Journal of Macromolecular Science, Part A: Pure and Applied Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lmsa20

# Synthesis and Characterization of Amphiphilic PEG Based Aliphatic and Aromatic Polymers and their Self-Assembling Behavior

Dhruba Jyoti Sarkar [a], Jitendra Kumar [a], N. A. Shakil [a], Totan Adak [a] & A. C. Watterson [b]

[a] Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi, India

[b] Institute for Nano-Science Engineering and Technology, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA

Available online: 30 Apr 2012

To cite this article: Dhruba Jyoti Sarkar, Jitendra Kumar, N. A. Shakil, Totan Adak & A. C. Watterson (2012): Synthesis and Characterization of Amphiphilic PEG Based Aliphatic and Aromatic Polymers and their Self-Assembling Behavior, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 49:6, 455-465

To link to this article: http://dx.doi.org/10.1080/10601325.2012.676845

*Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* (2012) **49**, 455–465

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2012.676845



# Synthesis and Characterization of Amphiphilic PEG Based Aliphatic and Aromatic Polymers and their Self-Assembling Behavior

DHRUBA JYOTI SARKAR[1], JITENDRA KUMAR[1,*], N. A. SHAKIL[1], TOTAN ADAK[1], and A. C. WATTERSON[2]

[1]*Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi, India*
[2]*Institute for Nano-Science Engineering and Technology, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA*

Received, Accepted January 2011



Twelve amphiphilic polymers were synthesized using poly(ethylene glycols) (PEGs) of different molecular weights, *viz.* 1000, 2000 and 4000 as hydrophilic block and linkers namely azelaic acid, sebacic acid, dimethyl isophthalate acid and dimethyl terephthalate as hydrophobic block in the presence of catalyst Conc. $H_2SO_4$. Synthesized polymers were characterized by using $^1$H-NMR, $^{13}$C-NMR and IR spectroscopy. Micellar sizes of the polymers were determined using Dynamic Light Scattering (DLS) which ranged from 51.6–174 nm for aliphatic polymers and 135.5–371 nm for aromatic polymers. Transmission Electron Microscope (TEM) results confirm the findings of DLS. Critical Micelle Concentrations (CMC) of the synthesized polymers were determined using electrical conductivity meter which ranged from 95 to 130 mg $L^{-1}$ for aliphatic polymers and 420–1500 mg $L^{-1}$ for aromatic polymers.

**Keywords:** Amphiphilic polymers, poly(ethylene glycols), aliphatic diacids, aromatic diacids, $^1$H-NMR, $^{13}$C-NMR, IR spectroscopy, DLS, TEM, CMC

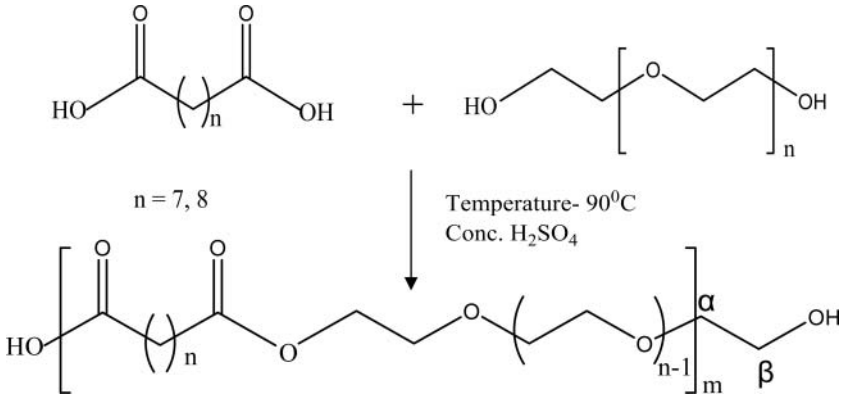
## 1 Introduction

Interest in the synthesis and characterization of amphiphilic block and graft copolymers has increased enormously in recent years. This is owing to their unique molecular structure, which consists of at least two parts with different chemical natures, constituting an amphiphilic (amphi: of both kinds; philic: having an affinity for) character. Amphiphilic block copolymers consist of a hydrophobic block that is insoluble in water and a water-soluble hydrophilic block (1). In fact, parallels can be drawn between typical surfactants and amphiphilic copolymers having both hydrophilic and hydrophobic blocks. The presence of two antagonistic parts in the molecular structure of amphiphilic molecules leads to particular characteristic properties in solution, such as adsorption at interfaces and surfaces, self-assembly into micellar aggregates with a wide variety of geometries (2). Such amphiphilic copolymers find numerous applications as emulsifiers, dispersants, foamers, thickeners, rinse aids, and compatibilizers (3). Generally, in comparison to classical surfactants, amphiphilic diblock copolymers exhibit reduced mobility and slower diffusion rates (4). Moreover, macro-surfactants have much lower critical micelle concentrations (CMC) than their low-molecular-mass counterparts (5, 6).

The micellar characteristics of amphiphilic block copolymers depend on the nature of both blocks. It was observed that surface properties of self-organized micelles are highly dependent on the structures of the hydrophilic blocks (7–9). The unique properties of poly(ethylene glycol) (PEG), including a wide range of solubility, lack of toxicity and non-interference with enzymatic activities, make them an ideal carrier of drugs and other bioactive materials (10).

The synthesis and self assembly of copolymers derived from PEGylated aromatic and aliphatic esters have been reported earlier (11–16). The amphiphilic polymers used in the self-assembly are based on poly(ethylene glycol) and various diesters, synthesized by chemical and enzymatic methods (13, 15).These copolymers were used in drug delivery systems as they were capable of encapsulating both hydrophilic and hydrophobic drugs (17, 18). They found that the design of the system and synthetic strategy is very flexible and provides a high degree of control over the polymer structures. This allowed the tuning of the properties of the micelle disruption, the critical micelle concentration and the size of micelles.

*Address correspondence to: Jitendra Kumar, Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi 110012, India; Email: jitendrakumar7@yahoo.com




**Sch. 1.** General method of polymerization of aliphatic di-acids (*viz.*, azelaic acid and sebacic acid) and PEG (MW-1000, 2000 and 4000).

In the present investigation, polymers with PEG as backbone and different aliphatic diacids and aromatic diesters as linker were synthesized and characterized for their future use in pesticide delivery and also to study their self assembling characters.

