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An investigation of the pH effect on the particle size and zeta potentials of poly (ethylene glycol) and poly ehtylene-block-poly (ethylene glycol) with various molecular weights

D. Sakar Dasdan*, G. Tosun, Y. Karahan

Yildiz Technical University, Faculty of Arts and Sciences, Department of Chemistry, 34220 Esenler, Istanbul, Turkey

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The aim of this study is to investigate the effect of the polyethylene (PE) segments on the charge and particle size of poly(ethylene glycol). For this purpose, in this current work, to compare the charge and particle size of poly(ethylene glycol) and PEG co-polymerized with PE segments polyethylene-block-poly(ethylene glycol) (PE-b-PEG) which is surfactant, emulsifier for coatings, ceramics, mold release agent and thickening with different molecular weights have been examined by Zeta Potential Analyzer. Zeta potential, mobility, and particle size of PEG and PE-b-PEG systems were determined by using the Zeta Potential Analyzer in water as a function of pHs.

Keywords: PEG, PE-*block*-PEG, Stability, Particle size, Zeta potential, pH effect

INTRODUCTION

Poly(ethylene glycol) is a polyether having strongly hydrogen bonds with water and is one of the most studied polymers in current materials science and biotechnology because of not only its unique behaviors in solution but also its wide applications. Poly(ethylene glycol) (PEG), otherwise known as poly(oxyethylene) or poly(ethylene oxide) (PEO), is a synthetic polyether that is readily available in a range of molecular weights. These polymers are amphiphilic and soluble in water as well as in many organic solvents (e.g., methylene chloride, ethanol, toluene, acetone, and chloroform). Low molecular weight (M_w <1,000) PEGs are viscous and colorless liquids, while higher molecular weight PEGs are waxy, white solids with melting points proportional to their molecular weights to an upper limit of about 67 °C. [1]

PEG has been found to be nontoxic and is approved by the FDA for use as excipients or as a carrier in different pharmaceutical formulations, foods, and cosmetics. Most PEGs with M_w <1,000 are rapidly removed from the body unaltered with clearance rates inversely proportional to polymer molecular weight. This property, combined with the availability of PEGs with a wide range of end-functions, contributes to the wide use of PEGs in biomedical research: drug delivery, tissue engineering scaffolds, surface fucntionalization, and many other applications. [2-5]

PEG was used as a nontoxic, water-soluble dispersant/stabilizer. Also known as Carboxwax®, it is present in health and beauty aids, including laxatives, toothpastes and eye drops, and is an excipient in tablet formulations. [6] PEG stabilizes organ and blood donations. Several studies have shown that PEG molecular weight and loading have a significant effect on extending circulatory life. [7-11]

Polyethylene (PE) based materials are widely used in many fields due to the combination of excellent physical and chemical properties along with low cost. However, the lack of chemical functionality and structural diversity is the common barrier for broadening their applications. Hence, it is urgent to develop the PE-based materials functionalized by polar groups such as glycols or polymer segments with some improved or modified properties. [12]

Zetasizer measurements which are zeta potential, particle size and mobility provide valuable properties of particles or molecules in liquid medium. These characteristics directly affect bioavailability, stability, dissolution and immunotoxicity of the molecules. [13-19]

In this work, to investigate the charge and particle size of PEG and PE-b-PEG with various molecular weights were measured by the zetasizer measurements such as the particle size, mobility and zeta potential as a function of pH.

EXPERIMENTAL

Instrument and materials

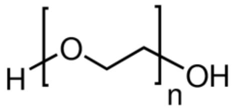
The particle size of PEG and PE-b-PEG solutions in water were measured via Brookhaven 90 Plus/BI-MAS (Multi Angle Particle Sizing, 15 mW solid state laser) and electrophoretic mobility and zeta potential measurements of all solutions were also determined by Brookhaven Zeta Potential

* To whom all correspondence should be sent:
E-mail: dolunaykar@yahoo.com

Analyzer (35 mW solid state laser in red at 660 nm wavelength) in water as a function of pH. The polymers PEG and PE-b-PEG were purchased from Sigma Aldrich. The properties of PEG and PE-b-PEG are given in Tables 1 and 2, respectively.

