Synthesis and properties of cross-linkable macromers from the selective substitution of poly(oxyalkylene)-amines and cyanuric chloride

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Abstract

Reactive macromers, consisting of hydrophilic poly(oxyethylene) and hydrophobic poly(oxypropylene) blocks and alternating chloro-triazine linking groups, were prepared from the tri-functional cyanuric chloride and poly(oxyalkylene)-diamines (POA-amines) in a selective manner. Macromers with multiple reactive chlorides could be structurally tailored by varying the ratios of amine/cyanuric chloride, types of the starting POA-amines and temperature (lower than 30 °C). At an elevated temperature (>140 °C), the macromers could be self-cured or cured with additional amine to form polymer films. The films exhibited high thermal stability, solvent-adsorption, and low surface electronic resistivity. The facile synthesis of cross-linkable macromers provides a new synthetic approach for preparing hydrophilic antistatic films with high electrostatic dissipating ($<10^5$ Ω/sq) property.
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1. Introduction

Block copolymers with electrostatic dissipation properties may have valuable applications as solid electrolytes and antistatic agents for electronic packaging and encapsulating materials [1,2]. As antistatic materials, the copolymers are required to be hydrophilic and moisture-absorbing. Early patents reveal the scope of polymer structure and their working principle [2–4]. In these disclosures, for example, the copolymers prepared from polyethylene glycol and aminocarboxylic acid were claimed for the ability to dissipate electrostatics because of their hygroscopic characteristics. A similar structure for the copolymers that are incorporated with poly(oxyethylene) (POE) blocks may result in the ability to chelate metal-ions [5]. Through ionic conduction, the copolymer surface resistivity is reduced to a low range of 10^{4-6} Ω/sq from $>10^{12}$ Ω/sq for a common polymers and from a moderate range of 10^{8-10} Ω/sq for a hydrophilic copolymer. Materials with a low surface

resistivity are suitable for anti-electrostatic accumulation or solid electrolytes, depending on the range of electronic resistivity. However, the mechanism of lowering a polymer's resistivity is often limited by the inherent crystallinity of the POE segments. Since, ionic conductivity is function of ionic concentration, charges and mobility in the matrix [6,7], these properties consequently depend on ionic solvating ability and flexibility of a polymer. Therefore, a low crystalline or amorphous polymer is more suitable for ion conduction compared to a crystalline polymer. The crystallinity of a POE-segmental copolymer may be mitigated by designing a partially cross-linking structure in order to limit the POE segregation in the matrices [8]. The POE-segmented copolymers designed with linear, hyper-branched, and dendritic structures have been widely reported [9–13]. Recent research indicates that the amphiphilic POE block copolymers acquire the unique ability to self-assemble and direct inorganic nanoparticles to form orderly arrays, which can be described as a 'bottom-up' process for synthesizing nanomaterials [14]. In an effort to synthesize functional POE copolymers, we have reported the copolymerization of water-soluble POE-diamines and a dibasic acid to form an electrostatic dissipating product [15–18]. By adopting a POE-amine grafting reaction of the maleated polystyrene–poly(ethylene/butylene)–

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polystyrene, we have also synthesized comb-shaped, amphiphilic copolymers [19]. In these previous studies, we realize that the use of 2000 g/mol molecular-weight POE-diamines as the constructing blocks results in copolymers that often contain a significant crystalline domain in the polymer matrices. Further improvements for minimizing the copolymer crystallinity required a convenient method to prepare cross-linking POE-copolymers. Here we report our extended work on the methodology of coupling amines with cyanuric chloride in a selective manner [20,21] to prepare hydrophilic POE-block and cross-linkable macromers which can be subsequently converted into flexible films for antistatic applications.

2. Experimental

2.1. Materials

Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine, mp 145–148 °C), was obtained from Aldrich Co. and purified by recrystallization from methanol before use. Poly(oxyalkylene)-diamines (POA-amines) were purchased from Aldrich Chemical Co. or Huntsman Chemical Co. The two types of POA-amines used are poly(oxyethylene)-(POE-) and poly(oxypropylene)- (POP-) diamine of different molecular weights, as shown in Fig. 1. The hydrophilic and water-soluble POE2000-diamine (white waxy solid, mp 35 °C, titrated amine content 0.95 meq/g) consists of a middle polyoxyethylene block and two short oxypropylene ending blocks with an average of 39.5/5 oxyethylene/oxypropylene unit ratio. Diethylene triamine (DETA) is a low molecular weight and tri-functional amine. The POP-diamines, on the other hand, have a generic poly(propylene glycol) backbone and two terminal 2-propyl-amine groups of molecular weights 230, 400 and 2000 g/mol (abbreviated as POP230, POP400 and POP2000, respectively). Among these POP-amines, high molecular weight of POP2000 is hydrophobic and water-insoluble, compared to the hydrophilic and water-soluble for low-molecular-weight ($<$ 400 g/mol) POP-amines as well as POE2000.