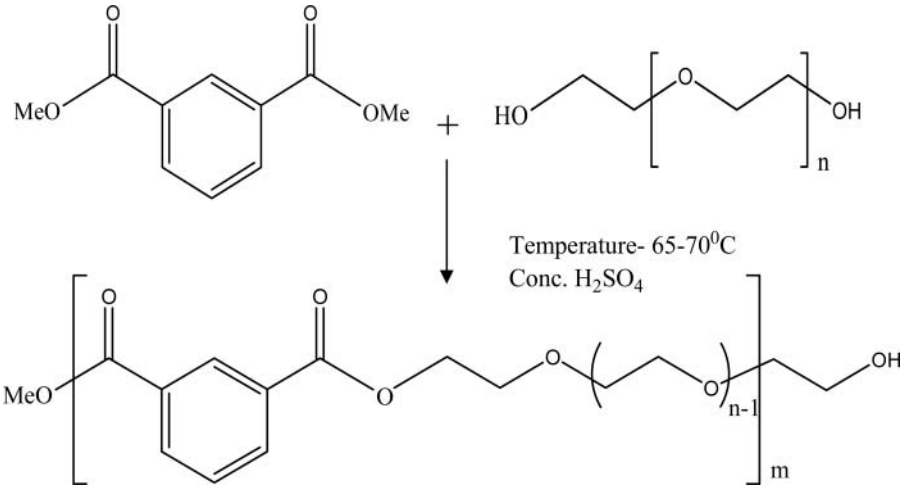
## 2 Experimental

### 2.1 Materials

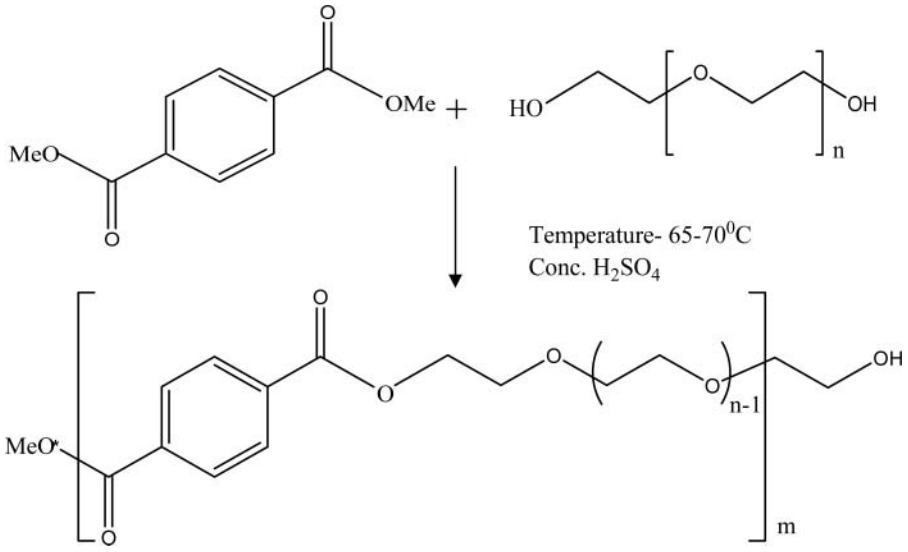
Poly(ethylene glycols) (PEGs) of different molecular weights *viz*. 1000, 2000 and 4000 were procured from Sigma Aldrich, India. Diacids namely azelaic acid, sebacic acid, dimethyl isophthalate and dimethyl terephthalate were supplied by Sigma Aldrich, India. 98% conc. $H_2SO_4$ and silicon oil bath on temperature controlled hot plate fitted with magnetic stirrer and vacuum pump were also used for synthesis of amphiphilic nanopolymers. AR grade solvents and chemicals were used for processing of the products.

### 2.2 General Methods for the Synthesis of Nano-ranged Amphiphilic Polymers

PEG-based amphiphilic polymers were synthesized with different aliphatic diacids and aromatic diesters as linker molecules (Schs. 1, 2 and 3). The numbers 1000, 2000 and 4000 represent the average molecular weights of PEG blocks, respectively which were used to form the main molecular chains of the copolymers. The monomers, diacids or esters and poly(ethylene glycols) of different molecular weights, *viz*. 1000, 2000 and 4000 were placed (in equimolar amount) in a two-necked round bottom flask and kept on a silicon oil bath at a constant temperature at 90°C for aliphatic and 65°C for aromatic diacids. The reaction was performed under vacuum with constant stirring. After proper mixing of both reagents, one drop of concentrated $H_2SO_4$ (0.1% with respect to monomers) was added in the round bottom flask. The reaction was allowed to proceed for 24 h and was monitored at different intervals by thin layer chromatography (TLC). After the completion of the reaction, the products were quenched by adding




**Sch. 2.** General method of polymerization of dimethyl isophthalate and PEG (MW-1000, 2000 and 4000).

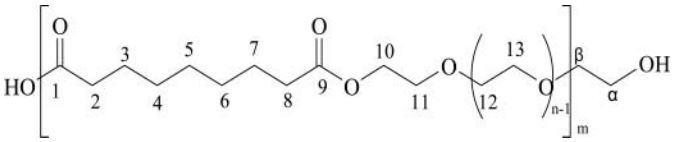



**Sch. 3.** General method of polymerization of dimethyl terephthalate and PEG (MW-1000, 2000 and 4000).

chloroform and unreacted $H_2SO_4$ was neutralized using a NaOH solution. The unreacted di-acids were removed by filtration. The organic solvent was then evaporated under vacuum and the residue was dialyzed using membrane filtration (MWCO 10000). The product polymers were freeze-dried and characterized with the help of Nuclear Magnetic Resonance (NMR) (Bruker 400MHz) and IR (Alpha ATR-Bruker) spectroscopy and the particle size was determined by Particle size analyzer and Transmission Electron Microscopy (TEM).

### 2.3 $^1$H-NMR, $^{13}$C-NMR and IR Spectroscopy Data

#### 2.3.1 *Poly[poly-(oxyethylene-1000)-oxyazelaioyl]* (A1)




**Polymer 1**. A1- Poly[poly (oxyethylene-1000)-oxy azelaoyl] polymer

**Polymer 2.** A2- Poly[poly (oxyethylene-2000)-oxy azelaoyl] polymer

**Polymer 3.** A4- Poly[poly (oxyethylene-4000)-oxy azelaoyl] polymer

**Structure of Azelaic Acid Based Polymers**

**$^1$H -NMR Data ($CDCl_3$):** $\delta$ 3.61–3.79 (*brs*, methylene PEG protons on C-12H and C-13H carbons of the repeating units and on C-11H), 4.21 (*t*, 2H, C-10H), 2.30 (*t*, 4H, C-2H and C-8H), 1.61 (*m*, 4H, C-3H and 7H), 1.30 (*m,* 6H, C-4H, 5H and 6H). PEG end OH group had shown peak at varied $\delta$ values.

**$^{13}$C-NMR ($CDCl_3$):** $\delta$ 24.75 (C-4, C-5 and C-6), 28.86 (C-3 and C-7), 34.06 (C-2 and C-8), 61.55(C-$\alpha$) 63.25 (C-$\beta$), 69.51 (C-11), 70.5 (C-12 and C-13 of PEG repeating units), 72.40 (C-10), 173.67 (C-9), 176.1 (C-1).

**IR data:** 3394 $cm^{-1}$ (OH stretching), 2862 $cm^{-1}$ (CH stretching), 1732 $cm^{-1}$ (C = O stretching), 1092 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit).

#### 2.3.2 *Poly[poly-(oxyethylene-2000)-oxyazelaoyl]* (A2)

**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.57–3.64 (*brs*, methylene PEG protons on C-12H and C-13H carbons of the repeating units and on C-11H), 4.21 (*t*, 2H, C-10H), 2.29 (*t*, 4H, C-2H and C-8H), 1.60 (*m*, 4H, C-3H and 7H), 1.31 (*m,*6H, C-4H, 5H and 6H). PEG end OH group had shown peak at varied $\delta$ values.

**$^{13}$C-NMR ($CDCl_3$):** $\delta$ 24.71 (C-4, C-5 and C-6), 28.81 (C-3 and C-7), 33.91 (C-2 and C-8), 61.49(C-$\alpha$) 63.1 (C-$\beta$), 68.92 (C-11), 70.32 (C-12 and C-13 of PEG repeating units), 72.57(C-10), 173.61(C-9), 175.49 (C-1).

**IR data:** 3500 $cm^{-1}$ (OH stretching), 2883 $cm^{-1}$ (CH stretching), 1732 $cm^{-1}$ (C = O stretching), 1097 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit)

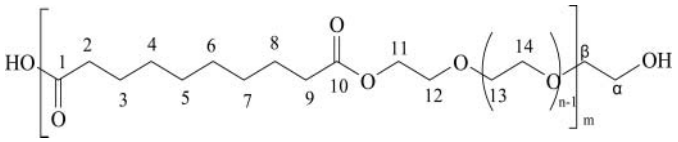
#### 2.3.3 *Poly[poly-(oxyethylene-4000)-oxyazelaoyl]* (A4)

**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.53–3.64 (*brs*, methylene PEG protons on C-12H and C-13H carbons of the repeating units and on C-11H), 4.27 (*t*, 2H, C-10H), 2.3 (*t*, 4H, C-2H and C-8H), 1.57 (*m*, 4H, 3H and 7H), 1.27 (*m,*6H, C-4H, 5H and 6H). PEG end OH group had shown peak at varied $\delta$ values.

