



# Microwave based synthesis of polymethyl methacrylate grafted sodium alginate: its application as flocculant

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## ABSTRACT

Polymethyl methacrylate grafted sodium alginate (SAG-g-PMMA) was synthesized by *microwave assisted method*. The grafting of the PMMA chains on the polysaccharide backbone was confirmed through intrinsic viscosity study, FTIR spectroscopy, elemental analysis (C, H, N, O and Na), SEM and TGA study. The intrinsic viscosity of sodium alginate appreciably improved on grafting of PMMA chains, thus resulting grafted product with potential application as superior viscosifier. Further, flocculation efficacy of the graft copolymer was studied in coal fine suspension through jar test procedure, toward possible application as flocculant.

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## 1. Introduction

### 1.1. Water scarcity: the impending disaster

Water is one of the key factors required for existence and flourishing of carbon based life form. The abundance of water is the single most important factor that distinguishes this planet from all others of this solar system. The importance of water for existence of life is so important that the search for water in other planets has become synonymous to search for life. However, most of the water on this planet is stored in oceans as saline water and hence is not fit for direct human consumption. The small percentage of freshwater that exists occurs in ice caps and inland water bodies, which are the key to fulfilment of our diverse needs.

In the present scenario, global warming is responsible for rapid disappearance of the ice caps (glaciers) which in turn in the near future will result in volume of water in the all season glacier fed rivers to dwindle. The ever increasing pollution of water bodies is making the scenario worse. Because of these factors, water or rather the shortage of it is emerging as one of the most significant problems of the recent times.

The other fundamental need of human civilization is energy. Coal has been the principal source of industrial energy for much

of the developing world. Although, petroleum based fuels are 'greener', the distribution of coal minerals on this planet are more even and hence, the importance of coal in development of world economy cannot be ignored. Washing coking coals with water before their utilization in thermal power plant and cement industry is a general practise and is gaining popularity. Washed coals have higher calorific value and cause lesser air pollution on burning. However, we seem to trade one type of pollution for the other. The very process of washing of coal produces effluent with coal fine suspension. These coal washery effluents have the potential to pollute huge stretch of the receiving water body. Further, once recovered, the fine coal particles of these effluents serve as a precious fuel commodity which otherwise would have gone waste. Thus, it is evident that treatment of coal washery effluent has both ecological as well as economical benefits.

For the removal of suspended solids from the coal washery effluent, flocculation aided by synthetic and semisynthetic flocculants (Pal, Sen, Karmakar, Mal, & Singh, 2008; Sen, Mishra, Usha Rani, Rani, & Prasad, 2012) seems to be a highly effective strategy.

### 1.2. Sodium alginate (SAG): a promising polysaccharide

Sodium alginate is the principal commercial water-soluble salt of alginic acid. Other commercially available water soluble salts are potassium alginate and ammonium alginate. Water-insoluble compounds that are marketed are calcium alginate and alginic acid. The only commercially important organic derivative is propylene glycol alginate.

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Sodium alginate is sourced from brown green algae (Phaeophyceae) and sea weeds. It binds 200–300-fold weight of water to give gel formation. Sodium alginate is insoluble in cold water. It has many applications in the food industry as thickeners in fruit jellies, marmalades, ice cream, etc. Propylene glycol esters of alginic acids are used as foam stabilizer. Sodium alginate and its derivatives has long been the focus of many scientific studies. Polyacrylamide grafted sodium alginate as a flocculant has been reported in recent times (Sen, Mishra, Jha, & Pal, 2010; Sen, Singh, & Pal, 2010).

### 1.3. Sodium alginate molecular structure

Alginate is composed of two building blocks of monomeric units, namely R-D-mannuronopyranosyl and L-guluronopyranosyl units. Ratio of D-mannuronic acid and L-guluronic acid and their sequence determines the alginate properties. Monomers occur in blocked sequences (M & G blocks) as shown in [Supplementary Fig. 1](#).

### 1.4. The concept of graft copolymers

Graft copolymers by definition, consists of a long sequence of one polymer (backbone polymer) with one or more branches (grafts) of another (chemically different) polymer (Gowariker, Viswanathan, & Sreedhar, 1986, Chapter 12; Odian, 2002). The process of graft copolymer synthesis starts with a preformed polymer (polysaccharide in this case). An external agent is used to create free radical sites on this preformed polymer. Once the free radical sites are formed on the polymer backbone (i.e. preformed polymer), the monomer (i.e. vinyl or acrylic compound) can get added up through the chain propagation step, leading to the formation of grafted chains. The various methods of graft copolymer synthesis actually differ in the ways of generation of the free radical sites on this preformed polymer.