$$H_2NCHCH_2\text{-}(OCH_2CH)_n\text{-}NH_2 \qquad H_2NCH_2CH_2NHCH_2CH_2NH_2$$

n= 2~3 (POP230)
n= 5~6 (POP400)
n= 33 (POP2000)

Diethylene triamine (DETA)

$$H_2NCHCH_2\text{-}(OCHCH_2)_a\text{-}(OCH_2CH_2)_b\text{-}(OCH_2CH)_c\text{-}NH_2$$
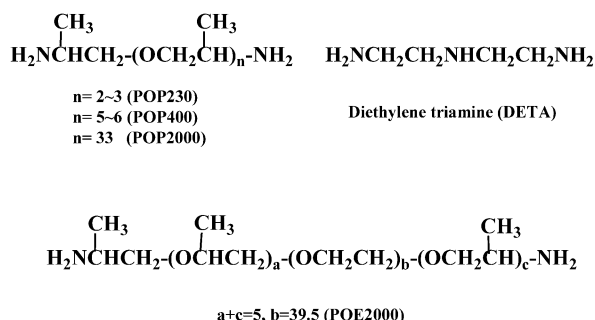
a+c=5, b=39.5 (POE2000)

Fig. 1. Chemical structures of the starting POP and POE amines.

2.2. Measurement

Thermal gravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 1, by heating the sample from room temperature to 500 °C at a rate of 10 °C min^{-1} in air or nitrogen. The analyses of melting and crystalline temperatures were carried out by using a differential scanning calorimeter (DSC, Perkin Elmer Pyris 6). Sample size of 3–8 mg on a sealed aluminum pan was generally used. The temperature range of −20–100 °C at a heating rate of 10 °C min^{-1} with a nitrogen flow of 20 ml min^{-1} was used. Surface resistivity was measured using a ST-3 model (Simco Co.) tester, according to the ASTM method D257-93. All samples were conditioned in an atmosphere of 50% relative humidity before measurement.

2.3. Synthetic procedures for macromers and their cross-linked polymers

The typical procedures for preparing amine-terminating and chlorotriazine-terminating macromers A and B are described below. A three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet–outlet lines and a thermometer was charged with POP2000 (10 g, 5.0 mmol) and THF (50 ml). The mixture was stirred at ambient temperature under nitrogen atmosphere. The powdered form of cyanuric chloride (0.8 g, 4.4 mmol) was added to the mixture in one portion, followed by adding triethylamine (0.9 g, 8.8 mmol). During the progress of the reaction, quaternary ammonium salt precipitate was observed. After continuous stirring for 24 h at ambient temperature, the solid was filtered (Whatman No. 5) and the filtrate was concentrated by rotary evaporation below 30 °C under a reduced pressure. The viscous liquid or semi-solid product (assigned as macromer A) was analyzed by using gel permeation chromatography, showing an average molecular weight (M_n) of 19,700 g/mol and polydispersity of 1.57. The analysis is consistent with the calculated molecular weight of 16,400 g/mol based on the starting material at 8:7 molar ratio. Similar procedures were applied for preparing other macromers involving POE2000 and also chloro-triazine rich, such as 2:1 starting material ratio of cyanuric chloride/amine at 0 °C.

