Effect of Poly(ethylene oxide)- Poly(ethylene glycol) Addition on Actuation Behavior of Cellulose Electroactive Paper

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ABSTRACT: This article reports the influence of poly-(ethylene oxide)- poly(ethylene glycol) (PEO-PEG) addition on its actuation behavior of cellulose electroactive paper. The actuator showed its maximum bending displacement of 5.0 mm with very low electrical power consumption (7 mW/mm) at an ambient condition. Increased displacement output and decreased electrical power consumption of the actuator might be due to the improved polymer chain flexibility and ion mobility. The ion migration effect might play a more important role in actuation principle. Present investigation reveals that cellulose/PEO-PEG-based EAPap actuators are suitable to construct an actuator working at normal ambient condition. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 847–852, 2009

Key words: cellulose; blending; FTIR; bending displacement; electroactive paper

INTRODUCTION

Polymeric composite materials of both natural and synthetic origin constitute by far the broadest and most diverse class of biomaterials. Many efforts have been devoted to the development of polymeric composites. Light weight, low cost, renewability and susceptibility, and environmental benefits are some of the advantages offered by these materials. Cellulose, a linear β-1,4-glucan, is the most abundant polymer found in nature and has a plentiful hydroxyl groups which usually give rise to a relatively strong interaction between the components in the blends and hence strongly affect the properties of the blends.[1] Cellulose has been discovered as a smart material that can be used as sensors, actuators, and smart devices.[2] This newly discovered material is termed as electroactive paper (EAPap) and has merits in terms of light weight, flexible, dryness, biodegradable, easy to modify chemically, cheap, and abundant. However, its actuator performance was sensitive to humidity conditions.[3,4] Cellulose blends with synthetic polymers, such as poly(vinyl alcohol), poly(ε-caprolactone), poly(ethylene oxide), poly(ethylene glycol)[5–8] and so on, have been envisaged for the past two decades as biodegradable polymer blends. Some new desirable properties that cannot be expected in the conventional materials can be obtained in polymer blends, which attracted much attention in the industrial research field.

Many researchers have reported the actuators working in air.[9,10] Which are generally multilayer structures where the internal layer is a solid polymer electrolyte (SPE) sandwiched between two conducting polymer (CP) layers (CP//SPE//CP) and the relative differential expansion between CP layers results in bending. However, such type of actuators has following draw backs: (a) delamination of layers due to poor cohesion between the CP film, the metal layer and flexible SPE; (b) evaporation of the solvent, when SPE is swollen with an electrolyte solution to improve its ionic conductivity; and (c) requires multistage processing due to their complicated configuration.

Objective of the present investigation is to study the possibility of using cellulose/poly(ethylene oxide)- poly(ethylene glycol) (PEO-PEG) blends to construct actuators working in normal ambient condition. We have chosen PEO-PEG as they have similar chemical structure, the hydrogen bonding between cellulose hydroxyl groups and skeletal

oxygen atoms of PEO-PEG whose presence was recently demonstrated by Fourier transform infrared (FTIR) analysis.[11] The combination of PEO-PEG may serve as an effective solid state polymer electrolyte. In other words, the polymeric blend of cellulose/ PEO-PEG, can offer a unique property of cellulose combined with electrolytic behavior of PEO-PEG to design an EAPap actuator working in normal ambient condition.

EXPERIMENTAL

Materials

Cotton cellulose (MVE, DPW 4580) was purchased from Buckeye Technologies (USA); N,N-dimethylacetamide (DMAc, anhydrous 99.8%) from Sigma Aldrich, (USA). Extra pure lithium chloride was purchased from Junsei Chemicals, Japan. Poly(ethylene oxide) with molecular weight 200,000 and poly(ethylene glycol) with average molecular weight 400 was purchased from Sigma Aldrich (St. Louis, MO). All the chemicals were used without any further treatment.

