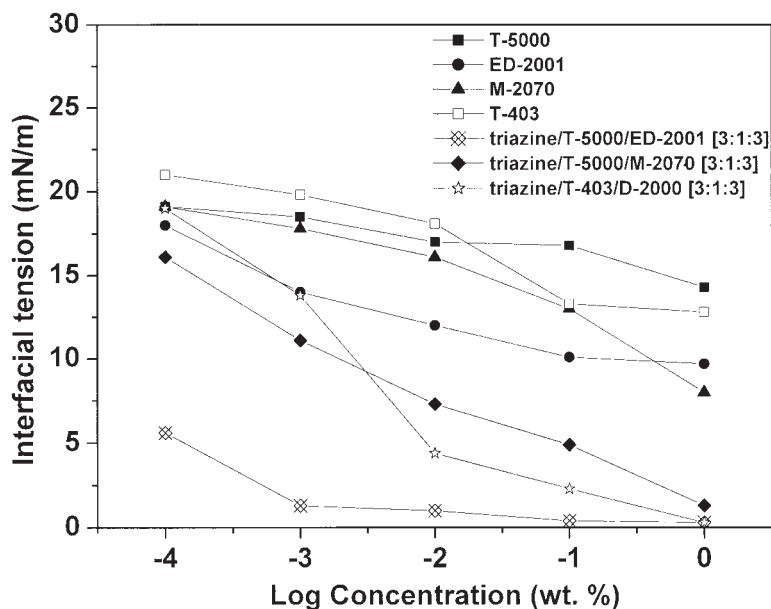

Figure 6 Interfacial tension profiles of the copolymers in toluene/water.

sumably, the linkage groups of triazine-NH may also provide additional hydrophilic hydrogen-bonding sites, as well as π–π stacking interaction among the triazine rings.

CONCLUSIONS

A new type of hyperbranched high-molecular-weight copolymers can be synthesized by the coupling reaction involving hydrophilic POE- and hydrophobic POP-block amines with 2,4,6-trichloro-1,3,5-triazine. The multiple POE/POP block copolymers are molecularly arranged in a hyperbranched star shape with a number-average molecular weight as high as 22,600 g/mol. With a suitable hydrophilic/hydrophobic balance, these copolymers may behave as excellent surfactants with the ability to reduce interfacial tension in toluene/water. The presence of triazine cores renders the copolymers thermally more stable than that of their POE- or POP-amine starting materials.

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