The sample plaque is prepared by stirring macromer A (2 g, 0.12 mmol), THF (5 ml) and cross-linking agents (DETA, POP230, POP400, POP2000 or POE2000 in a designated amount) together until homogeneous in an aluminum container at room temperature. The sample plaque was obtained after subjecting to solvent evaporation at 140 °C, 2 h in a vacuum oven (Diagram 1). In a separate experiment, macromer A was able to self-cure into cross-linked polymers under the similar condition without the addition of a cross-linking agent.
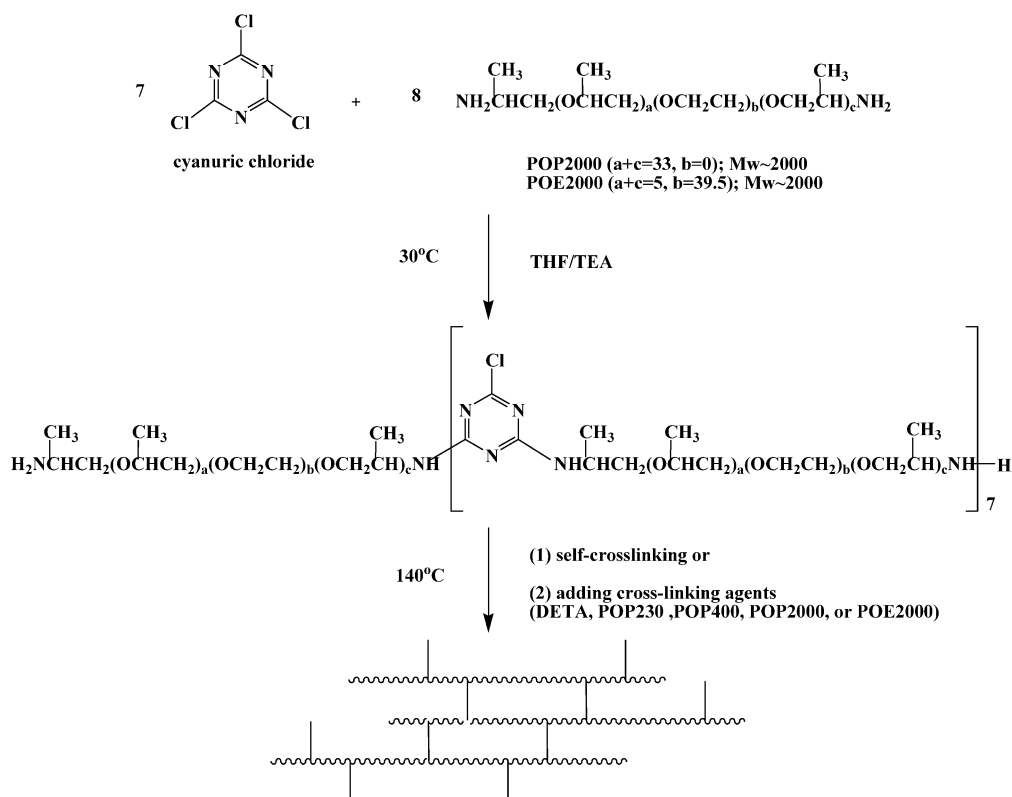
Diagram 1. Synthetic scheme and conceptual illustration of cross-linked structure from macromer A.

3. Results and discussion

3.1. Preparation and structures of macromers

Previously, we have developed a method for selectively coupling POA-amines with cyanuric chloride into block copolymers by controlling the condition of reaction [20,21].

The selective substitution of cyanuric chloride (triazine-Cl$_3$) toward primary amines allows us to prepare linear and branch block copolymers. By using POA diamines of 2000 g/mol molecular weight, the three chlorides in triazine-Cl$_3$ may be substituted in a sequential manner, controllable by varying temperatures at 0, 25 or >130 °C. Upon the addition of the first equivalent of primary amines,
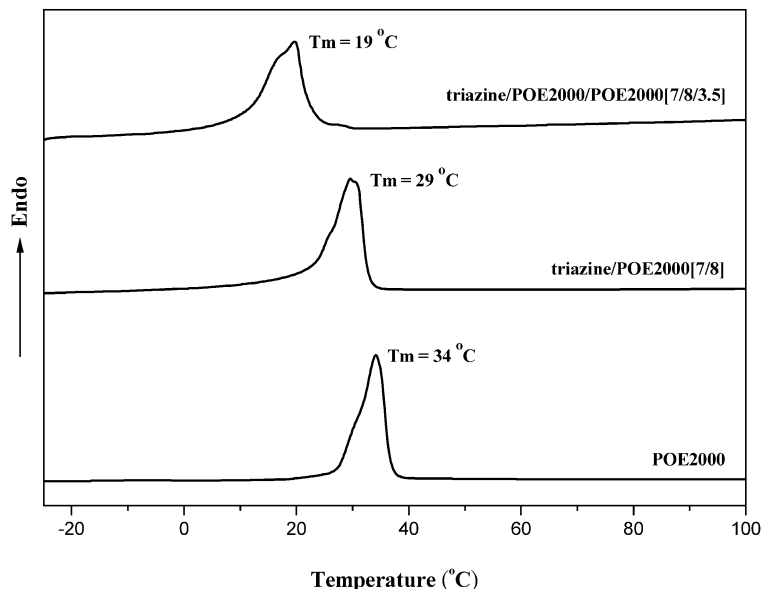
Fig. 2. Comparative DSC analyses of POE2000 starting amine, macromer and film.