Preparation of cellulose/ PEO-PEG blend films

DMAc was used as a common solvent to prepare cellulose and PEO-PEG solutions. Cellulose solution was prepared by following the method published elsewhere.[3] In brief, cotton cellulose pulp (16 g) and LiCl (80 g) were heated at 100°C for 2 h and the LiCl was dissolved in DMAc (720 mL), then the pulp was mixed with LiCl-DMAc solution and heated at 150°C for 30 min, followed by cooling and stirring. PEO-PEG solution (2.5%) was prepared by dissolving different ratio of PEO and PEG (namely 0.1 : 0.9, 0.25 : 0.75, 0.4 : 0.6, 0.5 : 0.5, 0.6 : 0.4, 0.75 : 0.25, and 0.9 : 0.1) in DMAc under simultaneous stirring and heating at 50°C.

Ten milliliters of 2.5% PEO-PEG solution was added to 100 mL of cellulose solution and were mixed by stirring for 24 h. Resulting blend solutions were spin coated on glass substrates at 600 rpm for 25 sec and were allowed to cure for 6 h. Based on the ratio of PEO : PEG, the blend films were named as CPP19, CPP27, CPP46, CPP55, CPP64, CPP72, and CPP91. The films are then transferred to oven and heated at 50°C for 3 days to remove the solvents. Further, films are heated at 50°C under high vaccum for 2 days to remove remnant solvents from the blends. The resulting blends were used for the analysis.

Characterization

Scanning electron microscope (SEM), X-ray diffraction (XRD), and FTIR analysis

The surface and cross section of the films were examined with a SEM (Hitachi S4300) to evaluate the effect of PEO-PEG on the morphology of films. The films were coated with platinum under vacuum conditions before the SEM experiments. The XRD patterns were recorded with thin film X-ray diffractometer (X'Pert MPD PRO/Philips) using CuKα target at 40 kV and 50 mA, at scanning rate of 0.015°/ min. The diffraction angle ranged from 5 to 40°. The IR spectra were obtained by Nicolet 6700 FTIR spectrometer with KBr beam splitter, detector at 4 cm^{-1} resolution and 32 scans per sample. The films were cut into very small particles and characterized by FTIR for evaluation of chemical structure using KBr pellet.

Actuator performance evaluation

The influence of PEO : PEG addition on the performance of actuators was evaluated at different humidity conditions. The measurement system consists of two laser displacement sensors (Keyence, LK-G85 and LK-G15), current probe (Tektronix, TCP 300), LabVIEW software on a personal computer and function generator (Agilent, 33,220A). PEO : PEG blended cellulose actuator is held in a gripper that has electric contacts wired to the function generator and current probe. When the function generator sends out the electrical signal to the actuator, it produces a bending displacement, and the laser displacement sensor measures it.

RESULTS AND DISCUSSIONS

SEM, XRD, and FTIR analysis

To investigate and compare the cause of PEO : PEG addition on morphology of cellulose, the surface and cross sections of pristine cellulose and its blend with PEO-PEG were studied by SEM. Figure 1(a,c) shows the surface and cross section of the pristine cellulose. It is quiet clear that pristine cellulose has a compact layer-by-layer structure with smooth surface roughness [root mean square (RMS) roughness value of 2.5 ± 0.3 nm]. However, on blending PEO-PEG with cellulose, surface became rough [Fig. 1(b)] with RMS value of 100 ± 0.8 nm. The layer-by-layer structure has been changed to aggregated structure at PEG = 0.75 as shown in Figure 1(d). When PEG = 0.1 the cross-sectional morphology of the blend was changed to roughly aggregated layered structure as shown in Figure 1(e). These observations clearly indicate their good miscibility between cellulose and PEO-PEG as well as the homogeneous dispersion of PEO-PEG in cellulose.