**$^{13}$C-NMR ($CDCl_3$):** $\delta$ 24.87 (C-4, C-5 and C-6), 27.40 (C-3 and C-7), 34.05 (C-2 and C-8), 61.38(C-$\alpha$) 63.31 (C-$\beta$), 68.94 (C-11), 70.30 (C-12 and C-13 of PEG repeating units), 72.61(C-10), 173.66(C-9), 175.52 (C-1)

**IR data:** 3554 $cm^{-1}$ (OH stretching), 2875 $cm^{-1}$ (CH stretching), 1732 $cm^{-1}$ (C = O stretching), 1099 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit).

### 2.3.4 *Poly[poly-(Oxyethylene-1000)-oxysebacoyl]* (S1)



**Polymer 4.** S1- Poly [poly (oxyethylene-1000)-oxysebacoyl] polymer

**Polymer 5.** S2- Poly [poly (oxyethylene-2000)-oxysebacoyl] polymer

**Polymer 6**. S4 Poly [poly (oxyethylene-4000)-oxysebacoyl] polymer

**Structure of Sebacic Acid Based Polymers**

**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.63–3.71 (*brs*, methylene PEG protons on C-13H and C-14H carbons of the repeating units and on C-12H, C-$\alpha$ and C-$\beta$), 4.21 (*t*, 2H, C-11H), 2.31 (*t*, 4H, C-2H and C-9H), 1.62 (*m*, 4H, C-3H and C-8H), 1.28 (m, 8H, C-4H, C-5H, C-6H and C-7H). OH group at PEG end had shown peak at varied $\delta$ values.

**$^{13}$C-NMR ($CDCl_3$):** $\delta$ 24.75 (C-4, C-5, C-6 and C-7), 29.13 (C-3 and C-8), 34.00 (C-2 and C-9) 61.36 (C- $\alpha$), 63.20 (C-$\beta$), 69.09 (C-12),70.40 (C-13 and C-14 of PEG repeating units), 72.55 (C-11), 173.63 (C-10), 176.58 (C-1).

**IR data:** 3560 $cm^{-1}$ (OH stretching), 2863 $cm^{-1}$ (CH stretching), 1732 $cm^{-1}$ (C = O stretching), 1093 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit).

### 2.3.5 *Poly[poly-(oxyethylene-2000)-oxysebacoyl]* (S2)

**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.59–3.70 (*brs*, methylene PEG protons on C-13H and C-14H carbons of the repeating units and on C-12H, C-$\alpha$ and C-$\beta$), 4.19 (*t*, 2H, C-11H), 2.29 (*t*, 4H, C-2H and C-9H), 1.58 (*m*, 4H, C-3H and C-8H), 1.27 (m, 8H, C-4H, C-5H, C-6H and C-7H). OH group at PEG end had shown peaks at varied $\delta$ values.

**$^{13}$C-NMR ($CDCl_3$):** $\delta$ 24.85 (C-4, C-5, C-6 and C-7), 28.96 (C-3 and C-8), 33.99 (C-2 and C-9) 61.47 (C- $\alpha$), 63.12 (C-$\beta$), 68.93 (C-12),70.29 (C-13 and C-14 of PEG repeating units), 72.6 (C-11), 173.67 (C-10), 176.62 (C-1).

**IR data:** 3566 $cm^{-1}$ (OH stretching), 2862 $cm^{-1}$ (CH stretching), 1732 $cm^{-1}$ (C = O stretching), 1093 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit).

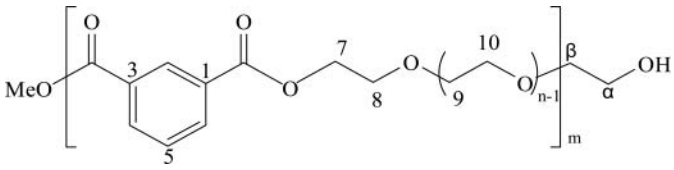
### 2.3.6 *Poly[poly-(oxyethylene-4000)-oxysebacoyl]* (S4)

**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.57–3.71 (*brs*, methylene PEG protons on C-13H and C-14H carbons of the repeating units and on C-12H, C-$\alpha$ and C-$\beta$), 4.20 (*t*, 2H, C-11H), 2.28 (*t*, 4H, C-2H and C-9H), 1.62 (*m*, 4H, C-3H and C-8H), 1.3 (m, 8H, C-4H, C-5H, C-6H and C-7H). OH group at PEG end had shown peaks at varied $\delta$ values.

**$^{13}$C-NMR ($CDCl_3$):** $\delta$ 24.39 (C-4, C-5, C-6 and C-7), 29.52 (C-3 and C-8), 33.89 (C-2 and C-9) 61.34 (C- $\alpha$), 63.05 (C-$\beta$), 68.87 (C-12),70.55 (C-13 and C-14 of PEG repeating units), 72.57 (C-11), 173.60 (C-10), 176.26 (C-1).

**IR data:** 3584 $cm^{-1}$ (OH stretching), 2877 $cm^{-1}$ (CH stretching), 1731 $cm^{-1}$ (C = O stretching), 1103 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit)

### 2.3.7 *Poly[poly-(oxyethylene-1000)-oxyisophthaloyl]* (I1)



**Polymer 7.** I1 Poly[poly (oxyethylene-1000)-oxyisophthaloyl] polymer

**Polymer 8.** I2 Poly[poly (oxyethylene-2000)-oxyisophthaloyl] polymer

**Polymer 9**. I4 Poly[poly (oxyethylene-4000)-oxyisophthaloyl] polymer

**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.58–3.73(*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-$\alpha$ and C-$\beta$), 3.82 (*t*, 2H, C-8H), 3.95 (*s*, 3H, -$COOCH_3$), 4.46 (*t*, 2H, C-7H), 7.54(s, 1H, C-5H), 8.22 (*m*, 2H, C-4H and C-6H) and 8.67 (*s*, 1H, C-2H).

**$^{13}$C-NMR Data ($CDCl_3$):** $\delta$ 52.29 (-$OCH_3$ end group) 61.42 (C-$\alpha$), 62.93 (C-$\beta$), 68.80 (C-8), 70.47 (repeating PEG units carbon), 72.59 (C-7), 128.59 (C-5), 130.55 (C-4 and C-6) 133.71 (C-2), 161.97 (-COO-) and 166.12 (-COOMe).

**IR-data:** 3465 $cm^{-1}$ (OH stretching), 2865 $cm^{-1}$ (CH stretching), 1725 $cm^{-1}$ (C = O stretching), 1093 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit), 734 $cm^{-1}$ (ring CH out-of-plane bending).

### 2.3.8 *Poly[poly-(oxyethylene-2000)-oxyisophthaloyl]* (I2)

**$^1$H NMR Data ($CDCl_3$):** $\delta$ 3.58–3.78 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-$\alpha$ and C-$\beta$), 3.82 (*t*, 2H, C-8H), 3.90 (*s*, 3H, -$COOCH_3$), 4.32 (*t*, 2H, C-7H), and 7.54(s, 1H, C-5H), 8.23 (*m*, 2H, C-4H and C-6H) and 8.69 (*s*, 1H, C-2H).