triazine-Cl_3 was converted to triazine-Cl_2 which may be consequently substituted by a second amine, at a mild temperature of 0–25 °C. The third chloride was only reactive at temperature above 130 °C. By taking advantage of three distinctly different rates of C–N bond formation as revealed in the previous reports, the macromers of various structures can be prepared and subsequently cured into flexible films. In particular, both amine- and triazine-terminating macromers were made by selecting molar ratios of diamine/triazine-Cl_3 at 8:7 and 1:2, respectively. With the use of more amine equivalents than triazine-Cl_3, macromer A is composed of several triazine-Cl linking cores and two primary amines at the terminals. In this structure, each linking triazine-Cl core still has one chloride, which is reactive and self-curable at 140 °C. On the other hand, the triazine-terminating copolymer consists of triazine-Cl_2, which may be cured with DETA at 30 °C. The idealized structure for macromer A consists of seven linking triazine cores and eight segments of POE- or POP-blocks, as depicted in Diagram 1.While the POP-derived macromers are amorphous and hydrophobic, the POE derivatives are actually crystalline copolymers. For example, the triazine/POE2000 (7:8) macromer has a melting point of 30 °C and melting enthalpy of 67 J/g (ΔH_m). By comparison, the crystallinity was lower than the starting POE2000 ($T_m = 34$ °C and $\Delta H_m = 119$ J/g) (Fig. 2).

Low melting temperature implies a possible higher POE backbone mobility in the polymer matrix and an increased dissipating ability for electrostatics. Therefore, the presence of triazine-Cl cores not only provide reactive cross-linking sites but also the advantage of lowering POE crystallinity which ultimately facilitating the electrostatic dissipating ability.

3.2. Insoluble and hygroscopic properties of the cross-linked films

The prepared macromers are generally soluble in organic solvents including THF, toluene and ethanol. With the addition of an amine cross-linker such as POP230, POP400, POP2000, and DETA, the macromers were cured into polymer films at an elevated temperature of 140 °C through the triazine-Cl reactive sites. The prepared films were insoluble in any organic solvents, but swelled in water and other solvents. As summarized at Table 1 and Fig. 3, the cross-linked network of triazine/POP2000/POP2000 (7:8:3.5 molar ratio) could absorb toluene up to 5.3 g/g of the film, as compared to 0.5 g/g for water absorption. In contrast, the POE-rich film, triazine/POE2000/POE2000 (7:8:3.5), absorbed more water (5.7 g/g) than toluene (1.3 g/g), indicating its high hygroscopic characteristics. The difference of their

Table 1
Solvent absorbing and swelling properties of the cross-linked films

Films[a]	H_2O[b]	Ethanol	THF	Ethyl acetate	Toluene	$CHCl_3$	IPA	DMSO	Hexane	CH_3CN	DMAc
Triazine/ POE2000/ POP230	4.1	3.2	3.4	2.0	1.4	10.9	0.8	4.2	0.02	2.6	3.7
Triazine/ POE2000/ POP400	4.8	3.9	3.9	2.3	1.7	11.4	1.0	4.9	0.04	2.7	4.2
Triazine/ POE2000/ DETA	3.8	2.9	2.6	1.6	1.4	9.5	0.6	3.5	0.04	2.2	3.0
Triazine/ POE2000/ POE2000	5.7	4.2	3.4	2.1	1.3	11.6	0.9	5.3	0.03	2.9	4.2
Triazine/ POP2000/ POP230	0.4	6.0	9.4	5.4	6.7	17.7	3.2	1.1	0.53	2.1	6.6
Triazine/ POP2000/ POP400	0.7	4.2	6.3	4.0	5.5	13.0	2.4	0.7	0.53	1.7	4.1
Triazine/ POP2000/ DETA	1.9	3.5	5.5	4.3	4.8	11.0	2.0	0.9	0.4	1.5	3.6
Triazine/ POP2000/ POP2000	0.5	5.6	6.3	4.5	5.3	14.0	3.0	0.5	0.5	1.9	4.6

[a] The films were prepared from triazine/POE2000 or triazine/POP2000 at 7:8 molar ratio and then cured into films with 3.5 equivalent amines, indicated as the third component.

