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Facile preparation of amphiphilic oxyethylene–oxypropylene block copolymers by selective triazine coupling

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Abstract

A novel synthetic route for preparing high molecular weight poly(oxyalkylene) block copolymers has been developed by using 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride, cc) as the coupling core. The coupling reaction involves the selective substitutions of oligo(oxyalkylene)-amines onto three chlorides of the triazine ring in a stepwise manner at 0, 25 and 130 °C. By judiciously selecting the starting amines and reaction conditions, one can tailor the copolymer structures with different block configurations (tri-block, multi-block, random and alternating block). The prepared copolymers can have a high molecular weight, up to 25,600 g/mol (GPC polydispersity = 1.48), and also high thermal stability due to the presence of triazine functionalities. The copolymers with hydrophilic and hydrophobic oligo(oxyalkylene) blocks are of versatile properties in solubility (water soluble or water insoluble) and morphology (crystalline or amorphous). With a specific structure of alternating oligo(oxyethylene)/oligo(oxypropylene) blocks (2000 g/mol each block), the copolymer exhibits the property of self-association. It reduces the interfacial tension of toluene/water as low as 0.5 dyne/cm at the critical micelle concentration of 0.01 wt%.

Keywords: Triazine; Amphiphilic copolymer; Surfactant

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1. Introduction

Amphiphilic copolymers consisting of poly(oxyethylene) (POE) and poly(oxypropylene) (POP) blocks are of great interest to both academic and industrial researchers, mainly due to their versatile properties and wide industrial applications [1–4]. Particularly, the presence of POE segments may allow the copolymers versatile properties such as metal chelation [5], hydrophilicity [6], crystallinity [7], surfactancy [8], etc. For practical applications, the POE-segmented copolymers are widely reported for use as drug carriers [9], emulsifiers [10], dispersants [6,7], solid electrolytes [11], and others [12,13]. However, the synthetic methods for making POE or POP block copolymers have a molecular weight limitation. The process generally involves the ring opening polymerization of ethylene oxide (EO) or propylene oxide (PO) with a suitable initiator [2,3]. For making a real high molecular weight POE copolymers, the procedure requires the introduction of large amounts of EO feed and long residence time in the reactor. The low level of water contamination in the feed often leads to the formation of poly(ethylene glycol) byproducts which are inseparable from the desired copolymers. In the PO polymerization, a side product often appears from the rearrangement of PO into allyl alcohol and followed by propoxylation. Hence, the commercial products of EO/PO block copolymers (trade name PLURONIC) have molecular weight limitations of approximately 8000 g/mol for POE, 2000 g/mol for POP and 11,000 g/mol for POE/POP copolymers. Besides the molecular weight limitation, the anionic EO/PO ring opening alkoxylation is not ideal for making functional copolymers [2,8,12,13]. For the synthesis of POE copolymers with specific functionalities and properties, alternative syntheses besides the direct EO/PO alkoxylation have been designed. In literature, e.g., the step growth copolymerization was reported to prepare a POE-segmented poly(ethylene terephthalate), which had enhanced properties such as hydrophilicity [14] and surfactant adsorptions [8]. Therefore, the development of new methods for making

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EO/PO copolymers with a high molecular weight or different functionalities are important for broadening this area of research.

Our approach for developing a novel synthetic methodology is to use 2,4,6-trichloro-1,3,5-triazine as the linking agent to couple oligo(oxyalkylene)amines into a family of high molecular weight EO/PO copolymers. The coupling reaction was studied with respect to the reaction conditions and parameters affecting the selectivity for the sequential triazine substitutions. Commercially available hydrophilic POE- and hydrophobic POP-backboned amines of 2000 g/mol were coupled in a stepwise and selective manner. Amphiphilic or hydrophilic/hydrophobic copolymers were constructed to have various configurations, molecular weights and POE/POP segmental ratios. Their fundamental surface/interfacial properties in toluene/water were also studied.