**$^{13}$C-NMR Data ($CDCl_3$):** $\delta$ 52.35 (-$OCH_3$ end group) 61.58 (C-$\alpha$), 63.00 (C-$\beta$), 68.80 (C-8), 70.41 (repeating PEG units carbon), 72.65 (C-7), 128.60(C-5), 130.59 (C-4 and C-6) 133.75 (C-2), 161.97 (-COO-) and 166.18 (-COOMe).

**IR data:** 3470 $cm^{-1}$ (OH stretching), 2867 $cm^{-1}$ (CH stretching), 1725 $cm^{-1}$ (C = O stretching), 1095 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit), 734 $cm^{-1}$ (ring CH out-of-plane bending).

### 2.3.9 *Poly[poly-(oxyethylene-4000)-oxyisophthaloyl]* (I4)

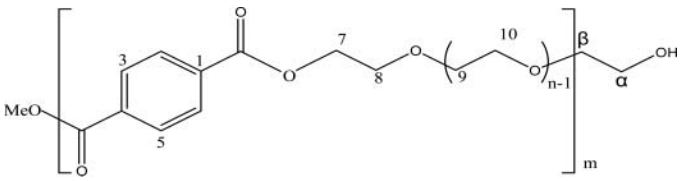
**$^1$H-NMR Data ($CDCl_3$):** $\delta$ 3.55–3.66 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-$\alpha$ and C-$\beta$), 3.78 (*t*, 2H, C-8H), 3.83(*s*, 3H,

-$COOCH_3$), 4.41 (*t*, 2H, C-7H), 7.52(s, 1H, C-5H), 8.19 – 8.21(*m*, 2H, C-4H and C-6H) and 8.65 (*s*, 1H, C-2H).

**$^{13}$C-NMR Data ($CDCl_3$):** $\delta$ 52.30 (-$OCH_3$ end group) 61.46 (C-$\alpha$), 62.80 (C-$\beta$), 66.83 (C-8), 70.40 (repeating PEG units carbon), 72.59 (C-7), 128.59(C-5), 130.53 (C-4 and C-6) 133.69 (C-2), 161.94 (-COO-) and 166.08 (-COOMe).

**IR Data:** 3470 $cm^{-1}$ (OH stretching), 2880 $cm^{-1}$ (CH stretching), 1726 $cm^{-1}$ (C = O stretching), 1103 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit), 735 $cm^{-1}$ (ring CH out-of-plane bending).

### 2.3.10. *Poly[poly-(oxyethylene-1000)-oxyterephthaloyl]* (T1)




**Polymer 10.** T1- Poly[poly (oxyethylene-1000)-oxyterephthaloyl] polymer

**Polymer 11.** T2 Poly[poly (oxyethylene-2000)-oxyterephthaloyl] polymer

**Polymer 12**. T4 Poly[poly (oxyethylene-4000)- oxyterephthaloyl] polymer

**$^{1}$H-NMR Data ($CDCl_3$):** $\delta$ 3.61–3.75 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-$\alpha$ and C-$\beta$), 3.81 (*t*, 2H, C-8H), 3.96 (*s*, 3H, -$COOCH_3$), 4.52 (*t*, 2H, C-7H), and 7.96 (s, 4H, C-2H, C-3H, C-5H, C-6H).

**$^{13}$C-NMR Data ($CDCl_3$):** $\delta$ 52.33 (-$OCH_3$ end group) 61.32 (C-$\alpha$), 64.36 (C-$\beta$), 69.92 (C-8), 70.30 (repeating PEG units carbon), 72.45 (C-7), 129.49 (C-2, C-3, C-5 and C-6), 133.74 (C-1 and C-4), 161.01 (-COO-) and 166.56 (-COOMe).

**IR data:** 3446 $cm^{-1}$ (OH stretching), 2869 $cm^{-1}$ (CH stretching), 1720 $cm^{-1}$ (C = O stretching), 1095 $cm^{-1}$ (stretching vibration from C-O-C of PEG repeating unit), 734 $cm^{-1}$ (ring CH out-of-plane bending).

### 2.3.11 *Poly[poly-(oxyethylene-2000)-oxyterephthaloyl] (T2)*

**$^{1}$H-NMR Data ($CDCl_3$):** $\delta$ 3.57–3.74 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-$\alpha$ and C-$\beta$), 3.79 (*t*, 2H, C-8H), 3.92 (*s*, 3H, -$COOCH_3$), 4.5 (*t*, 2H, C-7H), and 8.09 (s, 4H, C-2H, C-3H, C-5H, C-6H).

**$^{13}$C-NMR Data ($CDCl_3$):** $\delta$ 52.39 (-$OCH_3$ end group) 61.35 (C-$\alpha$), 62.89 (C-$\beta$), 68.72 (C-8), 70.06 (repeating PEG units carbon), 72.43 (C-7), 129.36 (C-2, C-3, C-5 and C-6), 133.72 (C-1 and C-4), 161.00 (-COO-) and 166.00 (-COOMe).

**IR Data:** 3450 $cm^{-1}$ (OH stretching), 2868 $cm^{-1}$ (CH stretching), 1721 $cm^{-1}$ (C = O stretching), 1097 $cm^{-1}$ (Stretching vibration from C-O-C of PEG repeating unit), 735 $cm^{-1}$ (ring CH out-of-plane bending).

### 2.3.12 *Poly[poly-(oxyethylene-4000)-oxyterephthaloyl]* (T4)

**$^{1}$H-NMR Data ($CDCl_3$):** $\delta$ 3.59–3.75 (*brs*, methylene PEG protons on C-9 and C-10 carbons of the repeating units and on C-$\alpha$ and C-$\beta$), 3.8 (*t*, 2H, C-8H), 3.95 (*s*, 3H, -$COOCH_3$), 4.49 (*t*, 2H, C-7H), and 8.1 (s, 4H, C-2H, C-3H, C-5H, C-6H).

**$^{13}$C-NMR Data ($CDCl_3$):** $\delta$ 52.42 (-$OCH_3$ end group) 61.45 (C-$\alpha$), 62.93 (C-$\beta$), 68.78 (C-8), 70.01 (repeating PEG units carbon), 72.31 (C-7), 129.26 (C-2, C-3, C-5 and C-6), 133.58 (C-1 and C-4), 161.73 (-COO-) and 165.93 (-COOMe).

**IR data:** 3460 $cm^{-1}$ (OH stretching), 2866 $cm^{-1}$ (CH stretching), 1721 $cm^{-1}$ (C = O stretching), 1094 $cm^{-1}$ (stretching vibration from C-O-C of PEG repeating unit), 735 $cm^{-1}$ (ring CH out-of-plane bending).

## 2.4 Determination of CMC of the Synthesized Polymers

CMC values of the polymers were calculated using electrical conductance data measured using a digital conductivity meter. The conductivity cell (dip-type with a cell constant of 0.92) was calibrated with KCl solutions in the appropriate concentration range. Various concentrations of amphiphilic polymers were prepared in the range of 25 to 300 mg $litre^{-1}$ for aliphatic esters and 100-4000 mg $litre^{-1}$ for aromatic esters. The conductivity of these solutions was measured at 25°C. The conductance was measured after thorough mixing and temperature equilibrium at each dilution. The measurement was started with a dilute solution and the subsequent concentrated solutions were used.

## 2.5 Sample Preparation for Particle Size Analyzer

Particle size analyzer (Zetatrac$^{TM}$) is based on Dynamic Light Scattering (DLS) which detects the fluctuation of the scattering intensity due to the Brownian motion of macromolecules or particles in suspension. DLS measurements were performed at 25°C and light scattering was detected at a fixed angle. Dual optical probe technology was used for particle size analysis. Optical light sources were dual solid-state laser diodes in 780 nm (near-infrared) wavelength.

