Crystallinity and surface morphology of the Poly Ethylene Glycol-added cholesteryl acrylate-ITO composites

A Afrizal*, S Budi, M Ismail, G Gracia, I Intan and B Bryan
Department of Chemistry, Universitas Negeri Jakarta, Jakarta, Indonesia

*afrizal@unj.ac.id

Abstract. Composite of cholesteryl acrylate-ITO nanoparticle was synthesized with the addition of polyethylene glycol (PEG). The crystallinity and surface morphology of the composites were investigated. XRD pattern of that product showed peaks in 2θ at 21° and confirmed a nematic phase. Therefore, added PEG could be changed the structures liquid crystal of cholesteryl acrylate. Percent crystallinity of the composites with different PEG variations of 0.001, 0.002, 0.003, 0.004, and 0.005 are 8.14%, 12.41%, 14.85%, 7.11, and 8.66%, respectively. SEM image of the composite with PEG 0.003 indicated showed the formation of rods and chains crosslinking indicating successful photopolymerizations process. Those conditions made polymer to be micelle that affect their conductivity due to aggregation.

1. Introduction
Cholesteryl acrylate is one of the liquid crystal for optic and sensor applications. This research focused on the properties of crystallinity of polymer cholesteryl acrylate that combined with poly ethylene Glycol (PEG). The properties of crystallinity and analysis of morphology of surface important for material applications [1]. Many advantages using PEG are their low-toxicity, low volatility, and biodegradability represent important environmentally, which are particularly attractive when combined with their relatively low cost as a bulk commodity chemical. The developed state of knowledge concerning the toxicological properties of PEG is of considerable current advantage compared to the paucity of knowledge for many other potential alternative solvent systems [2].

Some references explained that PEG could be as a surfactant, therefore in this research, PEG was added into the composite of cholesteryl acrylate-ITO. We hope that composite obtained from this research could enhance their physical and chemical properties. The goal of this research is to study crystallinity properties and surface morphology of composite of cholesteryl acrylate-ITO-PEG.

2. Materials and methods
Materials this research for synthesized precursor of acryloyloxy Buthyloxy benzoate (ABB) by reactions ethyl acetyloxy Buthyloxy benzoate by reactions eter Williamson and reactions process acrylation for making that precursor, using materials: chlorobutyl acetate, ethylhydroxybenzoate, KI, calcium carbonate, dimethylformamide, KOH, NaCl, PTSA, hydroquinone, chloride acid, acrylate acid, benzene, petroleum ether, and 2-propanol. Therefore, materials for synthesized of monomer cholesteryl acrylate were: cholesterol, acryloyloxy Buthyloxy benzoate (ABB), N2 gas, and solutions. For making composite were: dichloromethane solvent, Indium Tin Oxide (ITO), Polyethylene-block-polyethilene glycol. Characterizations of surface morphology using Scanning Electron Microscope (SEM), and crystallinity
properties using X-Ray Diffraction (XRD). Methods this research for making composite: using UV curing method that monomer of 10 mg cholesteryl acrylate was soluted in dichloromethane solvent. Then added 0.1% (1μL) initiator Darocure 1173 and ITO. The sample was added PEG with variations of concentrations. The variations ITO as follows: 10%, 20%, 30%, 40%, and 50% w/w. The homogeneous solution of cholesteryl acrylate-ITO-PEG is printed on the surface of the glass plate which has been placed on a hot plate set at 75-80°C. The photopolymerization process is carried out at a temperature of 75-80°C for 30 minutes using ultraviolet (UV) radiation in the UV Curing box [3].

3. Results and discussion
The result of crystallinity analysis of composite of cholesteryl acrylate-ITO nanoparticle was added PEG using X Ray Diffractions (XRD). The sample was measured in range 20 of 2-80°. According to literatures special peak for cholesteryl acrylates in 2θ : 2.6379°; 5.2457°; and 15.4697°. therefore special peak for ITO nanoparticle in 2θ : 30.5033°; 35.4018°; 50.9886°; and 60.6014°. the special peaks for PEG are 21.5344° and 23.8698° [4].

![Figure 1. XRD Diffractogram for composite of cholesteryl acrylate-ITO nanoparticle was added PEG.](image)

Diffractogram of XRD for sample composite of cholesteryl acrylate-ITO nanoparticle with the addition of PEG showed in figure 1. Composite of cholesteryl acrylate-ITO nanoparticle was polymerized using UV Curing showed percent crystallinity was 7.15%. Therefore, composite of cholesteryl acrylate-ITO nanoparticle with PEG more amorph compare without PEG. In general, cholesteryl acrylate has amorph phase [5].

When composite added PEG 0.004 and 0.005 crystallinity of composite decrease. This condition from the peak of ITO shoed only in 2θ : 30.5033 when added PEG 0.003. this phenomenon show cholesteryl acrylate was doped by ITO and PEG. As comparison, XRD diffractogram for cholesteryl acrylate, ITO nanoparticle, and PEG can be seen in Figure 2.
In general, based on figure 1, the peak of 2θ each of compositions PEG in the composite of polymer cholesteryl acrylate-ITO nanoparticle-PEG not different. The special peak for ITO showed in 2θ : 30°; 35°; 51°; and 60°. therefore peak for PEG showed in 20 is 21°. identifications index miller for that are 2θ is 21° is [001], for 2θ 30° lattice index miller are [110] [011] [101], 2θ 35° index miller lattice is [111], and 2θ 51° index miller lattice are [210] [120] [102] [201] [012] [021]. Based on that lattice that polymer cholesteryl acrylate doped ITO nanoparticle with PEG has nematic phase. According to Keike et. al nematic phase in index miller lattice [100] [200] [300]. Therefore, PEG can be effect structures of crystal that polymer.