2. Experimental

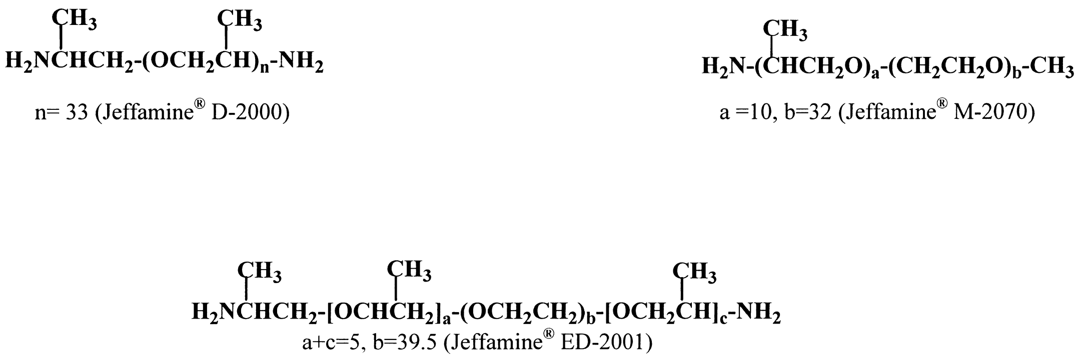
2.1. Materials

A family of commercially available poly(oxyethylene–oxypropylene)-amines, trade name Jeffamine® amines, were obtained from Huntsman Chemical Co. or Aldrich Chemical Co. and used without further purification. The chemical structures are illustrated in Fig. 1, including poly(oxypropylene) bis(2-propylamine) of ~2000 M_w (i.e. Jeffamine® D-2000, amine content 0.98 meqiv./g), poly(oxypropylene–oxyethylene–oxypropylene) bis(2-propylamine) of ~2000 M_w (i.e. Jeffamine® ED-2001, white waxy solid, mp 35 °C, amine content 0.95 meqiv./g), and methoxy-poly(oxyethylene–oxypropylene)-2-propylamine of ~2000 M_w (i.e. Jeffamine® M-2070). These poly(oxyalkylene)-amines can be classified as hydrophilic or hydrophobic amines. The POP-backboned amine (D-2000) is water insoluble and hydrophobic. In contrast, the oxyethylene-rich monoamine (M-2070) and diamine (ED-2001) are hydrophilic and water soluble. The detailed structures show the diamine ED-2001 having a backbone of poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxypropylene) tri-block and the M-2070 monoamine having a backbone of poly(oxyethylene)-*b*-poly(oxypropylene) diblock. According to the process disclosed in patents [15,16], these POE/POP amines are prepared by the ammonia amination of converting polyols into primary amines. The NMR and amine titration analyses confirmed the chemical structures as shown in Fig. 1. The ED-2001 diamine constituted of oxyethylene-rich tri-block backbone with an average of 39.5/5 EO/PO unit ratios, and D-2000 with an average of 33 PO units per molecule. For the monoamine, M-2070 is a water-soluble amine with an EO/PO ratio of 32/10 in the backbone.

The linking agent, 2,4,6-trichloro-1,3,5-triazine (abbreviated as cyanuric chloride or cc, mp 145.5–148.5 °C), was obtained from Aldrich Chemical Co.

2.2. Characterization and instruments

The average molecular weight was estimated by using gel permeation chromatography (Waters GPC, 515 HPLC pump, 717 autosampler, 2410 refractive index detector), calibrated by polystyrene standards. Elutions were performed using de-gassed THF as the eluent at a flow rate of 1.0 ml min^{-1}. The thermal analyses were performed on a differential scanning calorimeter (DSC 2010, TA instruments). Sample size of 5–8 mg on a sealed aluminum pan was generally used. The analyses were carried out in the temperature range of −100–180 °C at a heating rate of 10 °C min^{-1} with a nitrogen flow of 60 ml min^{-1}. The enthalpy of melting (ΔH_m) was determined by the integration of the peak area under a linear baseline, and peak values of the thermogram was reported as melting point (T_m). The thermal stability was observed using a thermal gravimetric analyzer (Seiko SII model SSC/5200). The temperature was ramped from rt to 500 °C at a rate of 10 °C min^{-1}. The interfacial tension was measured by the Wilhelmy method using a Kruss-K10 digital tensiometer equipped with a spherical ring.



$$\mathrm{H_2N\overset{CH_3}{C}HCH_2\text{-}(OCH_2\overset{CH_3}{C}H)_n\text{-}NH_2}$$

n= 33 (Jeffamine® D-2000)

$$\mathrm{H_2N\text{-}(\overset{CH_3}{C}HCH_2O)_a\text{-}(CH_2CH_2O)_b\text{-}CH_3}$$

a =10, b=32 (Jeffamine® M-2070)

$$\mathrm{H_2N\overset{CH_3}{C}HCH_2\text{-}[OCH\overset{CH_3}{C}H_2]_a\text{-}(OCH_2CH_2)_b\text{-}[OCH_2\overset{CH_3}{C}H]_c\text{-}NH_2}$$

a+c=5, b=39.5 (Jeffamine® ED-2001)

Fig. 1. Chemical structures of poly(oxyalkylene)-amines with averaged oxyethylene or oxypropylene units.

2.3. General procedures for the amination of cyanuric chloride

Typical procedures for the amination of cyanuric chloride are described by using poly(oxyalkylene)-monoamine as an example. To a three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet–outlet lines, and thermometer, was charged with Jeffamine® M-2070 (5.5 g, 2.7 mmol) and THF or xylene (50 mL). The solution was cooled to nearly 0 °C under a nitrogen atmosphere. To the solution was then added cyanuric chloride (0.5 g, 2.7 mmol) in one portion. While stirring and maintaining the temperature at 0 °C, triethylamine (0.27 g, 2.7 mmol) was added. During the process, hydrochloric acid/amine salt appeared as a solid precipitate. After 3 h, the reaction was terminated by removing the cooling bath to allow the mixture to warm up to rt. The mixtures were then filtered through filter paper (Whatman No.5) using a Buchner funnel attached to an aspirator. The filtrate was concentrated in a rotary evaporator at 30 °C under reduced pressure. The product is recovered in nearly quantitative yield. The solubility was measured by dissolving 0.1 g of product in 2.0 ml of the designed solvents. The viscous liquid or semi-solid products were analyzed to determine the molecular weight by using GPC and thermal properties by DSC and TGA.