Table 1. Properties of PEG

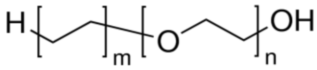
PEG



Property (M_V)	PEG1:100.000g/mol	PEG2:400.000g/mol	PEG3:900.000g/mol
T_g(°C)	-67	-	-
T_m(°C)	65	65	65
d(g/ml)	1.13	1.18	1.21
Viscosity(cP)	12-50	2.25-4.5	8.8-17.6

Table 2. Properties of PE-b-PEG

PE-b-PEG



Property (M_n)	PE-b-PEG1:575 g/mol	PE-B-PEG2:920g/mol	PE-b-PEG3:2250g/mol
Composition (EO, wt %)	20	50	80
T_m (°C) (DSC)	101	105	90
d (g/ml)	1.05	1.05	1.1
OH value (mg/KOH g)	85	55	-

Zetasizer measurements

Particle size. Particle size determination *via* dynamic light scattering (DLS) is a capable tool to determine the size of particles based on scattering of light [20]. DLS measures the (hydrodynamic) radius of a hypothetical solid particle scattering light with the same intensity as the particles under investigation while diffusing in the dispersion. DLS measures the (hydrodynamic) radius of a hypothetical solid particle scattering light with same intensity as the particles under investigation while diffusing in the dispersion.

DLS instrument calculates the particle size from the translational diffusion coefficient (D). The relationship is called Stokes-Einstein equation and is given by:

$$D = k_B T / 6\pi\eta R_H \quad (1)$$

where T is absolute temperature in degrees Kelvin, η is the liquid's viscosity, R_H is hydrodynamic radius, d_H is particle hydrodynamic diameter, $d_H=2R_H$ and k_B is Boltzmann's constant.

Mobility and zeta-potential: The velocity (in m/sec) for a unit field strength (1 Volt/m) is called electrophoretic mobility, and is given the symbol μ_e. The electrophoretic mobility of a charged particle is defined as the ratio between its stationary velocity, ν_c and the applied electric field, E:

$$\mu_e = \nu_c / E \quad (2)$$

It is related to the zeta potential. The electrostatic potential on that surface is called zeta potential and it is that potential which is measured, when one measures the velocity of the particles in a d.c. electric field. Zeta potential values provide an indirect measurement of the net charge on the particle surface. It is also an aid in predicting long-term stability. It is calculated from Marian Smoluchowski equation as follows:

$$\mu = \varepsilon\zeta / \eta \quad (3)$$

μ, is electrophoretic mobility, ε, is electric permittivity of the liquid, η is viscosity of liquid. [21]

RESULTS AND DISCUSSION

The particle size, mobility and zeta potential of PEG and PE-b-PEG solutions with different molecular weights in water were measured as a function of pH.

The pH effect on particle size, mobility and zeta Potential of PEG1, PEG2 and PEG3 solutions were given in Table 3, Table 4 and Table 5, respectively.

The pH effect on the particle size of PEG1, PEG2 and PEG3 solutions is given in Figure 1.

The particle size of PEGs is increasing up to pH 5, after pH 5, it sharply decreases up to pH 6 and after pH 6 it increases up to pH 8, after pH 8, it decreases with increasing pH. The particle size of PEGs is not stable between pH 5 and 8. The particle size of PEGs decreases with increasing molecular weight.

The pH effect on the zeta potential of PEG1, PEG2 and PEG3 solutions is shown in Figure 2.

The zeta potential of PEGs is slightly negative, i.e., -3 mV, at pH 2 for PEG1 and is gradually decreasing with increasing pH, reaching a minimum value of −1 mV for PEG1, -1,96 mV for PEG2 and -2.35 mV for PEG3 at pH 6. Zeta potential values of PEG1 and PEG2 are not chanching with increasing pH except for PEG3.

The pH effects on particle size, mobility and zeta potential of PE-b-PEG1, PE-b-PEG2 and PE-b-PEG3 solutions are given in Tables 6, 7 and 8, respectively.