The most contemporary technique in graft copolymer synthesis involves the use of microwave radiations to initiate the grafting reactions. Superiority of this technique over others has been well discussed in earlier studies (Mishra & Sen, 2011; Mishra, Mukul, Sen, & Jha, 2011; Mishra, Sen, Rani, & Sinha, 2011; Mishra, Rani, & Sen, 2012; Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011; Pal, Sen, Ghosh, & Singh, 2012; Sen & Pal, 2009a, 2009b; Sen, Kumar, Ghosh, & Pal, 2009; Sen, Mishra, et al., 2010; Sen, Singh, et al., 2010; Sen, Ghosh, Jha, & Pal, 2011; Usha Rani, Mishra, Sen, & Jha, 2012). Microwave radiations cause 'selective excitation' of only the polar bonds, leading to their rupture/cleavage – thus resulting in formation of free radical sites. The 'C–C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation, thus the structural integrity of the backbone remains intact, leading to a superior product (Mishra et al., 2012).

Microwave based graft copolymer synthesis is further classified into two types: microwave initiated synthesis (using microwave radiation alone to initiate grafting) and microwave assisted synthesis (using a synergism of microwave radiation and chemical free radical initiator to initiate grafting).

### 1.5. Plan of investigation

The study described in this paper involve the synthesis of graft chains of polymethyl methacrylate (PMMA) onto the backbone of sodium alginate, thus resulting in formation of polymethyl methacrylate grafted sodium alginate' (SAG-g-PMMA). The synthesis has been carried out by *microwave assisted method*, which involved a synergism of microwave radiations and ceric ammonium nitrate (CAN) to initiate the grafting reaction. The flocculation

efficacy of the grafted product has been studied in coal fine effluents toward its application in coal washery effluent treatment.

## 2. Materials and methods

### 2.1. Materials

Sodium alginate and methyl methacrylate were supplied by CDH, New Delhi, India. Ceric ammonium nitrate was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received; without further purification.

### 2.2. Synthesis of graft copolymer

#### 2.2.1. Microwave assisted synthesis of polymethyl methacrylate grafted sodium alginate (SAG-g-PMMA), using ceric ammonium nitrate (CAN) as free radical initiator

1 g of sodium alginate was dissolved in 40 ml distilled water. Desired amount of methyl methacrylate was added to above solution. They were mixed well and were transferred to the reaction vessel (250 ml borosil beaker) followed by addition of catalytic amount of ceric ammonium nitrate (CAN). The reaction vessel was placed on the turntable of a microwave oven and microwave irradiation at 800 W of power was performed. Periodically, the microwave irradiation was paused just as the reaction mixture starts boiling (~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to keep any probability of competing homo polymer formation reaction to the minimum.

This *microwave irradiation – cooling cycle* was repeated until a gel like mass was left or up to 3 min of irradiation time (if no gelling took place). Subsequently, the reaction vessel and its contents were finally cooled and kept undisturbed to complete the grafting reaction. Later, the gel like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of graft copolymer was collected and was dried in hot air oven. Subsequently, it was pulverized, sieved and purified (as explained in Section 2.2.2). The percentage grafting of this microwave assisted synthesized SAG-g-PMMA was evaluated as:

$$\% \text{ grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100$$

The synthesis details of various grades of the graft copolymer have been shown in [Table 1](#).

#### 2.2.2. Purification of the graft copolymer by solvent extraction method

In an attempt to check possibility of any competing homopolymer formation reaction, the whole synthesis process was repeated as above, but in absence of any polysaccharide (sodium alginate). In absence of the polysaccharide, no product is obtained. This implies that the above process either does not involve any parallel homopolymer formation reaction or if even any homopolymer happen to be formed, it cannot be precipitated in acetone.

However as an added precaution, any occluded polymethyl methacrylate (PMMA) formed by competing homo polymer formation reaction was removed from the graft copolymer synthesized as above, by extraction with acetone for 24 h (Kongparakul, Prasassarakich, & Rempel, 2008). The scheme of synthesis of the graft copolymer has been summarized in [Scheme 1](#).

### 2.3. Characterization

#### 2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (capillary diameter 0.46 mm)

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