Solution of both the aliphatic and aromatic polymers was prepared at their critical micelle concentration (CMC) value. 5 ml of the sample solution was placed in a glass vial. A minimum quantity (50$\mu$L) of chloroform was added to the polymer solution and the vial was sonicated for 5 min to form a proper emulsion. The resulting homogenized emulsions were then analyzed for the volume mean diameter and particle size distribution using the software Microtrac FLEX.

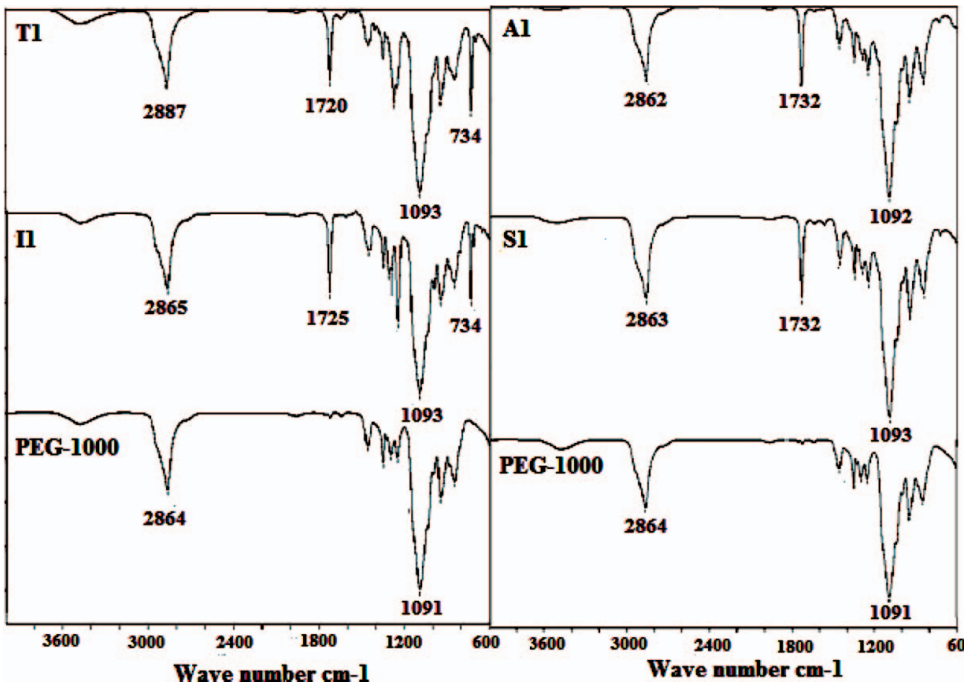



**Fig. 1.** FT-IR spectral patterns of representative aliphatic polymers (A1 and S1), aromatic polymers (T1and I1) and PEG. (Color figure available online.)

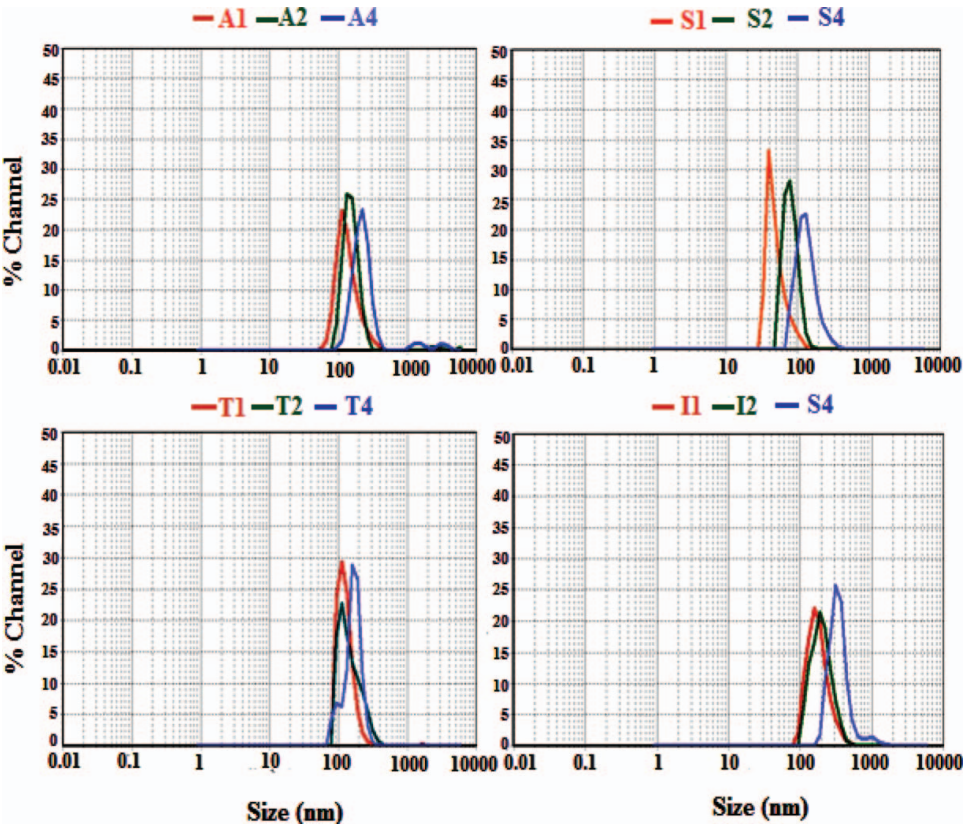



**Fig. 2.** Distribution of micelle sizes of differnet polymers as obtained from DLS. (Color figure available online.)

**Table 1.** Micelle sizes, polydispersity index and CMC of different amphiphilic polymers

| *Polymer name* | *Micelle size (nm) ± SD* | *PDI* | *CMC values ($\times 10^{-3}$ mg mL$^{-1}$)* |
|---|---|---|---|
| A1 | 104.1 ± 44.9 | 0.667 | 104 |
| A2 | 131.1 ± 38.9 | 0.562 | 110 |
| A4 | 174.9 ± 67.6 | 0.738 | 130 |
| S1 | 51.6 ± 13.38 | 0.844 | 95 |
| S2 | 81.4 ± 18.19 | 0.600 | 106 |
| S4 | 139.4 ± 40.50 | 0.887 | 132 |
| I1 | 185.6 ± 51.1 | 0.632 | 420 |
| I2 | 206.7 ± 64.8 | 0.498 | 475 |
| I4 | 371.0 ± 91.1 | 0.633 | 550 |
| T1 | 135.5 ± 28.6 | 0.916 | 665 |
| T2 | 155.9 ± 55.4 | 0.881 | 975 |
| T4 | 165.7 ± 42.8 | 0.776 | 1500 |

Polydispersity index (PDI) was calculated by the following formula (19):

$$\text{Polydispersity index} = (D_{0.9} - D_{0.1})/D_{0.5}$$

Where $D_{0.9}$, $D_{0.5}$ and $D_{0.1}$ are the particle diameters determined at the 90th, 50th and 10th percentiles of undersized particles, respectively. A PDI indicates the spread of size distribution and smaller value is indicative of narrow particle size distributions

### 2.6 Sample Preparation for the Transmission Electron Microscopy (TEM) Analysis

The diameter of the particles was determined using TEM. Polymer solutions of different concentrations were made in water. Then a drop of the polymer solution was put into the copper grid coated with a carbon film and stained with uranyl acetate. The excess water was dried gently using a blotting paper. The samples were used for the TEM analysis at different magnification levels.