The crystalline structure of cellulose is classified into four types, namely cellulose I, II, III, and IV.
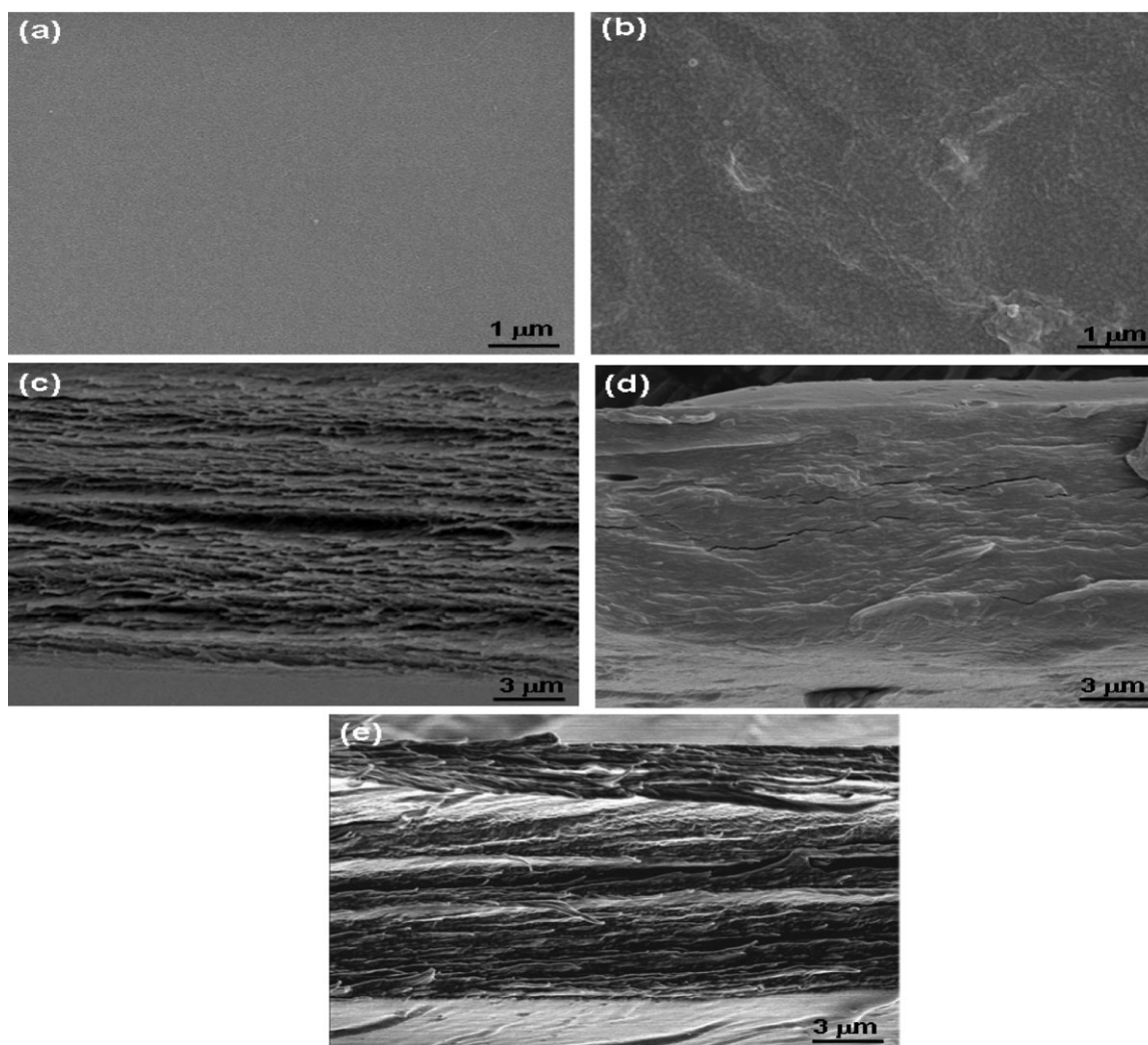
Figure 1 SEM images of surface (a) and cross section (c) of pristine cellulose, cross section of CPP27 (d), and surface (b) and cross section (e) of CPP91.

Cellulose crystalline structures are able to transform from one to another type.[12,13] Figure 2 shows the X-ray diffractograms of cellulose regenerated from DMAc/LiCl solvent system and PEO-PEG blended cellulose. From Figure 2(a), we can see the three peaks located at 12.5°, 20.3°, and 22° for DMAc-regenerated cellulose, which are assigned to (1 1 0), (1 −1 0) and (2 0 0), respectively.[14] This regenerated cellulose belongs to cellulose II structure. However, XRD patterns were remained unaltered when cellulose was blended with PEO-PEG as shown in Figure 2(b,c), suggesting no change in the structure of cellulose due to the addition of PEO-PEG.

