

New Limited Molecular Weight Polymeric Dispersants Prepared by Melt Condensation Polymerization

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Abstract

In this work, poly(sebacic anhydride) was prepared in a new method of condensation polymerization of sebacic acid monomer and sebacoyl chloride monomer in presence of triethyl amine, this polymer was purified, characterized by infrared spectroscopy.

Poly(sebacic anhydride) was used to prepare poly(ethylene glycol)-sebacic acid copolymers with carboxylic end groups and limited molecular weight using poly(ethylene glycol) having different chain length (400, 2000, 10000 and 20000 g/mole) by melt condensation polymerization. The copolymers were purified, characterized by infrared spectroscopy and end-group analysis of molecular weight determination technique. These polymers were tested as dispersants for ceramic alumina particles in ethanol as dispersion medium using centrifugation settlement method; High packing densities for alumina particles were obtained. It was found that the packing densities of alumina particles have been influenced by the polymer concentration and poly(ethylene glycol) chain length.

Their adsorption isotherms were also determined, it was found that the adsorption is molecular weight dependent and linear relationship was obtained between the maximum adsorption of the polymers and their molecular weights.

Keywords: melt condensation, poly(sebacic anhydride), poly(ethylene glycol)-sebacic acid, alumina, dispersants, isotherm adsorption

1. Introduction

In recent years, there has been a rapid development in research on achieving good ceramics suitable for various applications, such as mechanical, thermal, chemical, etc. To produce ceramic product meet the technology demands, has imposed requirements of producing high packing densities in the green state with closed packed, narrow-size distribution powders and uniform interparticle pores. This requires control of both powder-production and packing (Howard 1987; Landham 1987). However, it believed that the strength, homogeneity and quality of fired ceramic are difficult to meet while using crude powders as starting material.

The chemistry of the particle surfaces is an important factor in the formation of aggregates, which cannot be subsequently broken up. However, the critical first stage in production of a good ceramic is to disperse the primary particles into the suspending solvent so that they are separated to a stable dispersion without aggregation. Therefore, the selection of dispersants to maintain particles in a deflocculated state is dependent on both the ceramic powder and the dispersion medium. Each powder has an optimum dispersant requirement that will fully disperse and not flocculate the particles. The concentration required will also vary with each dispersant. Consequently, several theories were appeared to explain the mechanism of dispersed particles to achieve their stability by adsorbing polymeric chains (Napper 1989; Shi 2002; Platikanov & Exerowa 2009). Also, there are several ways and techniques to find out and evaluate polymeric dispersants for colloidal systems (Yanagioka & Frank 2008).

This work aims to focus on preparation and evaluation of some polymers prepared by melt condensation polymerization of poly(sebacic anhydride) with different molecular weights of poly(ethylene glycol), as dispersants for ceramic alumina particles. The adsorption behavior of these prepared polymers was explored and their adsorption isotherm was determined.

2. Materials

Toluene supplied by GCC, was dried by sodium wire, then it freshly distilled to obtain dry toluene before use. Triethyl amine was obtained from RDH. It was purified and dried to be used as a reagent for condensation polymerization. Poly(ethylene glycol) polymers having molecular weights (400, 2000, 10000 and 20000 g/mole)

and sebacic acid supplied by BDH and Aldrich respectively. The α -alumina particles supplied by MIT. It has a surface area $7.2 \text{ m}^2/\text{g}$ and diameter of $0.2\text{-}0.3 \text{ }\mu\text{m}$.

3. Methods

3.1 Synthesis of Poly(sebacic anhydride)

Sebacic acid (0.3 mole) was added to 150 ml of dry toluene in a three-neck round bottom flask fitted with mechanical stirrer, reflux condenser and thermometer. The solution was heated to $65 \text{ }^\circ\text{C}$ for 10 min. Then, (0.66 mole) of triethyl amine and (0.33 mol) of sebacyl chloride were added to reactant and the mixture was stirred mechanically for 6 hours. The white solid polymer was isolated and purified by petroleum ether and the yield was 89%.

3.2 Synthesis of Poly(ethylene glycol)-sebacic Acid Limited Molecular Weight

1 mole of poly(ethylene glycol) with molecular weights (400, 2000, 10000 and 20000 g/mole) was mixed with 1.1 mole poly(sebacic anhydride). The mixture was refluxed as a melt at $180 \text{ }^\circ\text{C}$ under dry nitrogen gas for two hours. Then, was dissolved by dichloromethane, filtered to remove sebacic acid formed. The product was reprecipitated in diethyl ether and dried at room temperature. The resulted polymer is a white solid with carboxylic acid end groups with 76% yield.