Table 3. Effect of pH on particle size, mobility and zeta potential of PEG1 in water.

pH	Particle Size (nm)	Mobility	Zeta Potential (mV)
2	2800	-0.17	-1.5
3	3050	-0.15	-1.57
4	3480	-0.13	-1.6
5	3700	-0.1	-1.25
6	3560	-0.09	-0.99
7	4750	-0.32	-4.5
8	5600	-0.35	-4.93
9	4690	-0.45	-5.21
10	3950	-0.43	-5.04
11	3690	-0.4	-5.02
12	3390	-0.4	-5.01

Table 4. Effect of pH on particle size, mobility and zeta potential of PEG2 in water

pH	Particle Size (nm)	Mobility	Zeta Potential (mV)
2	1570	-0.18	-2.33
3	1830	-0.21	-2.34
4	1970	-0.32	-2.14
5	2180	-0.38	-2.06
6	1900	-0.23	-1.96
7	2360	-0.29	-3.7
8	3820	-0.59	-5.85
9	3590	-0.48	-5.68
10	3290	-0.52	-5.55
11	3220	-0.44	-5.35
12	3000	-0.45	-5.48

Table 5. Effect of pH on particle size, mobility and zeta potential of PEG3 in water

pH	Particle Size (nm)	Mobility	Zeta Potential (mV)
2	1200	-0.25	-3.23
3	1630	-0.20	-3.11
4	1730	-0.18	-3.01
5	1970	-0.15	-2.65
6	1300	-0.11	-2.35
7	1460	-0.49	-5.44
8	1920	-0.51	-6.24
9	1670	-0.55	-7.56
10	1230	-0.81	-8.21
11	1200	-0.85	-8.51
12	1140	-0.88	-8.45

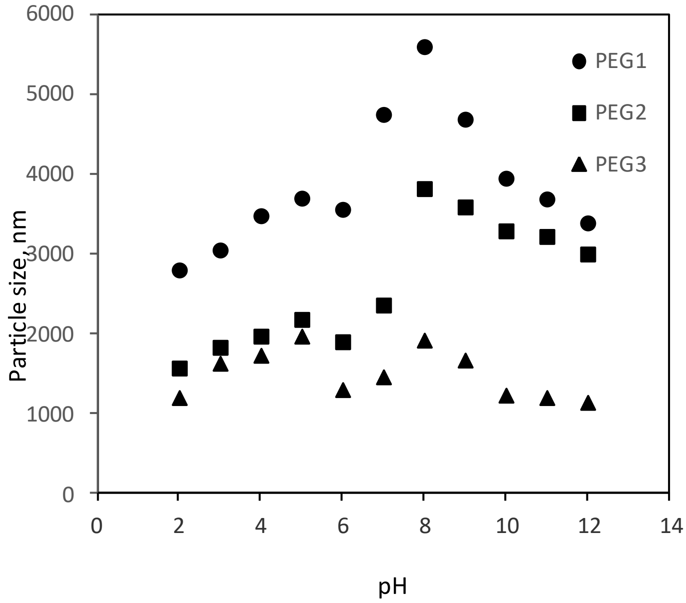


Fig.1. Effect of pH on the particle size of PEG1, PEG2 and PEG3 solutions

The pH effect on particle size of PE-b-PEG1, PE-b-PEG2 and PE-b-PEG3 solutions is shown in Figure 3.

The particle size of PE-b-PEGs increases up to pH 5, after pH 5, the particle size of PE-b-PEGs sharply decreases at pH 6. After this point, the particle size of PE-b-PEGs increases with increasing pH, however, it decreases with increasing molecular weight.

The pH effect on the zeta potential of PE-b-PEG1, PE-b-PEG2 and PE-b-PEG3 solutions is shown in Figure 4.