## 3 Results and Discussions

### 3.1 $^1$H-NMR Characterizations

The structures of all polymers were established from their $^1$H-NMR spectrum. The protons of the repeating PEG

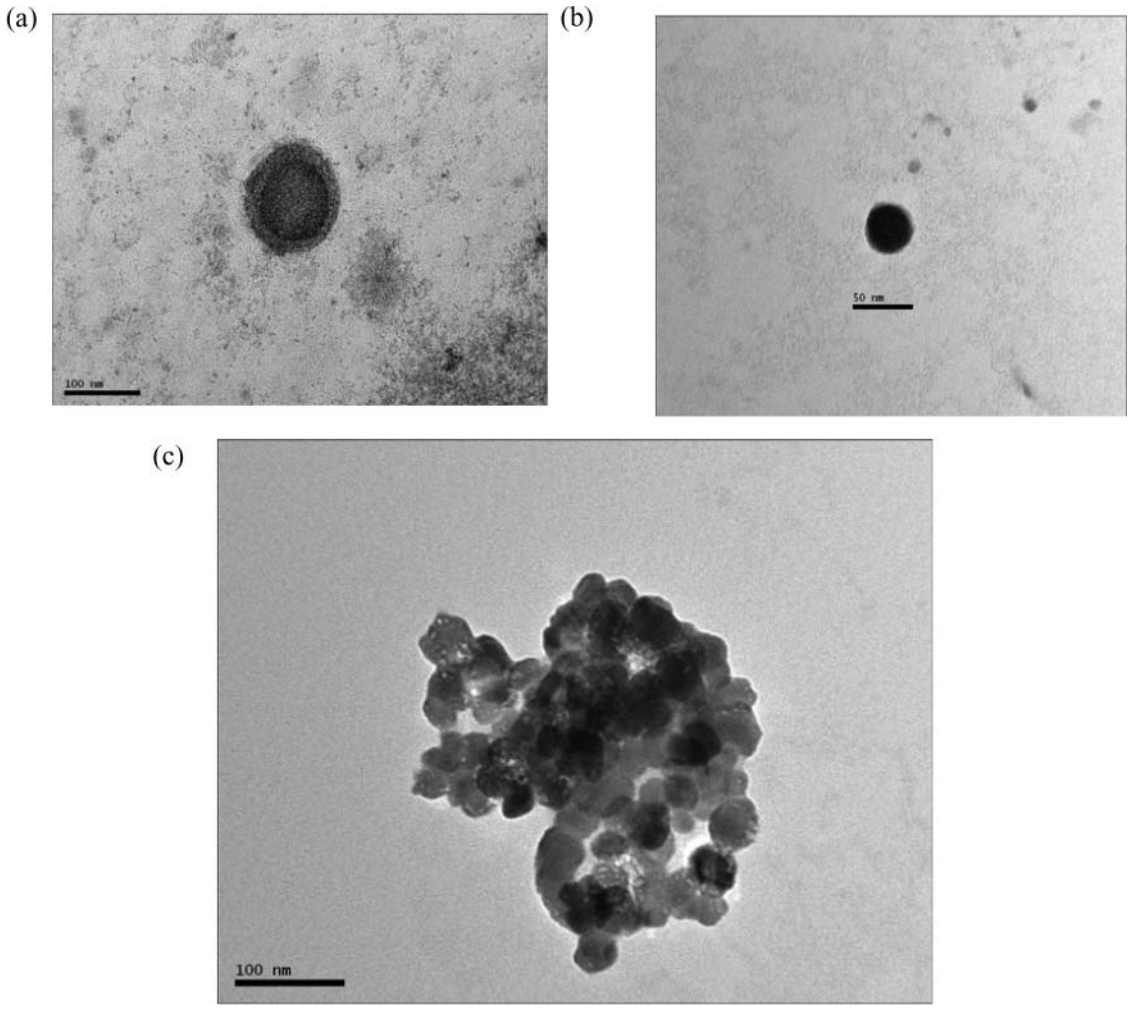



**Fig. 3.** TEM images of the polymers a) A1 (×120000) and b) S1 (×200000) c) I4 (×120000).

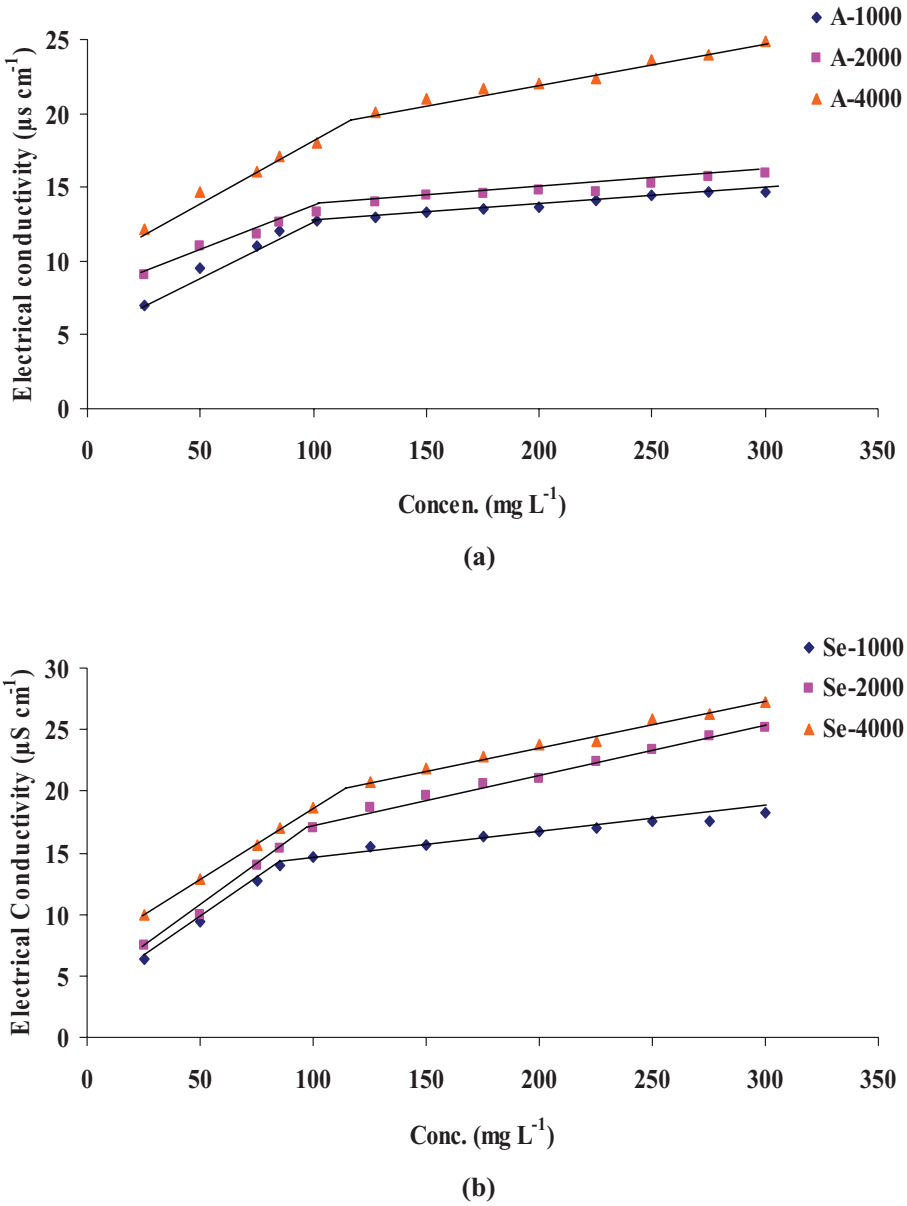



**Fig. 4.** Variation of specific conductivity vs. polymer concentration, for conductometric determination of the CMC of Azelaic acid polymers (a) and Sebacic acid polymers (b) at 25°C. (Color figure available online.)

units appeared as a broad singlet in the range $\delta$ 3.53-$\delta$ 3.78 in the case of both aliphatic and aromatic polymers. The two protons of the methylene group of the PEG chain appeared at $\delta$ 4.19 to $\delta$ 4.29 as triplet in the case of aliphatic polymers whereas, it ranged from $\delta$ 4.32 to $\delta$ 4.52 in the case of aromatic polymers. These methylene protons appear downfield compared to the corresponding methylene protons of PEG thereby confirming the formation of the ester linkage. It has already been reported that $^{1}$H-NMR of ester linkage of block copolymers of dimethyl 5-hydroxyisophthalate with polyethylene glycol (PEG) appeared at $\delta$ 4.5 (20). $^{1}$H-NMR spectrum of amphiphilic polymers based on glutaric acid, adipic acid, pimelic acid and suberic acid with PEG had similar characteristic peaks as reported (21). The end hydroxyl group of PEG chain had appeared at varied $\delta$ values. Therefore, we can say that the synthesized polymers were open chain.