3.3 Dispersion Process under Centrifugation Settlement

Dispersions were prepared by mixing four grams of alumina powder with a known concentration of the dispersing agent (0.5%, 1%, 2%, 3%, 4% and 5% wt. /wt.) in a 10 ml centrifuge tube. They were agitated manually for 15 minutes at room temperature to increase the surface area of adsorbent and preventing particles to accumulate. Then, dispersed particles were settled down by centrifugal forces that its rotation speed was regulated manually for one hour. The clearer solution above the compact particles layer was removed carefully. It was weighted before and after drying step with test tube and the results were expressed by %packing density (Al-Lami *et al.* 1992).

The packing density of the final particle bed is measured and expressed as a fraction of the theoretical density of a fully dense ceramic. For all the suspensions, the final packing densities were reproducible to within ± 0.2 in repeated experiments with same conditions.

3.4 Thermal Gravimetric Analysis

1 g of grafted alumina was placed on weighted ceramic crucible, which was dried and burned previously by furnace under the same firing conditions. Then, sample with crucible was heated gradually to $600 \text{ }^\circ\text{C}$ and hold at this temperature for one hour. Then it cooled down inside desiccators at room temperature. This step was repeated until constant obtained. The weight of adsorbed polymer onto alumina particle surface was calculated gravimetrically (Al-Lami 1998).

4. Results and Discussion

4.1 FTIR Analysis

The two types of polymeric products, poly(sebacic anhydride) and poly(ethylene glycol)-sebacic acid, were characterized by Shimadzu FTIR-8400S instrument. Figure 1 shows the FTIR spectrum for poly(sebacic anhydride); it exhibits two sharp and strong peaks at 1807 cm^{-1} and 1743 cm^{-1} which are assigned for stretching of acid anhydride carbonyl groups along the polymer backbone chains. In addition, strong peak at 1040 cm^{-1} assigned to the C-O bond of the acid anhydride groups. In addition, the carbonyl of the carboxylic acid groups at the end of polymer chains showed a peak at 1701 cm^{-1} and a broad peak at the range of $3300\text{-}2800 \text{ cm}^{-1}$ for their hydroxyl groups. Other peaks at 2921 cm^{-1} and 2856 cm^{-1} represent symmetric and asymmetric stretching of aliphatic C-H bond of methylene groups respectively. On the other side, poly(ethylene glycol)-sebacic acid was characterized by the presence of ester group, figure 2, which gave a strong peak at 1730 cm^{-1} for stretching carbonyl-ester group as well as two peaks at $1250\text{-}1040 \text{ cm}^{-1}$ for C-O bond of ester group. Disappearing of acid anhydride peaks at 1807 cm^{-1} and 1743 cm^{-1} implies the hydrolysis of acid anhydride groups to form carboxylic acid groups which gave a strong peak at 1699 cm^{-1} for its carbonyl groups and a broad peak at $3300\text{-}2800 \text{ cm}^{-1}$ for its hydroxyl groups (Silverstein 2005; Pretsch *et al.* 2009).

4.2 Determination of Polymers Molecular Weight

The number averages molecular weights of poly(ethylene glycol)-sebacic acid prepared polymers were determined by end-group acid analysis (Crompton 2009). The results obtained are listed on table 1. It was found that good compatibility of experimental molecular weights with theoretical molecular weights. This analysis confirms that each ethylene glycol-sebacic acid polymer chain has only one sebacic acid molecules in the each end of polymer chains. These results are in good agreement with reported in Jalal, 2011, and it confirmed that polymers with limited chain length have been prepared.