[b] The values are the absorbed weight (g) per gram of film samples.
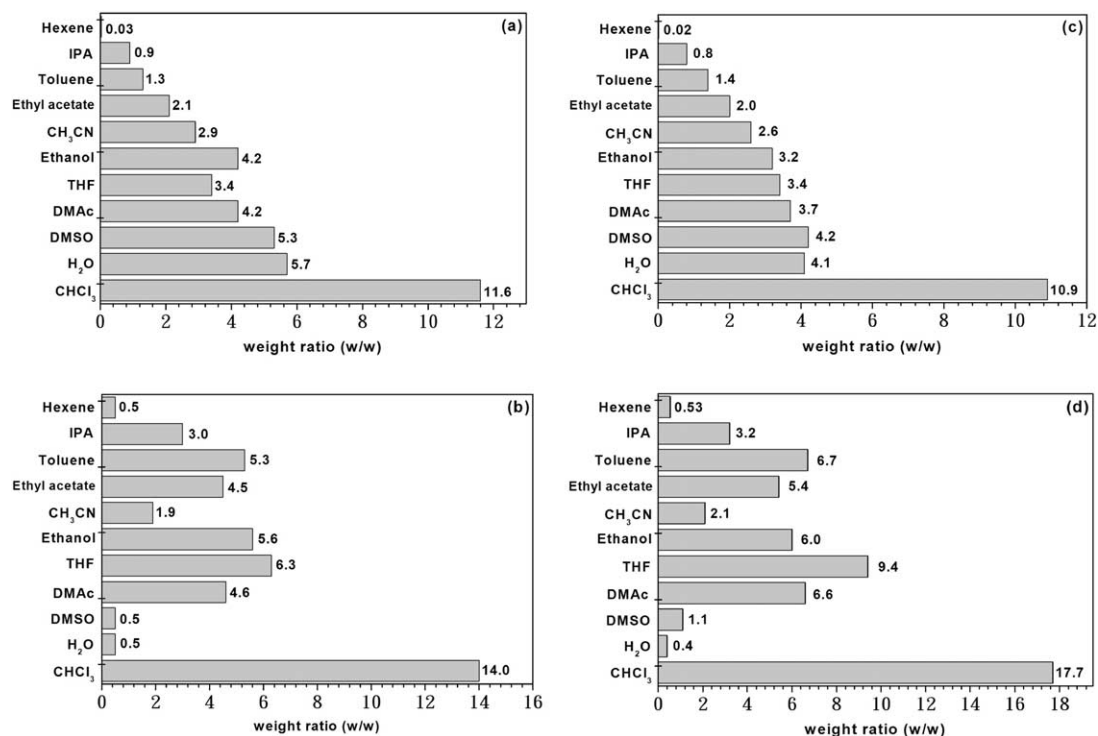
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Fig. 3. Solvent absorption (a) triazine/POE2000/POE2000, (b) triazine/POP2000/POP2000, (c) triazine/POE2000/POP230, (d) triazine/POP2000/POP230.

relative affinity for toluene and water is attributed to the presence of hydrophobic POP or hydrophilic POE segments in the structures. It is also noticed that chloroform is a good swelling solvent for both types of cross-linked networks (up to 10–14 g/g).