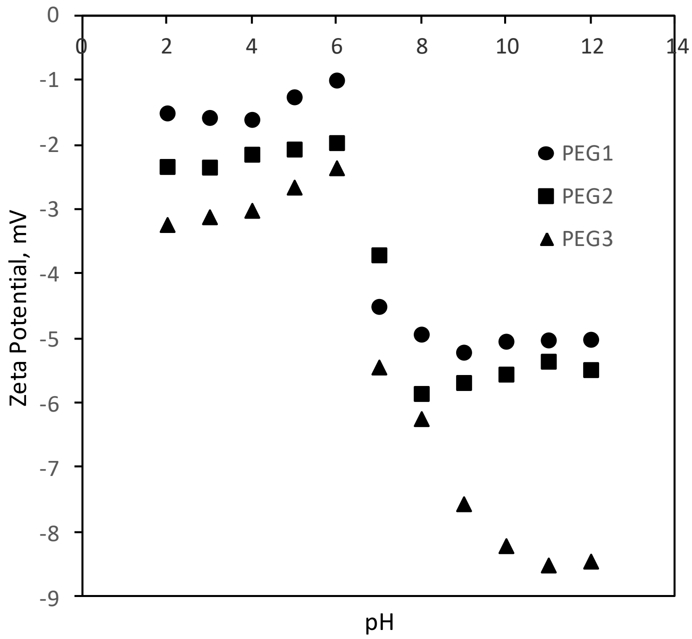


Fig.2. Effect of pH on zeta potential of PEG1, PEG2 and PEG3 solutions

Table 6. The pH effect on particle size, mobility and zeta potential of PE-b-PEG1 in water

pH	Particle Size (nm)	Mobility	Zeta Potential (mV)
2	2200	-1.64	-12,51
3	2300	-1.32	-11.44
4	2400	-1.27	-11.28
5	2600	-1.21	-11.02
6	2350	-1.79	-15.12
7	2700	-1.88	-16.56
8	3030	-1.78	-15.07
9	3080	-1.73	-13.79
10	3140	-1.68	-12.84
11	3090	-1.58	-12.05
12	3120	-1.19	-10.86

Table 7. Effect of pH on particle size, mobility and zeta potential of PE-b-PEG2 in water

pH	Particle size (nm)	Mobility	Zeta potential (mV)
2	1150	-0.24	-5.56
3	1180	-0.2	-4.51
4	1190	-0.27	-3.46
5	1290	-0.26	-3.30
6	960	-0.34	-4.37
7	1090	-0.55	-6.56
8	1070	-0.44	-5.57
9	1050	-0.26	-5.48
10	1150	-0.32	-4.65
11	1220	-0.29	-3.63
12	1240	-0.26	-3.33

Table 8. Effect of pH on particle size, mobility and zeta potential of PE-b-PEG3 in water

pH	Particle Size (nm)	Mobility	Zeta Potential (mV)
2	550	-0.38	-3.54
3	590	-0.28	-2.77
4	600	-0.25	-2.52
5	580	-0.1	-1.34
6	200	-0.31	-3.28
7	390	-0.34	-4.47
8	350	-0.44	-3.96
9	370	-0.44	-3.85
10	320	-0.26	-2.94
11	300	-0.18	-1.98
12	290	-0.15	-1.83

The zeta potential of PE-b-PEGs is negative, i.e., -12.51 mV, at pH 2 for PE-b-PEG1 and is gradually increasing with increasing pH up to pH 5, after this point, the zeta potential values of PE-b-PEGs are decreasing sharply up to pH7. After pH 7, the zeta potential of PE-b-PEGs is increasing with increasing pH. The zeta potential values are decreasing with increasing molecular weight. PE segments reduce the the particle size of PEG and increase the zeta potential of PEG.

CONCLUSIONS

According to the results, pH changes affect the particle size and zeta potential values of PEGs and PE-b-PEGs with increasing molecular weight. It means that It has to be considered that the charge and particle size of PEGs and PE-b-PEGs in different pHs when they are using as supporting material. PE segments reduce the particle size of PEG and increase the zeta potential of PEG.