FTIR is a useful tool for studying the structural changes. The width and intensity of the peaks are sensitive to the environment and conformation of molecules at molecular level.[15] FTIR spectra of cellulose and its blend with PEO-PEG of ratio 0.9 : 0.1 is shown in Figure 3. Peaks near 3436 and 1642 cm^{-1} represent OH band[16] and primary amide (DMAc),[17]

respectively. It is observed that the OH band became broarder on blending with PEO-PEG, meanwhile the intensity of 1642 cm^{-1} peak increased and sharpened on blending cellulose with PEO-PEG, which indicates the presence of remnant DMAc in blends. Peaks at wave number 2924 and 1072 cm^{-1} represent the CH and CO bands, respectively. On blending PEO-PEG with cellulose these bands were shifted to a negligibly higher wave numbers. This observation is in agreement with that of XRD results. Although SEM analysis revealed the change in morphology of cellulose due to PEO-PEG addition, both XRD and FTIR analysis suggest no substantial change in structure of cellulose due to PEO-PEG addition.
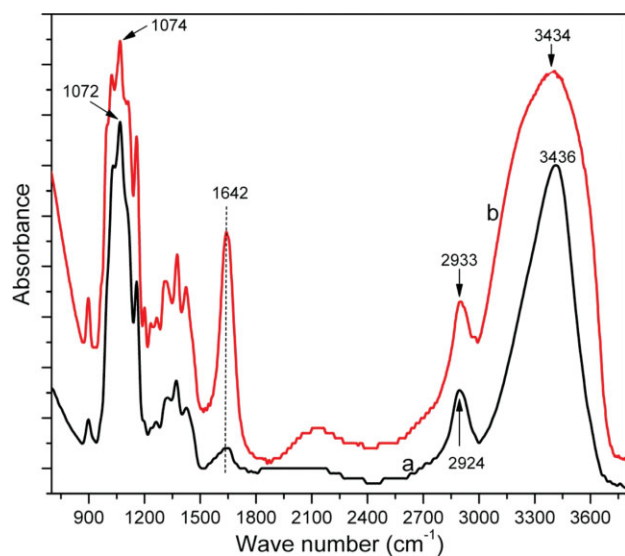
Influence of PEO-PEG addition on electromechanical performance

Bending actuators were fabricated by depositing gold electrodes on both sides of cellulose/PEO-PEG
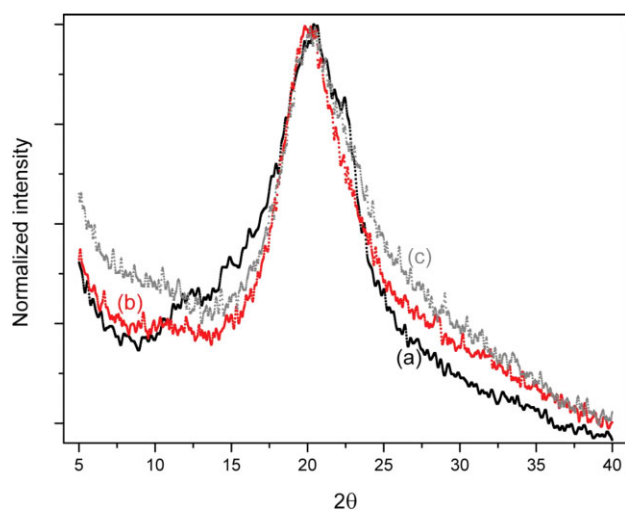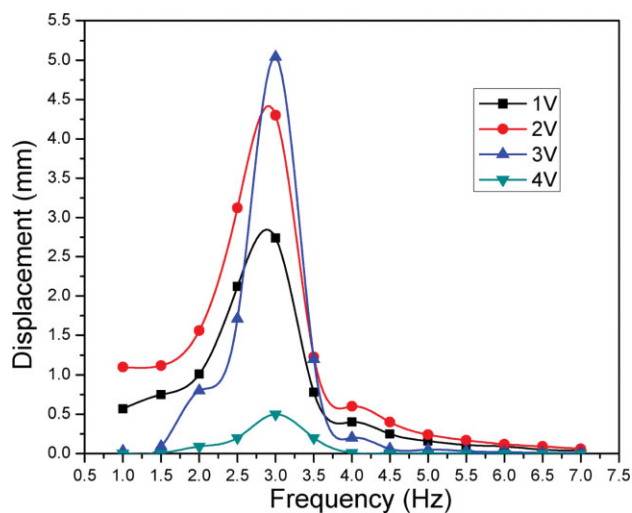
Figure 2 X-ray diffractograms of (a) regenerated cellulose, (b) CPP film with PEO : PEG = 0.25 : 0.75, and (c) CPP film with PEO : PEG = 0.9 : 0.1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 Bending displacement of the actuator made with cellulose/PEO-PEG blend film (CPP91) tested at an ambient condition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