3. Results and discussion

The reactions of cyanuric chloride with low molecular weight of alkyl and aromatic amines have been reported [17–28]. For example, the reaction of aromatic amines and cyanuric chloride afforded melamine derivatives [17]. It was reported that a stepwise and selective reaction of three symmetric chlorides in the triazine ring afforded dinitrobenzoyl derivatives [20] and modified melamine resins [25]. These amine substitutions were carried out at different reaction temperatures and solvents for three individual chlorides in the triazine ring. However, the use of cyanuric chloride as the linking core for amine polymerization, particularly for making high molecular weight poly(oxyalkylene) derivatives, has not been revealed in literature. In viewing all three reactive sites in cyanuric chloride for polymerization, the cross-linking gel formation is possible and must be avoided. Hence, an oligo(oxyalkylene)-monoamine of 2000 M_w has been first used in understanding the nature of cyanuric chloride reaction.

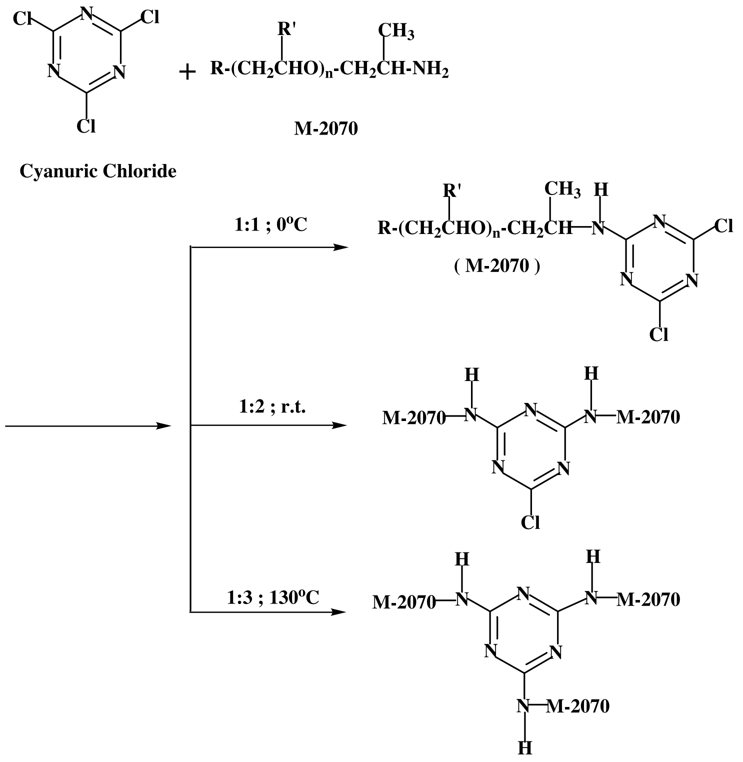
3.1. Selectivity for the reaction of cyanuric chloride and oligo(oxyalkylene)-monoamine of 2000 M_w (Jeffamine® M-2070)

The optimization of reaction temperatures and the selectivity of amine substitution on the three chlorides of cyanuric chloride were studied by using M-2070 as the starting amine. This polyetheramine M-2070 has only a single $-NH_2$ functionality for substitution on the triazine ring. To validate the selectivity mode for the substitutions of three chlorides, the reactions were carried out with different molar ratios of triazine to amine at 1:1, 1:2 and 1:3 (Scheme 1). After probing different temperatures, a single GPC product peak can be obtained by using the optimized reaction temperatures at 0, 25 and 130 °C (within ±5 °C precision) for three different molar ratios. The results indicate that the reaction temperature is the important parameter in controlling the amine substitution. Under the reaction temperature of 0 ± 5 °C, using THF as the solvent and under nitrogen atmosphere, the first chloride in the triazine ring was selectively substituted by 1 equiv. of M-2070 amine to produce a sole product. The substitution of second equivalent amines on the second chloride occurred at 25 ± 5 °C. Only at a high temperature such as 130 ± 5 °C does the third chloride in the triazine ring be reactive for the third equivalent of M-2070 monoamine. Mono-, di- and tri-substituted M-2070 products were easily identified by comparing the GPC distributions as shown in Fig. 2. These peaks generally have a polydispersity of 1.50 (M_w/M_n), in comparison with the polydisperisty of 1.17 for the starting M-2070. The gel permeation chromatograph unambiguously revealed the high selectivity of over 95% for each chloride substitution under the specific temperature. The reactions, using deviated temperatures from the optimized temperatures, afforded lower product selectivity. For example, the reaction of 1:3 molar ratio of triazine/M-2070 at 25 °C instead of 130 °C gave rise to a mixture of two GPC peaks, di-substituted and unreacted M-2070 starting material, without a trace of tri-substituted product. This implies the third chloride was not reacted at 25 °C. The differentiation of 0 °C from 25 °C was also realized in observing the presence of mono- and di-substitution mixtures in GPC chromatograms when the reaction was carried out under the condition of 1:1 reactant equivalent and 25 °C. In a similar manner, the high temperature of 130 °C was also optimized for the third chloride substitution.