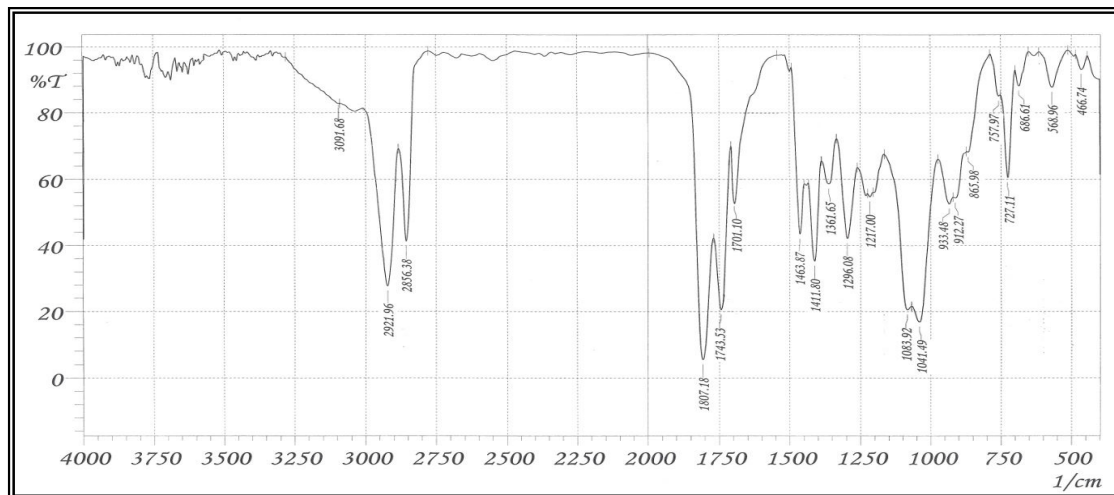


Figure 1. FTIR spectrum for poly(sebacic anhydride)

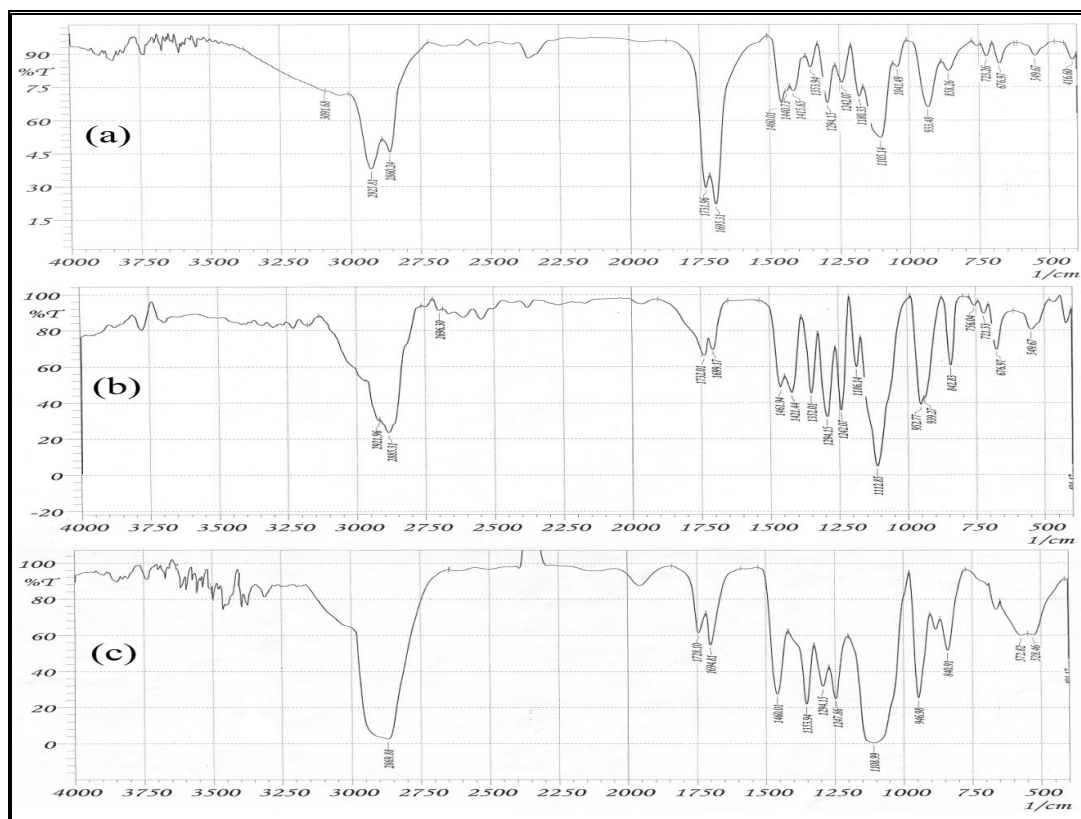


Figure 2. FTIR spectra for ethylene glycol-sebacic acid limited molecular weights polymers and the molecular weights (g/mole) of PEG are (a) 400, (B) 10000 and, (c) 20000