### 3.2 $^{13}$C-NMR Characterizations

$^{13}$C-NMR values of all polymers had shown two carbonyl groups at different $\delta$ values. In aliphatic polymers, the higher down fielded carbon at $\delta$ values more than 175 was the end carboxyl moiety of the polymer chain. The up field carbonyl moiety ($\delta$173.61-$\delta$173.67) was the ester bonded carbonyl group. In the case of aromatic polymers, the end carboxyl moiety showed $\delta$ values ranging from 165.93 to

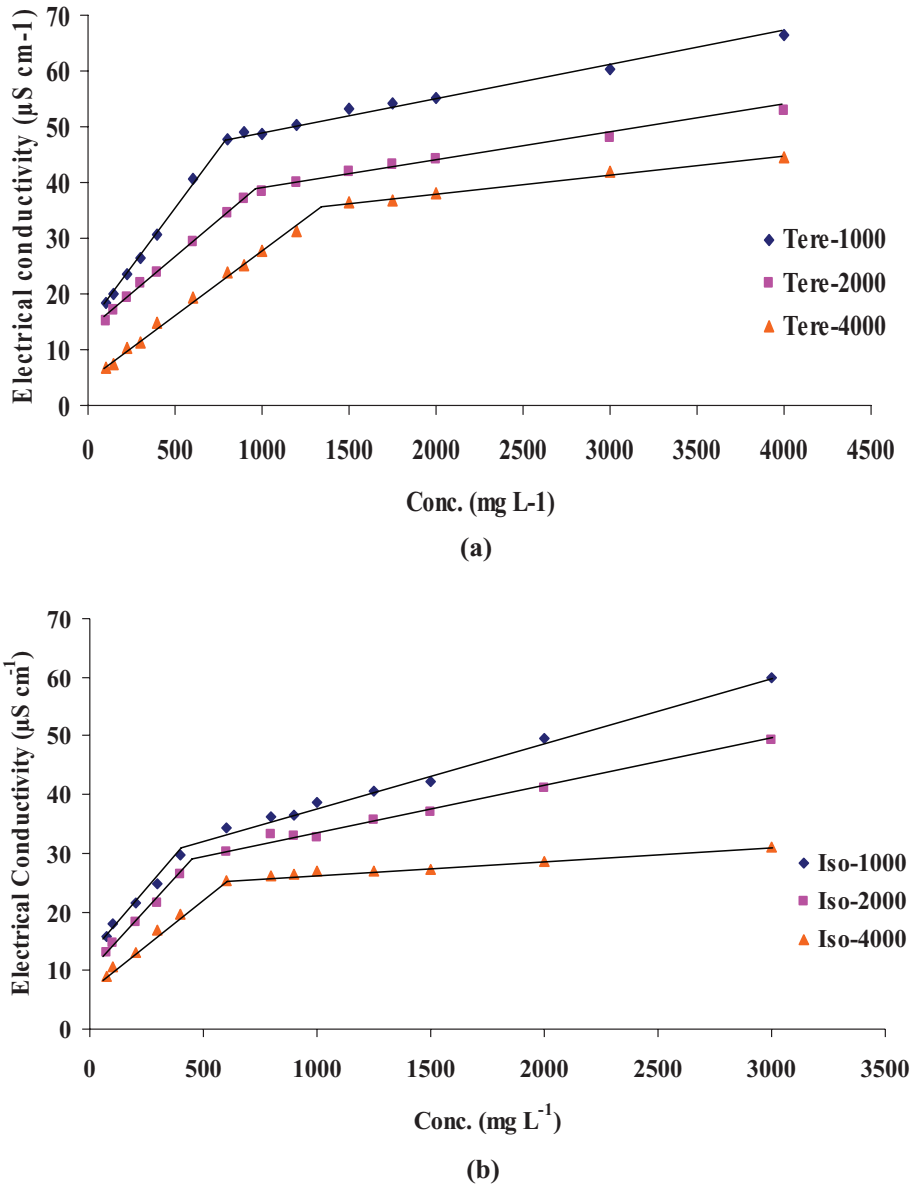



**Fig. 5.** Variation of specific conductivity vs. polymer concentration, for conductometric determination of the CMC of Terephthalate polymers (a) and Isophthalate polymers (b) at 25°C. (Color figure available online.)

166.56 and the ester bonded carbonyl carbon ranges from $\delta 161.00 - \delta 161.97$. This lower down field shift of carboxylic moiety in aromatic polymers may be due to electron withdrawing capacity of aromatic moiety. In both the aliphatic and aromatic polymers, the two protons of the methylene group of the PEG chain adjacent to ester linkage appears at $\delta$ 72.31–72.65. These two peaks at different $\delta$ values proved that the synthesized amphiphilic polymers were open chain. The other $\delta$ values corresponded to different carbon atoms in the macromolecules. $^{13}$C-NMR values of all polymers confirm the studies reported in the literature (20, 21).

### 3.3 IR Characterizations

The FT-IR spectra of the synthesized polymers are shown in Figure 1. A distinguished peak of carbonyl moiety around 1725 cm$^{-1}$ was shown by the polymers, whereas no such peak was observed in poly(ethylene glycol). An intense peak was observed at around 1090 cm$^{-1}$. This peak was identified as a C-O-C peak of PEG chain. The hydroxyl peak at around 3500 was observed in both monomer and polymer; however, in polymers, it was with much reduced intensity. The characteristic peak of CH stretching was observed for both polymers and PEGs. In the case of aromatic

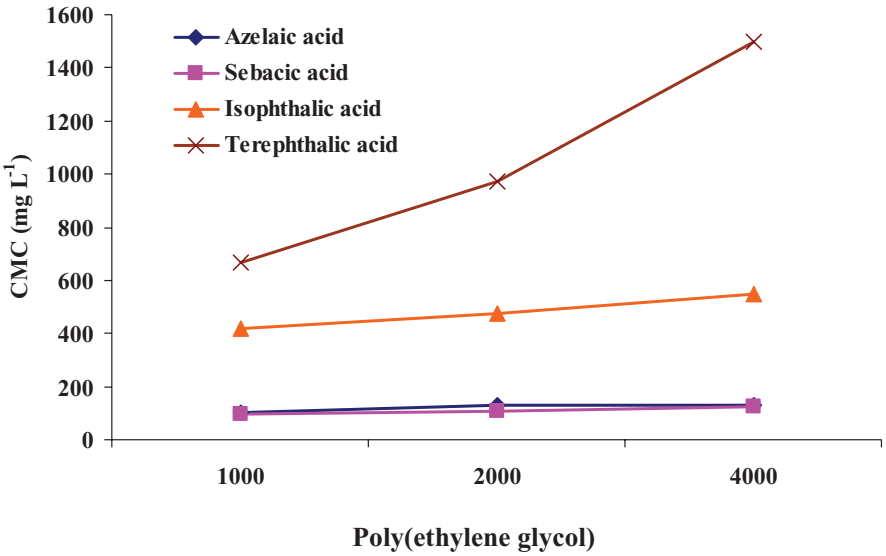



**Fig. 6.** Variation of critical micelle concentrations with respect to hydrophobic blocks of amphiphilic polymer. (Color figure available online.)



polymer, a distinct peak at around 734–735 $cm^{-1}$ attributed to the ring CH out-of-plane bending vibration.