3.3. Electrostatic dissipating property

Conventional polymeric materials that dissipate electrostatics were polymers coated with low-molecular-weight amines, amides, and quaternary ammonium salts. Due to

Table 2
Surface resistivity with respect to POE compositions and metal ions added into the cross-linked films

Film composition[a,b]	Molar ratio	POE-fraction (wt%)[c]	Surface resistivity (10^X Ω/sq)
POE2000 starting material	–	89	10.0
Triazine/POE2000 (self-cross-linked)	7:8	85	9.2
Triazine/POP2000/POP230	7:8:3.5	0	8.2
Triazine/POP2000/POP400	7:8:3.5	0	7.8
Triazine/POP2000/DETA	7:8:3.5	0	8.1
Triazine/POP2000/POP2000	7:8:3.5	0	7.8
Triazine/POE2000/POP230	7:8:3.5	82	4.7
Triazine/POE2000/POP400	7:8:3.5	79	4.9
Triazine/POE2000/DETA	7:8:3.5	84	4.8
Triazine/POE2000/POE2000	7:8:3.5	86	4.4
Triazine/POE2000/POP230 (Cu^{2+})	7:8:3.5	82	4.6
Triazine/POE2000/POP400 (Cu^{2+})	7:8:3.5	79	5.0
Triazine/POE2000/DETA (Cu^{2+})	7:8:3.5	84	4.8
Triazine/POE2000/POE2000 (Cu^{2+})	7:8:3.5	86	4.5
Triazine/POE2000/DETA (Li^+)	7:8:3.5	84	4.5
Triazine/POE2000/POE2000 (Li^+)	7:8:3.5	86	4.8

[a] Films were prepared from triazine/POP2000 (or POE2000) macromers and cured with the third component amines, except the self-crosslinked film.
[b] Cu^{2+} or Li^+ ion adsorbed film was prepared by a dipping process in $CuSO_4$ or LiCl aqueous solution.
[c] Calculated from the formula of macromers.

new requirements in electronic applications, polymeric types of antistatic materials were developed and blended in polymers. Previous studies indicated that the copolymers with POE blocks having the ability to chelate lithium ions were suitable for ionic conduction [12]. For an ionic hopping mechanism, the efficiency of electronic conduction is a function of the polymer mobility and ionic charges. The compromise for designing a suitable ionic conducting polymer is made by adjusting two requirements, high POE weight fraction for ionic chelation and low crystalline fraction for polymer flexibility. The cross-linked films prepared from the triazine/POE2000 (7:8) macromer had a generally low surface resistivity in the range of 10^{4-5} Ω/sq, significantly lower than the starting POE2000 at 10^{10} Ω/sq. It is noteworthy that the drop of resistivity as low as 10^{4-5} Ω/sq is unusual when comparing with other POE-derived copolymers as reported previously [15,18]. In general, the electrostatic dissipating ability can only reach the range of 10^{6-12} Ω/sq for POE-block copolymers. As summarized in Table 2, the POP2000-derived films had a relatively high surface resistivity (10^{8} Ω/sq) due to its inability to adsorb water. The presence of POE segments in the structure is essential for associating with water molecules through hydrogen bonding and possible ionization of water in contributing to the electronic conductivity (Fig. 4).

In general, the surface resistivity is expected to be lowered if the POE block coordinates with metal ions through dipole–dipole interaction [22,23]. The interaction between the ether oxygen of POE segments and the dissociated metal ions was suggested to be stoichiometric coordination with a molar ratio of 3/1 for $-CH_2CH_2O-$ to monovalent ions such as Na^+ and Li^+ [24,25]. When dipped in an aqueous solution of 0.1 M $CuSO_4$ for 24 h, the cross-linked films changed in color from light-yellow to blue-green due to the Cu^{2+} association. However, the adsorption of Cu^{2+} or other metal ions such as Li^+ did not further reduce the surface resistivity (10^{4-5} Ω/sq) of these films. It seems that the electrostatic dissipation was mainly affected by moisture adsorption rather than ionic conduction (Table 2 and Fig. 4).
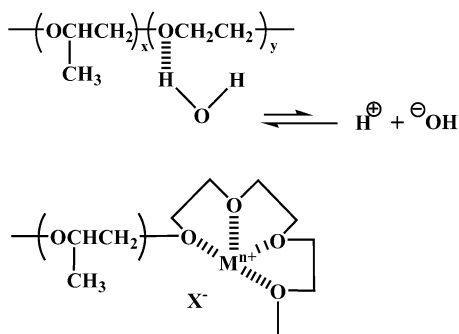

Fig. 4. Hygroscopic property and metal ion chelation of POE-segmented copolymers.