Table 1. Molecular weights of limited molecular weight prepared polymers

PEG segment molecular weight (g/mole)	Experimental molecular weight of poly(ethylene glycol)-sebacic acid (g/mole)	Theoretical molecular weight of poly(ethylene glycol)-sebacic acid (g/mole)
400	740	768
2000	2360	2368
10000	10383	10368
20000	20522	20368

4.3 Assessment of Prepared Polymers as Dispersants

The enormous development and use in the last three decades of ceramics for high technology has been made possible only by the paralleled development of specific dispersants and lubrication process. The steps to achieve well-packed sediment must include (a) deagglomeration and dispersion of the dry powder into the solvent, (b) settling of the powder without agglomeration due to interparticle attractive forces, and (c) high mobility and low friction within the sediment to allow optimum packing (Napper 1983).

In any dispersion process although a ceramic slip should consist of individual particles stabilized against aggregation, the large density differences between the alumina particles and the dispersion medium ethanol means that the particles will usually settle out faster with some alumina particles adhering to the wall. Therefore, %packing density measurement was used to assess the ability of prepared polymeric dispersant to flocculate or deflocculated alumina particles in the suspending medium. Although all dispersants contributed to the dispersion of alumina particles, some of them increased the packing factor more than the other and affected by poly(ethylene glycol) chain length and dispersant concentration.

Examining figure 3, concerning the packing densities obtained from different concentrations of different polymeric dispersants examined, one can easily observe that higher packing densities are obtained with dispersant having the longest poly(ethylene glycol) chains, i.e. 20000, reflecting better dispersion was obtained originally from its suspensions, although the active group was the same, i.e. carboxyl end groups.

From the above discussion of powder packing, the emphasis has been placed on the second stage as being the key to achieving good packing by the elimination of the attraction between alumina particles. It can be say that increasing the poly(ethylene) molecular weight in polymeric dispersants has improved the dispersion and enhance the settlement of alumina powders in terms of packing density, similar observation was made by Doroszkowski & Lambourn 1987. They found that increasing the length of the acetate side chain by just three (-CH₂-) links caused very large increase in stability. This implies that surface concentration is very important in influencing origin dispersions.

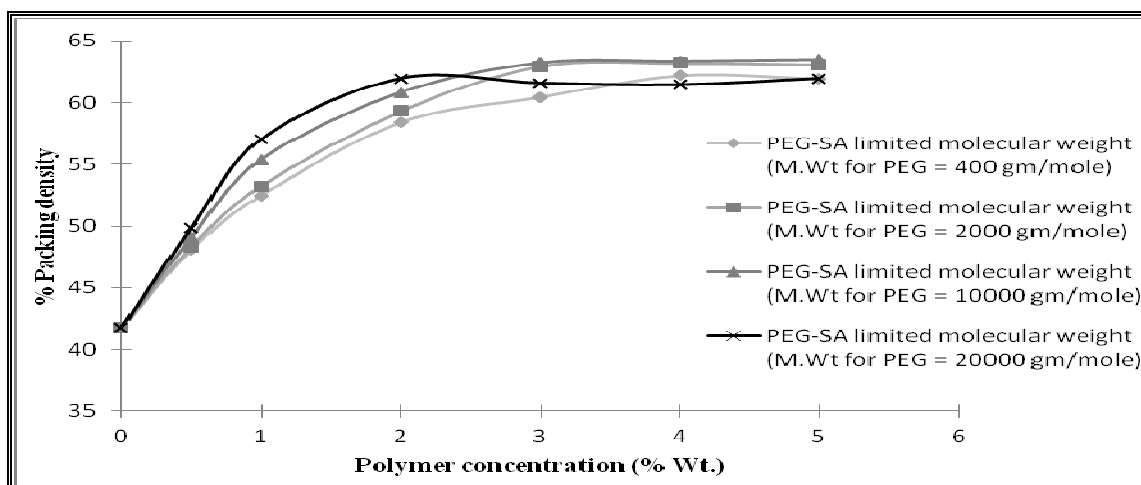


Figure 3. Effect of concentrations of poly(ethylene glycol)-sebacic acid limited molecular weight on packing densities of alumina particles dispersed in ethanol

4.4 Adsorption Isotherms

The amount of adsorbed polymer on surface of alumina particles was determined by thermal gravimetric analysis method and then, adsorption isotherm was specified by relation between the estimated amount of polymer adsorbed onto alumina and polymer concentration at equilibrium, figure 4. The adsorption isotherm, in general, exhibits a rapid rise in the adsorption at low solution concentration and start to level off at high polymer concentration.

