



## Research article

## Oil loving hydrophobic gels made from glycerol propoxylate: Efficient and reusable sorbents for oil spill clean-up



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## ABSTRACT

Glycerol propoxylate based oil loving sorbents were prepared through bulk polymerization, without using of an activator, initiator, or catalyst. Fourier transform infrared spectroscopy (FTIR),  $^{13}\text{C}$  and  $^{29}\text{Si}$  CPMA nuclear magnetic resonance (NMR), as well as elemental analysis and thermal gravimetric analysis (TGA) were operated in order to identify the structural and thermal features of sorbents. The synthesized gels were employed as absorbents for various organic solvents and oils. The swelling capacity, absorption-desorption kinetics, reusability, and selective removal from an oil/water mixture were also examined. To explore the effects of a crosslinker's concentration on oil absorption capacity, star type propoxylate monomers were reacted at different concentration of tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS) crosslinker; swelling capacity was calculated using dichloromethane as an organic solvent. Oil removal ability from the water surface is another important section contained within this article.

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## 1. Introduction

Over the past several decades, water pollution caused by oil spillage, tanker accidents, natural events, vandalism, war, earthquakes, and personal accidents has been one of the most important problems needing to be solved by mankind. (Bi et al., 2014; Dong et al., 2014; Li et al., 2013; Wang et al., 2013). Spilled oil on the water surface can severely impact on the environment of marine life (by inhibiting the penetration of sunlight) as well as on human life (by adversely impacting on fishing, coastal beaches and resorts, etc.) (Alayande et al.; Lin et al., 2015; Yang et al., 2014; Yu et al., 2015a, 2015b; Zang et al., 2015).

BTEX (benzene, toluene, ethyl benzene, xylene) have been extensively utilized in the industrial field as organic solvents; they also exist in fuels, including: gasoline, diesel, and crude oil. Therefore, they can appear in water as a result of environmental accidents (Bolden et al., 2015; Ranieri et al., 2013). The spillage of BTEX into water may destroy drinking water and could negatively affect human life (Nourmoradi et al., 2012). For this reason, it is necessary to clean up such pollutants from the water surface/environment (Hu et al., 2014; Zou et al., 2014). Until now, various

methods have been proposed for the removal of spilled oil from water surfaces; these can be categorized into three classes: physical (sorbents, booms, skimmers); chemical (dispersion, burning, use of solidifier), and biological methods (bioremediation) (Atlas, 1995; Biswas et al., 2005; Bitting, 1999; Delaune et al., 1999; Fritz, 2003; Lessard and DeMarco, 2000; Yang et al., 2009).

It is well known that, among traditional techniques related to oil/organic spills, there exist biological, physical, and chemical treatments, membrane filtration, and electro-coagulation using a sorbent material is one of the most efficient methods (Khemis et al., 2005; Obaid et al., 2015; Yang, 2007). Sorbent materials with hydrophobicity and oleophilicity can selectively absorb oil from water and are known as "oil removing" materials (Xue et al., 2014). In order to produce a good sorbent, it should be synthesized as a cross-linked polymer (Atta et al., 2006). Cross-linked polymer materials must have some features that can be used as absorbents for oil slicks, including: hydrophobicity, retention over time, low density, high uptake capacity, lower water pickup, exhibition of high selectivity, etc (A. Tanobe et al., 2009; Alayande et al.; Lin et al., 2013).

Nowadays, much attention has been paid to the production of sorbent materials for the purpose of cleaning up oils and organic solvents from the water surface/environment. Therefore, a variety of materials, including magnetics nanocomposites (Gu et al.), plastic waste (Saleem et al.), natural products (activated carbon,

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milkweed, coconut shells etc.) (Choi and Cloud, 1992), multi-walled carbon nanotube (Pourjavadi and Doulabi, 2014), graphene (Iqbal and Abdala, 2012), fibers (Wang et al., 2015), foams (A. Tanobe et al., 2009), sponges (Bi et al., 2012), butyl rubber (Ceylan et al., 2009), cross-linked poly(orthocarbonate)s (Karadag et al., 2011; Sonmez and Wudl, 2005; Yati et al., 2013), cross-linked poly(orthosilicate)s (Karadag et al., 2010; Karadag and Sonmez, 2013a; Sonmez et al., 2011), polysulfone microspheres (Yu et al., 2012), poly(alkoxysilane) sorbents (Aydin and Sonmez, 2016; Karadag and Sonmez, 2013b; Kizil et al., 2015; Kizil and Sonmez, 2016a, 2016b; Ozan Aydin and Bulbul Sonmez, 2015), cyclodextrin based sorbents (Ding et al., 2011), polyethyleneglycol (Yati et al., 2015), polypropylene glycol (Tezcan Demirel et al., 2017), polytetrahydrofuran (Yati et al., 2016) and alkyl acrylate (El-Ghazawy and Farag, 2014) based sorbents have been employed as oil clean-up agents due to their characteristic features. While these sorbent materials show many advantages, there are some limitations that need to be addressed such as preparation techniques, reusability of sorbents, oil removal efficiency from wastewater, etc.