3.4. Relative thermal stability of the films

In order to establish the relative thermal stability, several representative macromers, film materials and their starting amines were examined using thermal gravimetric analysis (TGA) in nitrogen (Table 3 and Fig. 5). The major factor influencing their thermal stability was the structural difference between the POE and POP blocks. The following thermal stability trend is observed with respect to the 50% weight loss in the TGA curve: triazine/POE2000/POE2000 > triazine/POE2000/POP230 = triazine/POE2000/DETA > triazine/POE2000/POP400 > triazine/POP2000/POP400 > triazine/POP2000/POP230 > triazine/POP2000/DETA > triazine/POP2000/POP2000. More specifically, the POE blocks contributed at least 14 °C difference of thermal stability compared to the POPs. The tertiary carbon ($-CH_2-C^*H(CH_3)O-$) in the POP backbone may facilitate free radical formation, and hence decreased stability compared to the secondary carbon ($-CH_2CH_2O-$) in the POE structure [26].

It is also found that the thermal stability of these films is influenced by the presence of the triazine linking cores and
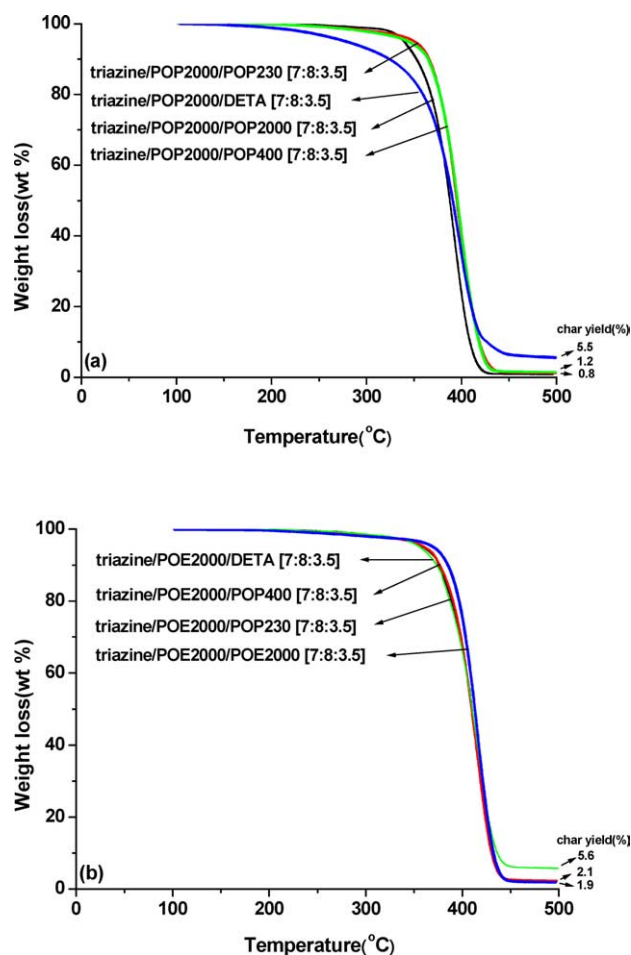

Fig. 5. Relative thermal stability in N_2 (a) triazine/POP2000/amine, (b) triazine/POE2000/amine.

Table 3
Thermal gravimetric decomposition in nitrogen

Composition	Temperature (°C)				Char yield (%)
	Weight remained (wt%)				500 °C
	95	75	50	25	
Triazine/POP2000/POP230 (7:8:3.5)	350	381	394	407	1.2
Triazine/POP2000/POP400 (7:8:3.5)	344	381	395	408	1.3
Triazine/POP2000/DETA (7:8:3.5)	278	368	390	406	5.5
Triazine/POP2000/POP2000 (7:8:3.5)	339	372	387	399	0.8
Triazine/POE2000/POP230 (7:8:3.5)	359	394	410	422	2.1
Triazine/POE2000/POP400 (7:8:3.5)	360	395	409	421	2.3
Triazine/POE2000/DETA (7:8:3.5)	356	392	410	423	5.6
Triazine/POE2000/POE2000 (7:8:3.5)	370	400	413	423	2.0
Triazine/POE2000/DETA (2:1:2)	303	394	413	433	5.0
Triazine/POP2000/DETA (2:1:2)	298	396	417	429	5.7

amine functionalities. For example, the triazine/POE2000/POE2000 (7:8:3.5) has a 50% retention temperature at 413 °C, which is more stable than the 395 °C for the starting POE2000 under the same conditions (Table 4). When measured in air for their oxidative stability, the presence of terminal amine functionalities was found to be effective for scavenging radicals thus stabilizing the copolymer backbones. As shown in Fig. 6, the use of triamine as the cross-linking agent such as DETA provided additional secondary-amines in the structure and rendered the cross-linked film more stable than the diamine cured film. The relative oxidative stability in air is as follows: triazine/POE2000/DETA > triazine/POE2000/POP400 > triazine/POE2000/POP230 > triazine/POE2000/POE2000 > triazine/ POP2000/DETA > triazine/POP2000/POP400 > triazine/POP2000/POP230 > triazine/POP2000/POP2000. The