### 3.4 Particle Size Analysis

The hydrodynamic diameters of the micelles of the synthesized polymers are summarized in the following Table 1. The hydrodynamic diameter of the polymers' micelle varied from 51.6 nm to 206.7 nm as analyzed by dynamic light scattering (Fig. 2). There was a clear trend in the size of the micelle with PEG's molecular weight, as well as with different linker molecules. With an increase in the molecular weight of PEG, the size of the micelle of synthesized polymer also increased. This was in agreement with the report where aromatic polymers based on dimethyl 5-hydroxyisophthalate showed an increase of radius of gyration (Rg) with the increase in the size of hydrophilic segment (PEG size) (15, 16).

TEM figures (Fig. 3) confirmed the data observed from the dynamic light scattering. TEM figures also indicate that the micelle of the polymer in water was spherical in shape.

### 3.5 Determination of CMC

The variation of specific conductivity with varied polymer concentrations is shown in for aliphatic polymers and for aromatic polymer Figures 4 and 5, respectively. In the case of aliphatic polymers, it was seen that polymers with higher molecular weight hydrophilic segments showed higher electrical conductivity than polymers of lower molecular weight hydrophilic segments. Whereas, in the case of aromatic polymers, as the molecular weight of hydrophilic segment increases, the electrical conductivity showed a gradual decrease.

Critical Micelle Concentration (CMC) was recorded as a point where a sudden change in any physical properties (specific conductance) occurred. When the conductivity of solutions with increasing concentration of polymers was measured, the specific conductivity– surfactant concentration plots showed two straight lines with different slope. The first one corresponded to the concentration range below the CMC, when only single polymer units exist in solution. At higher concentrations, micelles start to form and a change of slope appeared because the conductivity increases in a different manner. The intersection of these two straight lines was taken as the CMC value of the surfactant (Figs. 4 and 5). The CMC values are presented in the Table 1. CMC values of the synthesized polymers ranged from 95 to 1500 mg $L^{-1}$. It was seen that in both aliphatic and aromatic polymers, as the molecular weight or chain length of the hydrophilic segment i.e., PEG increased, the CMC values also increased which was in agreement to the studies reported earlier in the literature (22, 23) (Fig. 6). The effect of molecular weight on CMC was much higher in aromatic polymers, whereas it was not that pronounced in the case of aliphatic polymers. It also was seen that the aromatic polymerrs were having higher CMC values than the aliphatic polymers. It was observed that S1 showed the lowest CMC value whereas, polymer I2 showed narrow size distribution in terms of PDI.

## 4 Conclusions

Synthesis and characterization of twelve amphiphilic polymer molecules have been achieved and their self assembling micelles were studied. The size of these polymeric micelles showed size in the nano range. Their particle size and

critical micelle concentration make them favorable to be used in a delivery system. In a delivery system, they can be used for encapsulating both hydrophilic and hydrophobic bioactive molecules. The novelty of amphiphilic polymers through aliphatic and aromatic polymers can also be extended from drug delivery to agrochemical delivery.

## References


1. Riess, G. (2003) *Prog. Polym. Sci.*, 28, 1107–1112.
2. Holmberg, K., Jonsson, B., Kronberg, B., and Lindman, B. (2002) *Surfactants and Polymers in Aqueous Solution*, John Wiley & Sons, Ltd.
3. Förster, S., and Antonietti, M. (1998) *Advanced Materials*, 10(3):195–217.
4. Creutz, S., van Stam, J., De Schryver, F.C., and Jerome R. (1998) *Macromolecules*, 31, 681–689.
5. Astafeva, I., Zhong, X., and Eisenberg, F.A. (1993) *Macromolecules.* 26, 7339–7352.
6. Vieira, J.B., Thomas, R.K., Li, Z.X., and Penfold, J. (2005) *Langmuir*, 21, 4441–4446.
7. Kwon, G.S., Suwa, S., Yokoyama, M., Okana, T., Sakurai, Y., and Kataoka, K. (1994) *J. Controlled Rel.*, 29, 17–23.
8. Gao, Z., Varshney, S.K., Wong, S., and Eisenberg, A. (1994) *Macromolecules*, 27, 7923–7927.
9. Yu, K., and Eisenberg, A. (1996) *Macromolecules*, 29, 6359–6361.
10. Zalipsky, S.E., Lee, S. *Poly(ethylene glycol) Chemistry: Biotechnological and Biochemical Applications*; Harris, J.M., Ed. Plenum Press: New York, p. 347, 1992.
11. Kumar, R., Shakil, N.A., Chen, M.H., Parmar, V.S., Samuelson, L.A., Kumar, J., and Watterson, A.C. (2002) *J. Macromol. Sci., Pure & Appl. Chem., Part A*, A39, 1137–1149.
12. Danprasert, K., Kumar, R., Chen, M.H., Gupta, P., Shakil, N.A., Prasad, A.K., Parmar, V.S., Kumar, J., Samuelson, L.A., and Watterson, A.C. (2003) *Eur. Polymer J.*, 39, 1983–1990.
13. Kumar, R., Chen, M.H., Parmar, V.S., Samuelson, L.A., Kumar, J., Nicolosi, R., Yoganathan, S., and Watterson, A.C. (2004a) *J. Am. Chem. Soc.*, 126(34), 10640–10644.
14. Kumar, R., Tyagi, R., Parmar, V.S., Samuelson, L.A., Kumar, J., and Watterson, A.C. (2004b) *Green Chem.*, 6 (10), 516–520.
15. Shakil, N.A., Singh, M.K., Pandey, A., Kumar, J., Pankaj, B., Parmar, V.S., Pandey, R.P., and Watterson, A.C. (2010) *J. Macromol. Sci., Pure & Applied Chemistry, Part A*, 47, 241–247.
16. Loha, K.M., Shakil, N.A., Kumar, J., Singh M.K., Adak, T., and Jain, S. (2011) *J. Env. Sci. and Health, Part B*, 46, 201–206.
17. Sharma, S.K., Kumar, R., Kumar, S., Mosurkal, R., Parmar, V.S., Samuelson, L.A., Watterson, A.C., and Kumar, J. (2004) *Chem. Commun.*, 23, 2689–2691.
18. Kumar, R., Tyagi, R., Shakil, N.A., Parmar, V.S., Kumar, J., and Watterson, A.C. (2005) *J. Macromol. Sci., Pure & Appl. Chem., Part A*, 42, 1523–1528.
19. Natarajan, V., Krithica, N., Madhan, B., and Sehgal, P.K. (2011) *Journal of Pharmaceutical Sciences*, 100(1): 195–205.
20. Kumar, R., Shakil, N.A., Chen, M.H., Parmar, V.S., Samuelson, L.A., Kumar, J., and Watterson, A.C. (2002) *J. Macromol. Sci., Pure & Appl. Chem., Part A*, A39, 1137–1149.
21. Adak, T., Kumar J., Shakil, N.A., Walia, S., Kumar, A., and Watterson, A.C. (2011) *J. Macromol. Sci., Pure & Appl. Chem., Part A*, 48, 767–775.
22. Priev, A., Zalipsky, S., Cohen, R., and Barenholz, Y. (2002) *Langmuir*, 18(3): 612–617.
23. Ashok, B., Arleth, L., Hjelm, R.P., Rubinstein, I., and Önyüksel, H. (2004) *Journal of Pharmaceutical Sciences*, 93, 2476–2487.