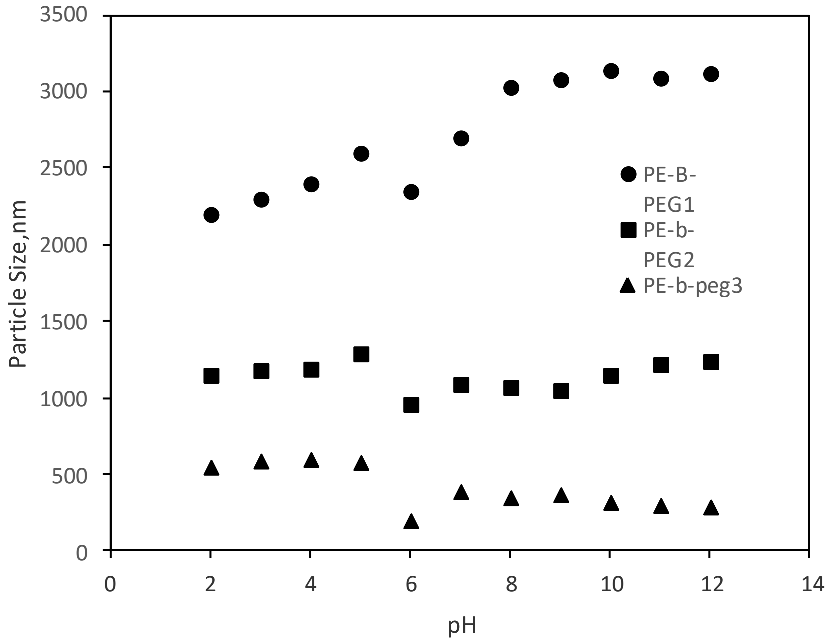


Fig. 3. Effect of pH on the particle size of PE-b-PEG1, PE-b-PEG2 and PE-b-PEG3 solutions

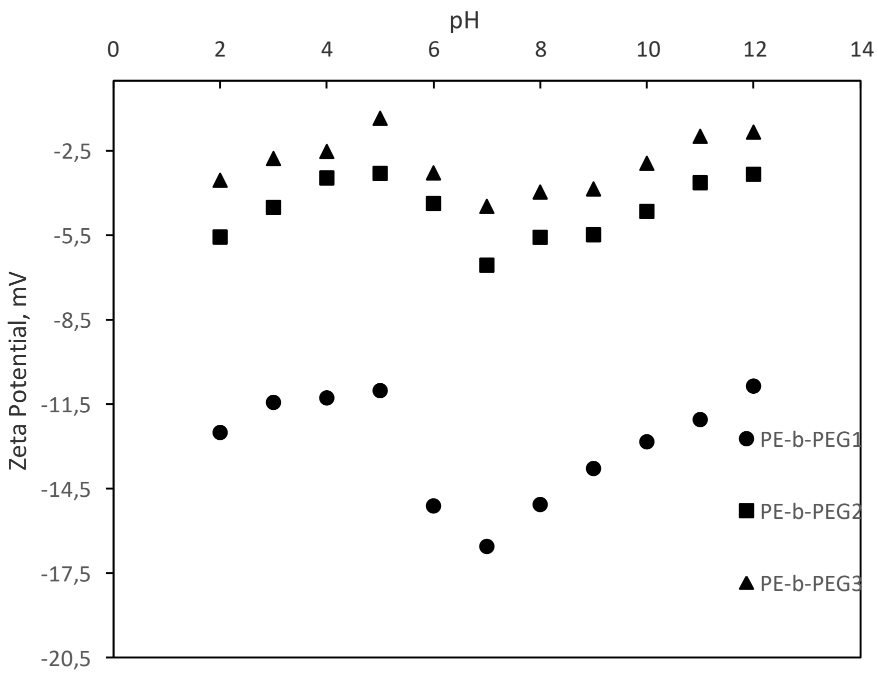


Fig. 4. Effect of pH on zeta potential of PE-b-PEG1, PE-b-PEG2 and PE-b-PEG3

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REFERENCES

1. J. Chen, N. Li, Y. Gao, F. Sun, J. He, Y. Li, *Soft Matter*, **11**, 7835 (2015).
2. F.E. Bailey, J.V. Koleske, Poly (ethylene oxide), Academic Press, New York, 1976.
3. F. Fuertges, A. Abuchowski, *J. Controlled Release*, **11**, 139 (1990).
4. P. K. Working, Safety of poly(ethylene glycol) and poly(ethylene glycol) derivatives, in: J.M. Harris, S. Zalipsky, (eds.), Polyethylene Glycol Chemistry and Biological Applications, American Chemical Society, Washington, DC, 1997.