Table 4
Thermal gravimetric decomposition in air

| Composition	Temperature (°C)				Char yield (%)
	Weight remained (wt%)				500 °C
	95	75	50	25	
Triazine/POP2000/POP230 (7:8:3.5)	239	329	360	379	5.9
Triazine/POP2000/POP400 (7:8:3.5)	288	344	362	375	4.7
Triazine/POP2000/DETA (7:8:3.5)	258	358	375	389	7.2
Triazine/POP2000/POP2000 (7:8:3.5)	247	296	330	358	4.6
Triazine/POE2000/POP230 (7:8:3.5)	319	370	388	406	8.0
Triazine/POE2000/POP400 (7:8:3.5)	320	370	390	407	7.7
Triazine/POE2000/DETA (7:8:3.5)	329	379	396	413	8.9
Triazine/POE2000/POE2000 (7:8:3.5)	290	360	385	404	7.5
Triazine/POE2000/DETA (2:1:2)	246	321	385	437	17.9
Triazine/POP2000/DETA (2:1:2)	256	345	404	438	16.2
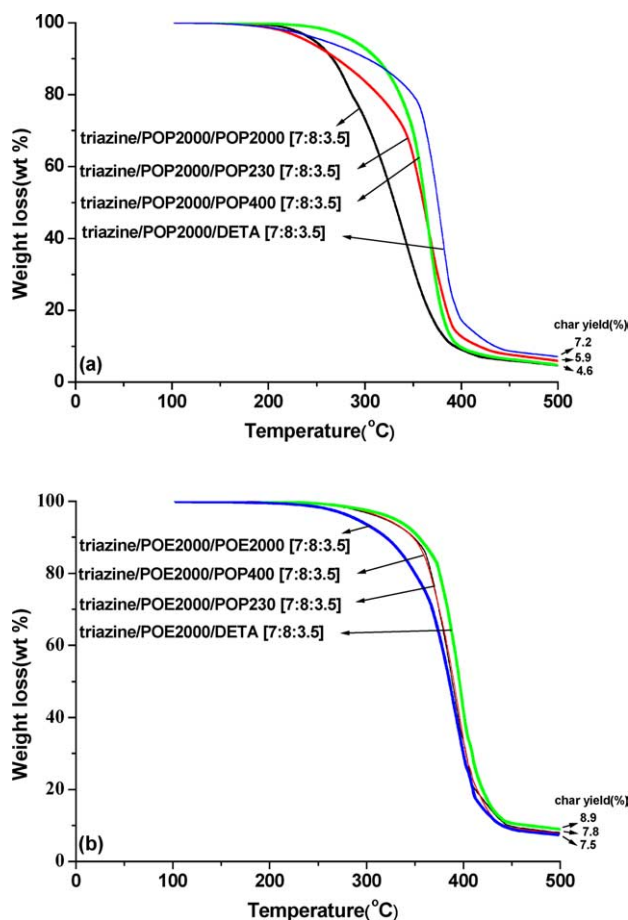
Fig. 6. Relative thermal stability in air (a) triazine/POP2000/amine, (b) triazine/POE2000/amine.

the types of curing amines, the resultant cross-linked films are hygroscopic and thermally stable. The low surface resistivity ($10^{4.4}$ Ω/sq) suggests that these films are suitable for electrostatic dissipation applications. The low resistivity is attributed to both the high composition of hydrophilic POE and the low crystallinity due to the cross-linked structure, while the thermal stability is largely due to the triazine and amine functionalities.

Acknowledgements

trend of thermal stability is correlated with the structural functionalities, in which, the presence of the triazine cores, amines and POE backbone greatly contribute to the film stability.

4. Conclusions

Cross-linkable macromers from the coupling reaction of POA-diamines and cyanuric chloride were prepared according to previously developed procedures. Depending on the different backbones such as POE- and POP-block and also

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