Recently, we synthesized amphiphilic poly(ethylene glycol) gels through the reaction of different molecular weights of poly(ethylene glycol)s with an ICS monomer (Yati et al., 2015) and hydrophobic sorbents by the reaction of polytetrahydrofuran with ICS (Yati et al., 2016). The effect of molecular weight of macromonomers, reaction conditions on solvent absorbency, as well as the absorption-desorption features of the sorbents, were investigated; this was the main purpose of the studies. It was found that using a macromonomeric structure to obtain crosslinked materials, rather than using a small monomer, positively develops the swelling capacity of sorbents.

Within this study, on the basis of the aforementioned idea, in order to increase the swelling capacity of absorbents we used both macromonomeric and branching structures to obtain hydrophobic oil loving sorbents. For this purpose, glycerol propoxylate (GP) has been chosen as a star-like hydrophobic macromonomer that having PPG unit with three hydroxyl end groups. The average molecular weights are approximately 266 and 1500 in the branched structure, respectively (Kohga, 2013; Wang et al., 1983). Due to the unique topology of hyperbranched polymers, their physical and chemical properties differ from those of corresponding linear polymers. Their multiple reaction sites result from a branched structure, making them good candidates for the preparation of crosslinked polymers (Gitsov and Zhu, 2002). GP is a triol material lacking linear structure; the final polymers would have good rubber-like elasticity, resulting in increased solvent absorbing ability. The crosslinker that was used ICS is the same as the one used in other studies of a similar nature. It is an organosilane monomer with a bridging core group. The core is an isocyanurate ring and has trimethoxysilyl groups through propyl chains. The propyl chains, which are connected to the isocyanurate ring as well as the trimethoxysilyl groups, provide increased flexibility for the synthesis of crosslinked polymer networks (Cho et al., 2009).

The preparation of sorbents was achieved via bulk polymerization of glycerol propoxylate and the ICS cross-linker without using any initiator, activator, solvent, or catalyst. It was shown that the hydrophobic oil loving sorbents can be used several times for the selective removal of oil without any capacity loss.

## 2. Material and methods

### 2.1. Materials

The materials used in this paper including glycerol, glycerol propoxylate (Mw: 266 and 1500 g/mol), and ICS were obtained from Sigma-Aldrich and used without any purification.

Dichloromethane, tetrahydrofuran, benzene, toluene, xylene, and ethyl benzene were obtained from Sigma-Aldrich. 1-[4-(Phenylazo)phenylazo]-2-naphthol (Sudan III) were also purchased from Sigma-Aldrich. 95 octane gasoline and euro diesel were purchased from British Petroleum (BP) and crude oil was obtained from TUPRAS (Turkish Petroleum Refineries Co.). All organic solvents and oils were used as received.

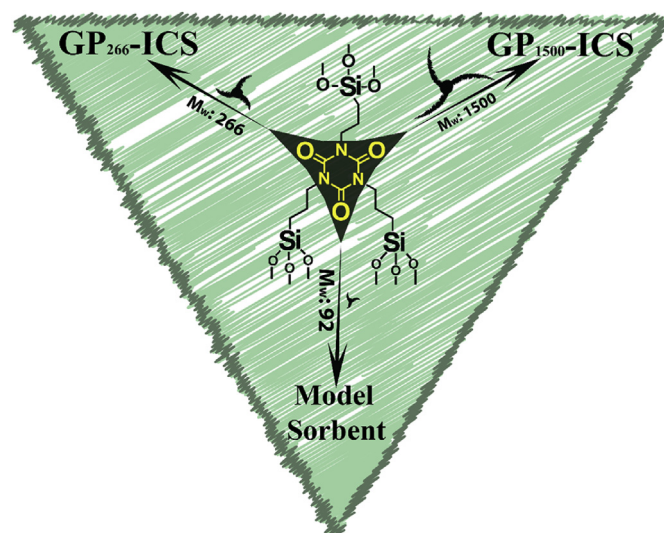
### 2.2. Characterization techniques

Fourier transform infrared spectroscopy (FT-IR) was recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer with an attenuated total reflectance (ATR) objective. The crosslinked polymers were exposed to increasing from 25 °C to 900 °C (as increasing 10 °C per minute) under an argon atmosphere by using a Mettler Toledo model TGA/SDTA 851 (Mettler Toledo, Greifensee, Switzerland). <sup>13</sup>C and <sup>29</sup>Si solid-state nuclear magnetic resonance (CP-MAS NMR) spectra were recorded Bruker Superconducting FT-NMR spectrophotometer Avance TM 300 MHz WB. The total content of carbon, hydrogen, nitrogen and oxygen was determined by using a LECO, CHNS-932 analyzer. Innova 2000/platrom shaker was used in order to increase the polymer-solvent interaction. All swelling experiments were carried out at room temperature (25 ± 2 °C).

### 2.3. Preparation of sorbents

The preparation of sorbents was achieved via bulk polymerization of propoxylate and the ICS cross-linker without using any initiator, activator, solvent, or catalyst; this is represented in Scheme 1.

After completion of polymerization, the resulting product was washed with several solvents (water, ethanol, and acetone) in order to remove the unreacted monomers. These were then vacuum dried to obtain a cross-linked polymer. The molecular weight of the star-type macromonomer, as well as the cross-linker ratio, have been examined. Additionally glycerol was condensed with the ICS cross-linker in order to obtain a model polymer. The amount of used monomers, the reaction conditions, and some properties of the synthesized polymers, are provided in Table 1.



**Scheme 1.** Preparation route of hydrophobic sorbents with ICS and different molecular weight of glycerol propoxylate and glycerol.

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