blend films by using a physical vapor deposition technique. Figure 4 shows the bending displacement of the CPP91 film with frequency variation. Cellulose regenerated from DMAc/LiCl solvent system has produced a very small bending displacement of ∼ 0.5 mm.[3] Tenfold increase in bending displacement of the actuators were observed on PEO : PEG addition of ratio equal to 0.9 : 0.1 (5.0 mm at 3 V, 3 Hz). Figure 5 depicts the effect of PEO-PEG ratio on the maximum bending displacement of actuators. It is observed that the maximum displacement increased with changing the PEO : PEG ratio from

0.1 : 0.9 to 0.9 : 0.1. In other words, the bending displacement increased linearly with decreasing the PEG content in the blend films.

Further, electrical power consumed by the actuators per unit displacement output was calculated by measuring their electrical current. Figure 5 also shows the electrical power consumption of actuators with varying PEO : PEG ratio. When the PEO : PEG ratio was changed from 0.1 : 0.9 to 0.9 : 0.1, the electrical power consumption of the actuators was decreased from 55 to 7 mW/mm, respectively. This is ∼ 50% lower than that of cellulose actuator (15 mW/mm). SD of the bending displacement and electrical power consumption of actuators was found to
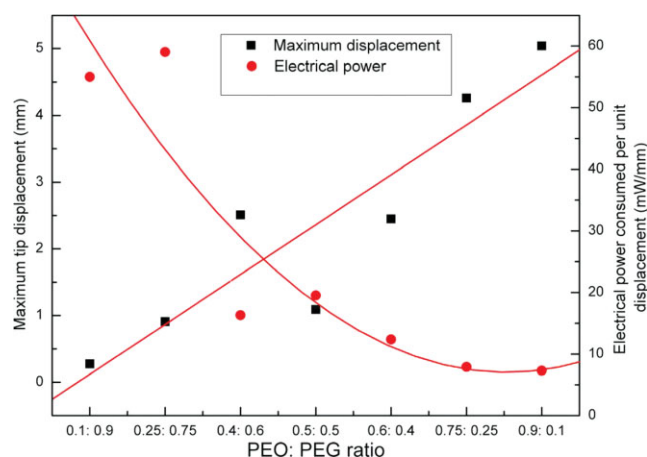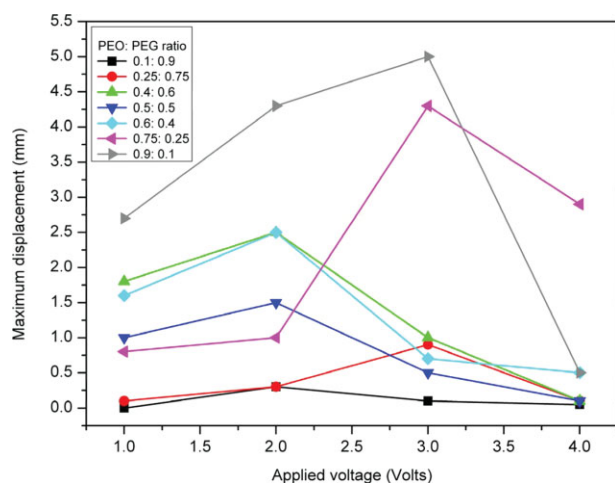

Figure 3 FTIR spectra of (a) cellulose, (b) cellulose blended with PEO-PEG of ratio 0.9 : 0.1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Effect of PEO : PEG ratio on maximum bending displacement (SD: ±0.6–0.7) and electrical power consumption (SD: ±0.81–1.9) of actuators made with CPP blend films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

be ±0.6–0.7 and ±0.8–1.9, respectively. The increase in displacement output and decreased electrical power consumption of actuator with decreasing PEG content might be due to the reduction in formation of salt complexes with entrapped LiCl in the blend films. This resulted in improved polymer chain flexibility and ion mobility accounted for larger bending displacement output with low electrical power consumption.