The clear distinction of the relative reactivity among three chlorides revealed a possible synthetic methodology for tailoring the copolymer structure and composition. Linear, star-shaped and comb-branched block configurations can therefore be designed and prepared.

3.2. Preparation of linear poly(oxyalkylene) block copolymers

Two types of poly(oxyalkylene)-amines, hydrophilic poly(oxyethylene)-amine (POE-amine) and hydrophobic poly(oxypropylene)-amine (POP-amine) were employed to construct real high molecular weight of various hydrophobic, hydrophilic and amphiphilic linear block copolymers.



Scheme 1. Selectivity of cyanuric chloride with polyether-amine (M-2070) in THF or xylene/triethylamine.

3.2.1. POP multiple blocks of hydrophobic copolymers

Since the second chloride substitution in cyanuric chloride is highly selective for 25 °C from 130 °C, the linking agent can be considered as a di-functional linking core when reacting with diamine at 25 °C. At this temperature, a series of block copolymers were derived from the POP-diamine of 2000 M_w (i.e. D-2000) at various molar ratios (Scheme 2). At a 1:1 molar ratio, the copolymer at the highest molecular weight (25,600 M_n) and with a polydispersity of $M_w/M_n = 1.48$ was prepared. With an excess amount of amine at progressively increasing molar ratios in the range from 9/10 to 3/4, the copolymers, with a decreasing molecular weight ranging from 20,600 to 10,300 were observed (Table 1). On the basis of GPC analyses, the maximum degree of polymerization was achieved in approximately 12 of D-2000 segments, estimated by dividing M_n by segmental weight. The physical properties of these POP-backboned copolymers are similar to the amorphous D-2000 starting material. They are hydrophobic and water insoluble, but fairly soluble in common organic solvents such as tetrahydrofuran, toluene, chloroform and ethanol.

3.2.2. POE multiple blocks of hydrophilic copolymers

In contrast to those POP-amine derivatives, the hydrophilic POE-amines were coupled into copolymers of high molecular weights. The preparation involved the use of various equivalent ratios of POE-amine of 2000 molecular weight (i.e. ED-2001 in THF with triethylamine as HCl scavenger, and reacted at 25 °C for 24 h. Their chemical structures and the reaction scheme are illustrated (Scheme 3). Similar to the preparation of POP copolymers at ambient temperature, the POE/triazine coupling can reach a maximum molecular weight of 18,100 M_n. The degree of

Table 1
Reaction products and molecular weights of cc/D-2000 polymerization

Composition	Molar ratio	Theoretical[a] (g/mol)	GPC, M_w	GPC, M_n	M_w/M_n[b]
Cyanuric chloride (cc)	–	–	–	–	–
D-2000	–	2000	2500	2200	1.14
cc/D-2000	3:4	8100	15,200	10,300	1.48
cc/D-2000	5:6	12,300	19,300	13,800	1.40
cc/D-2000	7:8	16,400	31,000	19,700	1.57
cc/D-2000	9:10	20,500	32,900	20,600	1.60
cc/D-2000	1:1	–	38,000	25,600	1.48

[a] Theoretical molecular weights based on the idealized structures.
[b] Polydispersity.