Comparisons of these adsorption isotherm indicated that the isotherm of the dispersant polymer having the shorter segment of poly(ethylene glycol) have the highest amount adsorbed. This can be attributed to that the alumina surface might needed more adsorbed polymer to reach the monolayer coverage(Napper 1983; Perrino 2009), and increasing polymer concentration led to decrease adsorption. The obtaining shapes of adsorption isotherm curves have taken the same shapes of Langmuir isotherm (Langmuir 1918).

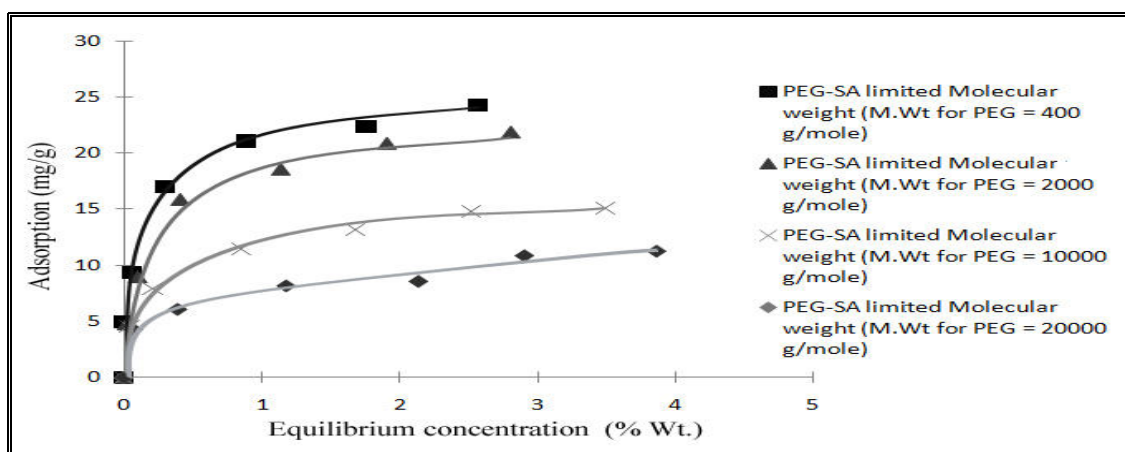


Figure 4. Adsorption isotherm for ethylene glycol-sebacic acid limited molecular weight polymers on alumina particles at ethanol

4.5 The effect of molecular weight on conformation of adsorbed polymer

The conformations of adsorbed polymers were studied by determination of maximum amount of adsorbed polymer at particular molecular weight. It has been often reported for maximum adsorption of polymers on solid surface that the dependence on molecular weight is in accord with the following equation (Ellerstein & Ullmann 1961):

$$A_s = K \times M^\alpha \quad \dots (1)$$

The terms; (M) represents the polymer molecular weight, (A_s) is maximum amount of adsorbed polymer and (K) is constant. The exponent (α), in this case, is a function of the shape of the adsorbed molecule, and hence the degree of coiling that has to describe conformation of adsorbed polymers.

Good linear correlation is obtained for the adsorption of the prepared dispersants between logarithm of maximum amount of adsorbed polymers and logarithm of their limited molecular weight, figure 5. The straight line of this relation gave an exponent (α) value 0.22 which implies that the polymer molecule would be adsorbed in the form of coil on the alumina particle surface, and again the amount of adsorbed polymer depends on its molecular weight. These results are in a good agreement with other results reported using monodispers n-butyl methacrylate/methacrylic acid block copolymers prepared by groups-transfer polymerization (Howard 1987; Al-Lami & Ibrahim 1993).