Prosen crystallinity of composite polymer cholesteryl acrylate-ITO-PEG which variations of PEG are: PEG 0.001 is 8,14%, PEG 0.002 is 12,41%, PEG 0.003 is 14,85%, PEG 0.004 is 7,11, and PEG 0.005 is 8,66%. The highest percent crystallinity when added PEG 0.003. Therefore, PEG 0.003 as surfactant doing optimum. The structure of cholesteryl acrylate can be happened in mesophase conditions in range temperatures are 75°C-85°C. the temperatures ranges that the structures of phase of cholesteryl acrylate formed liquid crystal nematic or nematic crystal. Those conditions showed from the analysis peak of XRD in d_{001} that peak at 2θ is 21° [6].

Analysis morphology of surface composite of polymer cholesteryl acrylate-ITO-PEG can be seen in SEM photo of polymer cholesteryl acrylate-ITO-PEG can be seen in figure 3. Analysis SEM with magnification of 1000x.

Figure 3 showed that polymer without PEG is more amorphous than those after the addition of PEG. That photo of surface polymer not uniform of that structures crystal.
4. Figure 4. Photo SEM Polymer Cholesteryl acrylate-ITO nanoparticle at PEG 0.003 PEG 0.004.

Figures 4 showed photo SEM composite of polymer cholesteryl acrylate-ITO-PEG can be seen string fibers which branch off and form crosslinked that indications process of photopolymerizations success. The structure of morphology uniform, same, and solid. Based on result this research added of PEG as surfactant composites be homogen and has two sides as hydrophobic and hydrophilic. Although in photo SEM was added 0.004 PEG a little not uniform/homogen. That conditions because happened agglomerations cause by ITO nanoparticle fill inside chains polymer cholesteryl acrylates [7].

The other happened PEG form micell as surfactant, so maybe nanoparticle ITO not dispersed homogens. Because that nanoparticle ITO cannot fill pores of polymer cholesteryl acrylate and give effect to crystallinity of composite polymer cholesteryl acrylate-ITO. According to resulted thus research, much more PEG was added, so compositions of crystal in that composite better. But if excess of PEG added will effect crystallinity composites [8].

4. Conclusion
Composite of cholesteryl acrylate-ITO nanoparticle was polymerized using UV Curing showed prosen crystallinity was 7.15%. The composite of cholesteryl acrylate-ITO nanoparticle with PEG was found to be more amorph compare to those without PEG. In general cholesteryl acrylate has amorph phase, based on result this research added of PEG as surfactant composites be homogen and has two sides as hydrophobic and hydrophilic. Although in photo SEM was added 0.004 PEG a little not uniform/homogen. That conditions because happened agglomerations cause by ITO nanoparticle fill inside chains polymer cholesteryl acrylates.

Acknowledgement
This research was supported by Program Hibah Penelitian Kompetitif Fakultas MIPA UNJ, Tahun 2020.

References
[1] Akbarzadeh A, Zarghami N, Mikaeili H, Asgari D, Goganian A M, Khiabani H K, Samiei M and Davaran S 2012 Synthesis, characterization, and in vitro evaluation of novel polymer-coated magnetic nanoparticles for controlled delivery of doxorubicin Nanotechnol. Sci. Appl. 5 13
[2] Furuichi K, Oaki Y, Ichimiya H, Komotori J and Imai H 2006 Preparation of hierarchically organized calcium phosphate–organic polymer composites by calcification of hydrogel Sci. Technol. Adv. Mater. 7 219
[3] Pfeifer S and Bandaru P R 2014 A methodology for quantitatively characterizing the dispersion of nanostructures in polymers and composites Mater. Res. Lett. 2 166–75
[4] Peng S, Pan Y, Wang Y, Xu Z, Chen C, Ding D, Wang Y and Guo D 2017 Sequentially programmable and cellularly selective assembly of fluorescent polymerized vesicles for monitoring cell apoptosis Adv. Sci. 4 1700310
[5] Xia L, Cheng B F, Zeng T Y, Nie X, Chen G, Zhang Z, Zhang W J, Hong C Y and You Y Z 2020 Polymer Nanofibers Exhibiting Remarkable Activity in Driving the Living Polymerization under Visible Light and Reusability Adv. Sci. 1902451
[6] Sakamoto T, Ogawa T, Nada H, Nakatsuji K, Mitani M, Soberats B, Kawata K, Yoshio M, Tomioka H and Sasaki T 2018 Development of Nanostructured Water Treatment Membranes Based on Thermotropic Liquid Crystals: Molecular Design of Sub-Nanoporous Materials Adv. Sci. 5 1700405

[7] Nahum T, Dodiuk H, Kenig S, Panwar A, Barry C and Mead J 2017 The effect of composition and thermodynamics on the surface morphology of durable superhydrophobic polymer coatings Nanotechnol. Sci. Appl. 10 53

[8] Bosman A W, Sijbesma R P and Meijer E W 2004 Supramolecular polymers at work Mater. Today 7 34–9

[9] Xia L, Cheng B, Zeng T, Nie X, Chen G, Zhang Z, Zhang W, Hong C and You Y 2020 Polymer Nanofibers Exhibiting Remarkable Activity in Driving the Living Polymerization under Visible Light and Reusability Adv. Sci. 7 1902451