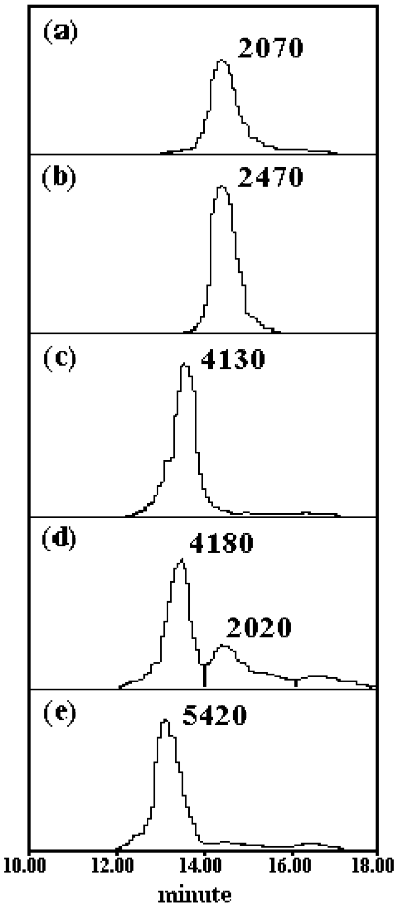


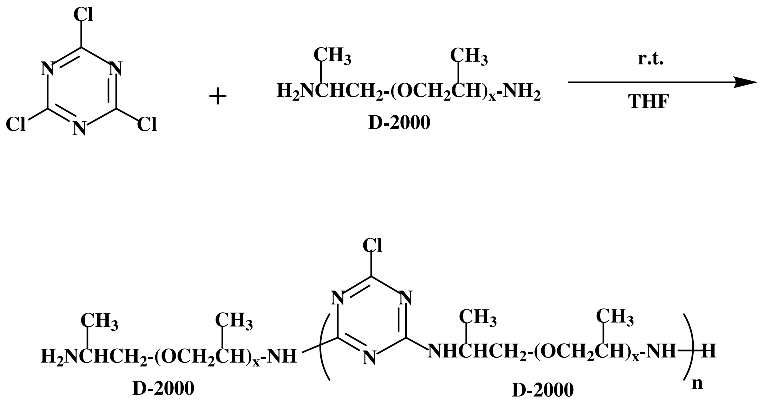
Fig. 2. GPC distribution of crude reaction products: (a) M-2070 starting material; (b) cc/M-2070 (1:1) at 0 °C; (c) cc/M-2070 (1:2) at rt; (d) cc/M-2070 (1:3) at rt; (e) cc/M-2070 (1:3) at 130 °C.

polymerization was estimated to be approximately 7. With an excess amount of POE-diamine to cyanuric chloride at the molar ratios of 9/10, 7/8, 5/6 and 3/4, the reactions afforded a series of copolymers with molecular weights progressively lower from 17,200 to 11,900. Since the POE-diamine equivalents were always in excess to the cyanuric chloride, it was believed that the coupled copolymers were amine-terminated. This was confirmed by the total amine titration showing the slight basicity for these products.

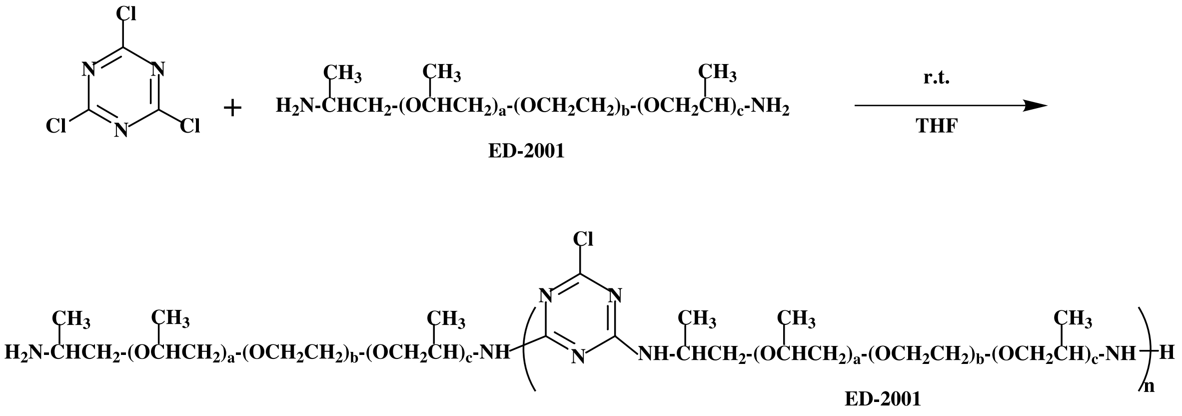
The properties of these POE-amine-coupled copolymers are significantly different from that of POP-amine-derived copolymers with respect to their hydrophilicity and crystallinity. As the starting materials, the POE-amine is hydrophilic and semi-crystalline (mp = 35 °C), while the POP-amine is hydrophobic and amorphous. Through the triazine linking, the POE-segmented copolymers, as analyzed by DSC, had a generally lower melting point (T_m) and melting enthalpy (ΔH_m) in the range of 31–21 °C (T_m) and 63–53 J/g (ΔH_m), respectively, than the starting ED-2001 ($T_m = 35$ °C and $\Delta H_m = 111$ J/g) (Table 2). The lowering of the segmental crystallinity is attributed to the interference of POE alignments by the triazine linking groups in the polymer strain. The POE segments are restricted with respect to their molecular chains by their inhomogeneous portions in the linking location. Otherwise, the high molecular weight of POE copolymers would allow a higher crystallinity than those observed. As a reference, the pure POE-amine of 6000 M_w has a crystalline phase with a $T_m = 54$ °C and $\Delta H_m = 144$ J/g [29], which is considerably higher than that of the 2000 M_w POE-amine.