Influence of the activation voltage on the maximum bending displacement of the actuators with varying PEO : PEG ratio is illustrated in Figure 6. It is observed that for CPP19, CPP55, CPP46, and CPP64 cases, the actuators exhibited their maximum bending displacement at 2 V, whereas CPP27, CPP72, CPP91 cases were at 3 V. However, when the voltage was increased beyond these values, the bending displacement was reduced to <1 mm. To investigate this phenomenon, the surface of the actuators was examined by SEM after actuation test, shown in Figure 7. It is observed that the surface of the gold electrodes were severely damaged due to the presence of the remnant DMAc solvent and the reactive Li^+ ions in the blend films,[18,19] which might account for the drastic reduction in the bending displacement of the actuators on increasing the voltage.

As mentioned in the experimental part, LiCl/DMAc solvent system has been used to dissolve the pulp. According to the dissolution mechanism of cellulose in LiCl/DMAc solvent system, hydroxyl protons of the anhydrous units are associated with chloride anion by hydrogen bonding, and Li^+ ions forms a macrocation complex with DMAc $[Li^+(DMAc)_x]$.[20] In other words, Li^+ ions are tightly bounded than the Cl^- ion, which requires more activation energy to break free and migrate under elec-
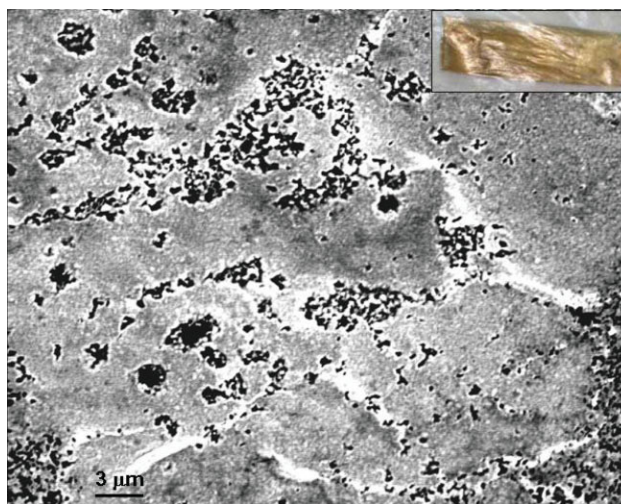
Figure 7 Damaged gold electrode surface of the actuator (inset, photograph after actuation). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tric field. In addition, radius of Cl^- ion is larger than that of Li^+ ion.[21] Also, ionic velocity of Cl^- is 65 and that of Li^+ is 35[22] these factors make Cl^- ion hasten on before the Li^+ ions and contribute for the bending motion at room condition. On the basis of these factors, we believe that its actuation mechanism of CPP-based EAPap actuator may be based on ion migration effect associated with motion of flexible polymer chains due to addition of small amount of PEO-PEG in cellulose matrix.

CONCLUSIONS

The effect of PEO-PEG addition on the actuation behavior of cellulose EAPap was investigated. Cellulose/PEO-PEG blend films were fabricated with varying PEO : PEG ratios from 0.1 : 0.9 – 0.9 : 0.1 via traditional solution blending technique. Although SEM images showed the change in morphology of cellulose due to the addition of PEO : PEG, both XRD and FTIR analysis revealed no substantial change in its structure. From bending actuation test, we found that the maximum bending displacement of the actuator was linearly increased with decreasing the PEG content in blends. The electrical power consumption of the actuator was reduced with decreasing the PEG content. This might be due to the reduced formation of salt complexes with entrapped LiCl in the blend films. This improved the polymer chain flexibility and ion mobility that were accounted for increased bending displacement of the actuator with low electrical power consumption. These results allow the potential of the cellulose/PEO-PEG blend to build an actuator working in normal ambient condition.

Figure 6 Influence of activation voltage on the maximum bending displacement of the actuators with varying PEO : PEG ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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