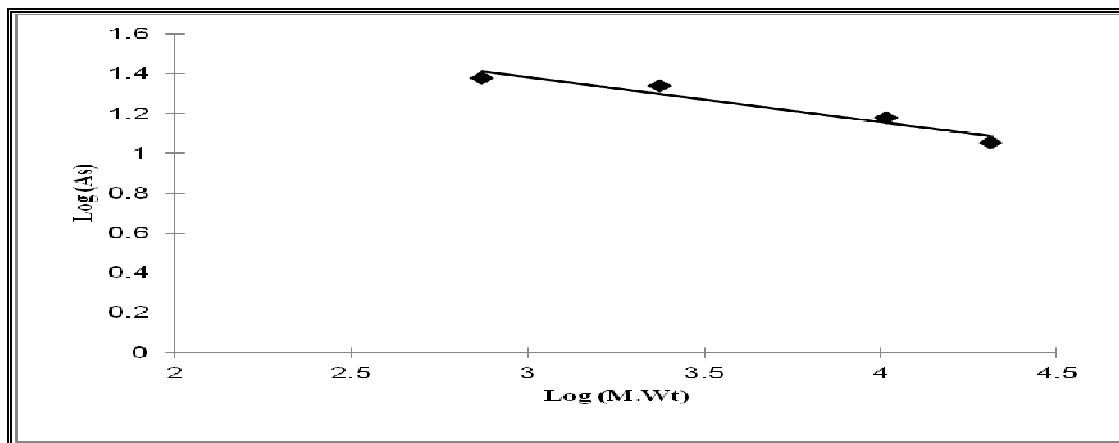


Fig. 5. The effect of molecular weight of ethylene glycol-sebacic acid polymers limited molecular weight on amount of adsorbed polymer onto alumina particles surface

On the other hand, the obtained non-linear curve for unlimited molecular weights polymers imported from Jalal, 2011 is shown in figure 6. This implies that the unlimited molecular weight polymer chains adsorbs with more than one active site by physical adsorption as well as chemical adsorption on surface of alumina particle and the amount of adsorbed polymer doesn't depend on its molecular weight.

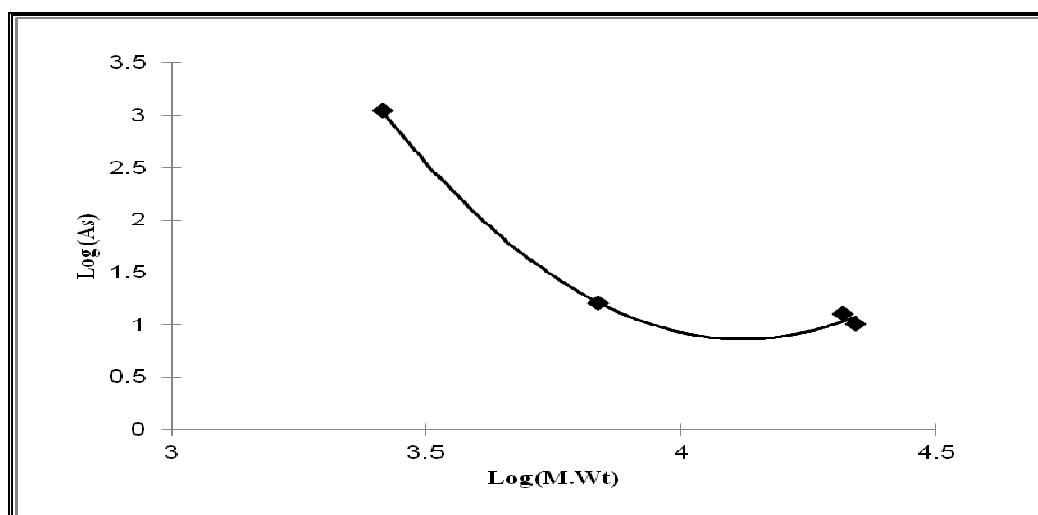


Figure 6. The effect of molecular weight of unlimited molecular weight glycol ethylene-sebacic acid polymers on amount of adsorbed polymer on alumina particles surface (Jalal, 2011)

5. Conclusions

Polymers of ethylene glycol-sebacic acid limited molecular weights were successfully prepared and it found that each polymer chain has only one poly(ethylene glycol) segment and two of sebacic acid end groups of polymer chain. This was confirmed by end group and FTIR analyses. Testing them as dispersants for alumina particles in ethanol showed much better packing densities comparing with unlimited molecular weight polymers and they are molecular weight dependence with adsorption isotherm followed Langmuir isotherm.

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