3.2.3. POE–POP–POE tri-block of amphiphilic copolymers

In demonstrating the selectivity between the first and the second chloride of cyanuric chloride, we prepared a POE–POP–POE tri-block copolymer. When a 1:2 molar ratio of POP-diamine to cyanuric chloride was employed, the first chloride substitution occurred selectively at low temperature (preferably 0 °C). The resultant POP-derived di-triazine intermediate was allowed to further react with 2 equiv. of monoamines in a second step at a higher temperature (25 °C) to afford the tri-block copolymer (A). The synthetic route is shown in Scheme 4. Specifically, the hydrophobic intermediate of D-2000/triazine at 1:2 molar ratio was prepared at 0 °C and allowed to further react with 2 equiv. of hydrophilic M-2070 at 25 °C. As a result, the M2070–D-2000–M2070 tri-block copolymer was selectively prepared. The segmental arrangement of hydrophilic/hydrophobic/hydrophilic blocks, with a molecular weight of 2000 M_w each and with the hydrophilic POEs as the ends, gave rise to



Scheme 2. Preparation of hydrophobic prepolymer by cyanuric chloride and Jeffamine® D-2000 at various molar ratios.



Scheme 3. Preparation of hydrophilic prepolymer by cyanuric chloride and Jeffamine® ED-2001 at various molar ratios.

an amphiphilic copolymer having a molecular weight around 7800 g/mol (M_n).

3.2.4. POE–POP alternating multiple blocks of copolymers

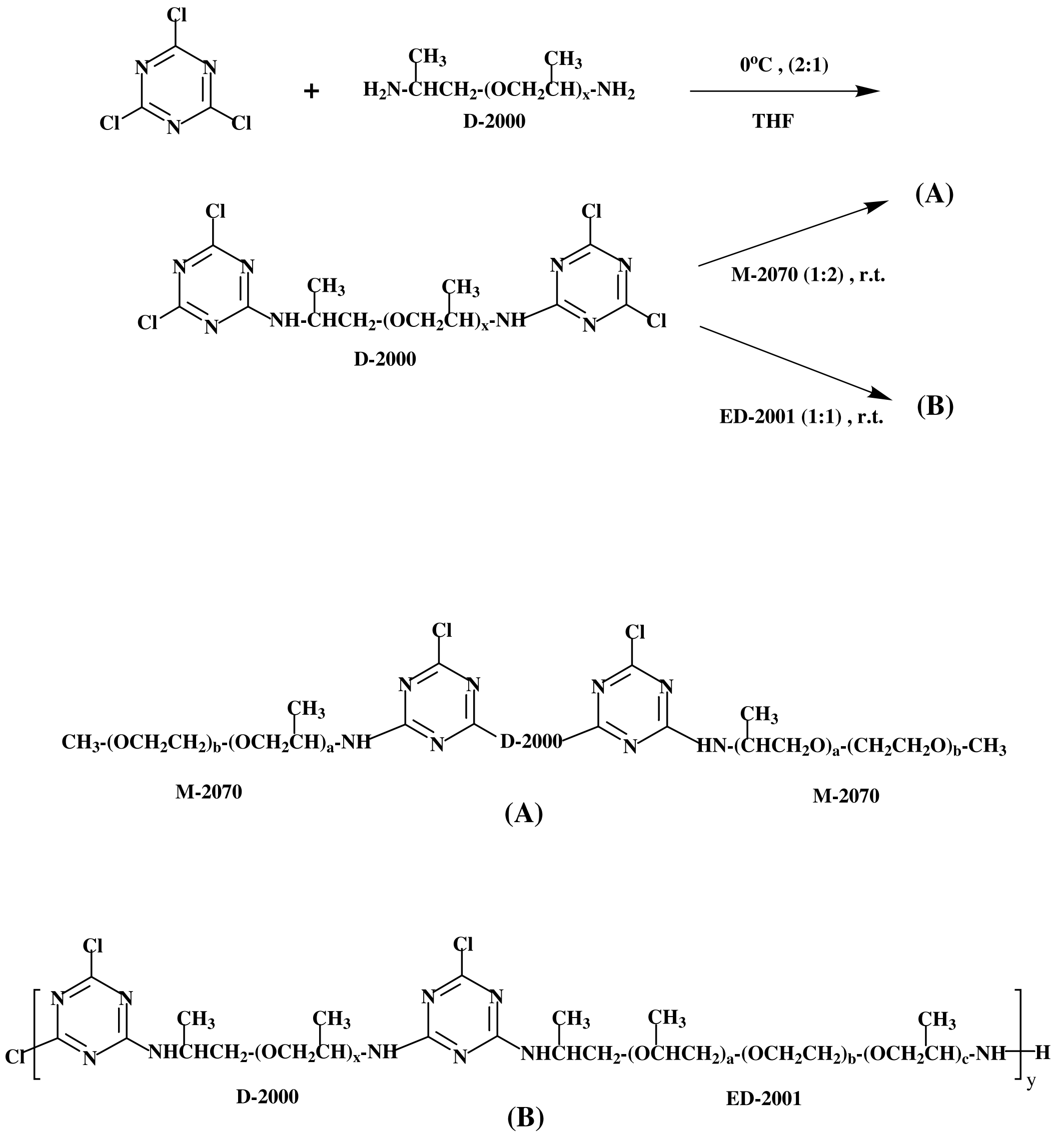
Another combination of block arrangement was also made according to Scheme 4. In this synthetic strategy, the same intermediate for preparing copolymer (A) is used to make copolymer (B). However, the di-functional POE-diamine (ED-2001) instead of M-2070 was subjected to the polymerization to afford a POE–POP block copolymer (B). The specific structure is arranged in a manner of alternating POE and POP blocks at approximately 2000 g/mol for each block. The linking of hydrophilic and hydrophobic diamines led to amphiphilic block copolymers. Hence, both POE–POP–POE tri-block and alternating POE–POP multi-block copolymers were prepared from the same D-2000/triazine (1:2) macromonomer. It is noteworthy that the synthesis is straightforward in terms of the reaction conditions at mild temperatures of 0 or 25 °C. Furthermore, the reaction involves only the first two chlorides in cyanuric chloride and the third triazine chloride in the copolymer still exists for further reaction at a higher temperature.