5. R. I. Mahato, Biomaterials for delivery and targeting of proteins and nucleic acids, CRC Press, 2005.
6. R. G. Strickley, *Pharm. Res.*, **21,** 201 (2004).
7. M. C. Woodle, K. K. Matthay, M. S. Newman, J. E. Hidayat, L. R. Collins, C. Redemann, F. J. Martin, D. Papahadjopoulos, *Biochim. Biophys. Acta*, **1105**, 193 (1992).
8. T.M. Allen, C. Hansen, F. Martin, C. Redemann, A. YauYoung, *Biochim. Biophys. Acta*, **1066,** 29, (1991).
9. A.L. Klibanov, K. Maruyama, A.M. Beckerleg, V.P. Torchilin, L. Huang, *Biochim. Biophys. Acta*, **1062**, 142 (1991).
10. K. Maruyama, T. Yuda, A. Okamoto, S. Kojima, A. Suginaka, M. Iwatsuru, *Biochim. Biophys. Acta*, **1128**, 44 (1992).
11. A. Mori, A. L. Klibanov, V. P. Torchilin, L. Huang, *FEBS Lett.*, **284**, 263 (1991).
12. D. D. Lasic, D. Needham, *Chem. Rev*., **95,** 2601 (1995).
13. http://www.horiba.com/uk/scientific/products/particle-characterization/applications/drug-delivery/
14. V. G. Kadajji, G. V.Betageri, *Polymers*, **3**, 1972 (2011).
15. K. Knop, R. Hoogenboom, D. Fischer, U.S. Schubert, *Angew. Chem. Int. Ed*. **49**, 6288 (2010)
16. M. Wisniewska, *J. Dispers. Sci. Technol.*, **32**, 1605 (2011).
17. H. L. Kutscher, P. Chao, M. Deshmukh, S. S. Rajan, Y. Singh, P. Hu, L. B. Joseph, S. Stein, D. L. Laskin, P. J. Sinko, *Int. J. Pharm*., **402,** 64 (2010).
18. D. Sakar Dasdan, A. Dizdar, G. Karakus, *Bul. Chem. Commun.*, **49,** Special Issue I, 43 (2017).
19. F. Noyan Tekeli, *Bul. Chem. Commun.*, **49**, Special Issue I, 146 (2017).
20. J. Ziegler, H. Wachtel, *J. Aerosol Med.*, **18**, 311 (2005).
21. http://zeta-potential.sourceforge.net/zeta-potential.shtml#SmoluchowskiEquation

ИЗСЛЕДВАНЕ ВЛИЯНИЕТО НА pH ВЪРХУ РАЗМЕРА НА ЧАСТИЦИТЕ И ЗЕТА ПОТЕНЦИАЛА НА ПОЛИЕТИЛЕНГЛИКОЛ И ПОЛИЕТИЛЕН-БЛОК-ПОЛИЕТИЛЕНГЛИКОЛ С РАЗЛИЧНО МОЛЕКУЛНО ТЕГЛО

Д. Сакар Дашдан*, Г. Тосун, Я. Карахан

Йилдиз Технически университет, Факултет по науки и изкуства, Департамент по химия, 34220 Есенлер, Истанбул, Турция

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(Резюме)

Полиетилен-блок-полиетиленгликол (PE-b-PEG) – повърхностно активно вещество, емулгатор за покрития и керамики, агент, спомагащ за освобождаване от леярната форма и сгъстяващ агент, е материал на основата на полиетилен. Той е модифициран с PEG сегменти за разширяване на областите на приложение. Целта на настоящата работа е да се изследва влиянието на PEG сегментите върху стабилността на PE-b-PEG във вода.За сравняване на товара и размера на частиците на полиетиленгликол и полиетилен-блок-полиетиленгликол с различно молекулно тегло е използван анализатор на зета потенциала. Зета потенциалът, мобилността и размерът на частиците на PEG и PE-b-PEG състемите са определени във вода в зависимост от pH.