3.3. Relative thermal stability of POE- or POP-amine-coupled copolymers

Structurally, all of these analogous copolymers consist of POE- or POP-backbones and triazine cores. The relative thermal stability or thermo-oxidative degradation was analyzed by thermal gravimetric analysis (TGA) in air. The chemical nature of the structural difference between POE and POP backbones is the major factor contributing to the stability. Several representative copolymers in this study and their starting amine were analyzed as shown in Fig. 3. The following trend for thermal stability was observed: triazine/ED-2001 (7:8) > triazine/D-2000/ED-2001 (2:1:1) > ED-2001 > D-2000 > triazine/D-2000 (7:8). There are several factors determining this trend. First, the POE-rich backbone appears to be more stable than the POP derivatives. The thermal degradation of POE derivatives is known to undergo a random chain scission. Presumably, the mechanism involves the formation of free radicals and followed by C–O or C–C scissions in polymer backbones. The easiness of radical formation on the secondary carbon of $-[CH_2CH(CH_3)O]_x-$ over the primary carbon of $-(CH_2CH_2O)_x-$ is the key factor for controlling the relative thermal stability. In this order, the ED-2001-derived copolymers are generally more stable than the D-2000 derivatives. The second factor for stabilizing the copolymers is the presence of nitrogen functionalities such as amine and triazine. It was reported previously that the tethered amines could behave as antioxidants in stabilizing polymer backbones. In this study, it is shown that the triazine functionalities in the polymer structure can contribute to the backbone stability in a catalytic manner. For example, the triazine/ED-2001 (7:8) has a 50 wt% retention temperature at 369 °C, which is much higher than 306 °C for the starting ED-2001 under the identical TGA

Table 2
Reaction products and characterization of cc/ED-2001 polymerization

Composition	Molar ratio	Theoretical, M_w	GPC, M_w	GPC, M_n	M_w/M_n	ΔH (J/g)	T_m (°C)
Cyanuric chloride (cc)	–	–	–	–	–	–	–
ED-2001	–	2100	3200	2700	1.18	111.4	35.0
cc/ED-2001	3:4	8900	18,000	11,900	1.51	62.8	31.3
cc/ED-2001	5:6	13,400	18,700	14,000	1.33	59.0	23.9
cc/ED-2001	7:8	18,000	24,600	15,700	1.57	53.3	21.1
cc/ED-2001	9:10	22,500	26,600	17,200	1.55	54.7	23.2
cc/ED-2001	1:1	–	28,700	18,100	1.59	54.7	25.0



Scheme 4. Two-step oligomerization and polymerization of tri-block and multi-block hydrophilic/hydrophobic copolymers.

heating condition. Similarly, the triazine/D-2000/ED-2001 (2:1:1) is more thermally stable than the starting amines, ED-2001 or D-2000. It is reasonable to consider triazine cores to be antioxidants or free radical scavengers for the thermo-oxidative process. The built-in triazine functionalities in the copolymer backbones greatly stabilize the POE- and POP-portions, with an exception of the triazine/D-2000 copolymer.

3.4. Self-associating property in toluene

The block copolymers with POE/POP combinations were investigated with respect to their surfactant behaviors in solutions, particularly the interfacial tension in toluene/-water. With the designed balance between hydrophilic and hydrophobic segments, the copolymer behaved like surfactants. Dissolved in toluene at different concentrations, the copolymers were capable of reducing the interfacial tension in toluene/water significantly (Fig. 4). In the case of the alternating hydrophilic/hydrophobic block copolymer or triazine/D-2000/ED-2001 at 2:1:1 molar ratio, the interfacial tension was reduced as low as 2.1 dyne/cm. Remarkably, the critical micelle concentration (cmc), obtained by extrapolating from the curve of interfacial tension versus concentration, is estimated to be only 100 ppm. The extremely low cmc implies the high efficacy as a surfactant. The low interfacial tension indicates the broad coverage of surface area per copolymer molecule. From the viewpoint of bonding forces, the POE block interacts with water through hydrogen bonding in balancing with the hydrophobic alkyl effect of POP block with toluene. Both types of non-covalent bonds compete and attract the molecules in the interfacial layer between toluene and water. However, it is not clear if the presence of triazine cores in the structure contributes significantly to the bonding force through aromatic interactions. Presumably, the

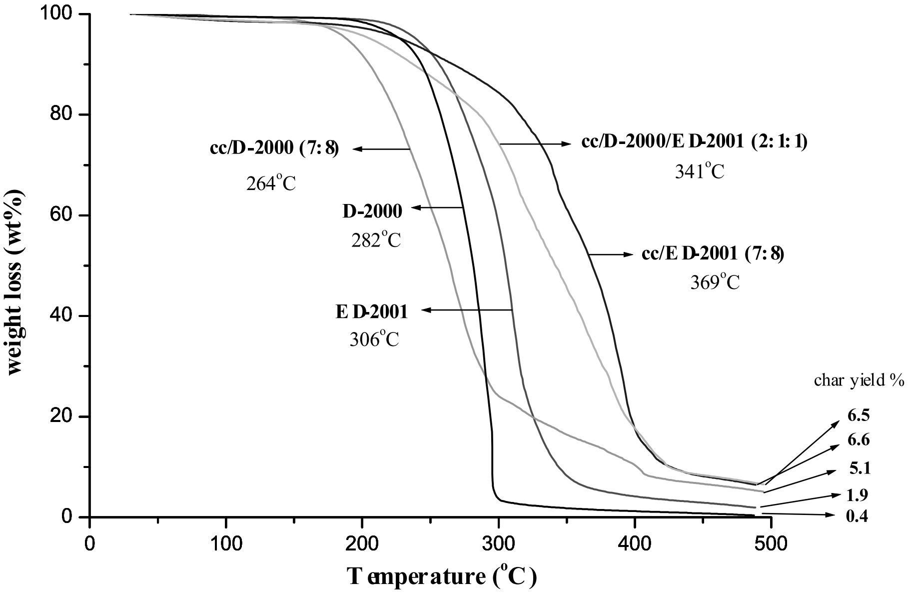


Fig. 3. Relative thermal stability and 50% decomposition temperature of the starting amines and their block copolymers in air.

linkage groups of triazine-NH may provide additional hydrogen-bonding sites as well as the triazine π–π-stacking interaction. With a similar POE/POP weight ratio as the hydrophilic and hydrophobic components but different structural arrangements, the analogous copolymers have the similar behavior in reducing interfacial tension (Fig. 4).

4. Conclusions

A new synthetic methodology of linking POE- and POP blocks into high molecular weight poly(oxyalkylene)-amines by using 2,4,6-trichloro-1,3,5-triazine as the coupling agent has been developed. The coupling reaction is highly selective for three triazine chlorides in preparing copolymers with various configurations including alternating or random POE/POP multiple blocks. The presence of triazine cores renders the copolymer less crystalline but higher thermal stability than their POE- and POP-amine starting materials. The copolymers with the proper balance of hydrophilic and hydrophobic POE/POP blocks can exhibit a self-associating property in toluene, evidenced

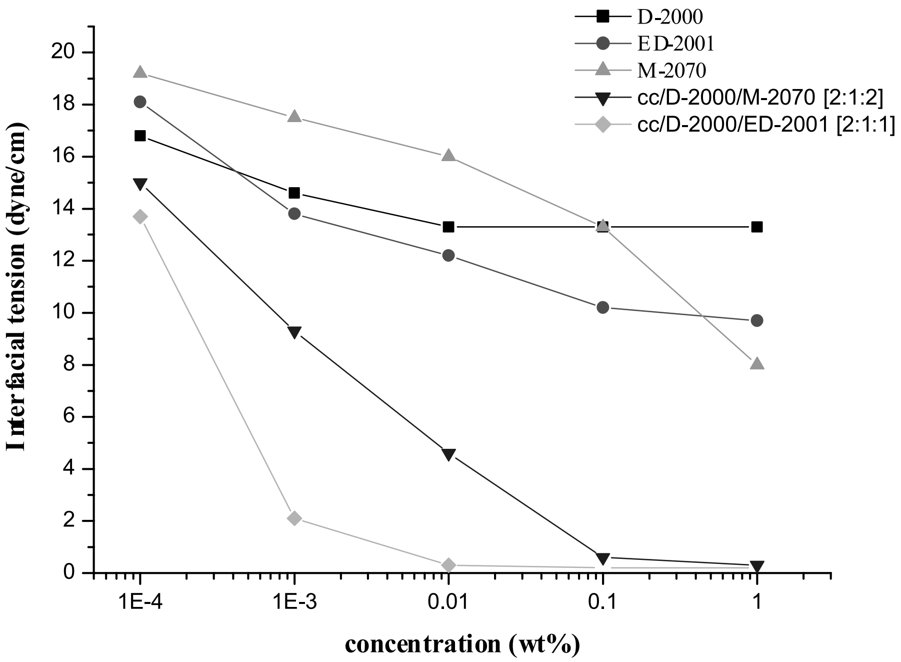


Fig. 4. Interfacial tension of surfactants in toluene/water.

by observing the significant reduction of interfacial tension at low cmc.

Acknowledgements

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