



Suspension stability control using light-sensitive polymers

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ABSTRACT

In this paper a novel approach to the flocculation phenomenon was investigated, i.e. application of light-sensitive polymers. A hypothesis was proposed that the energy delivered by an electromagnetic wave will trigger the photo-dimerization reaction, which in turn will lead to the destabilization process via bridging phenomenon. In research two polymers differing in content of light-sensitive component, i.e. cinnamoyl groups, were synthesized by means of conventional free radical copolymerization and postreaction. In the flocculation experiments a model suspension of CaCO₃ precipitate in deionized water was used. The experiments were performed using two different mixer configurations. Unfortunately, the postulated mechanism was proved to be wrong. Although both polymers acted as good destabilization agents directly after injection to suspension, the UV radiation had no impact on the process.

1. Introduction

Recently, various kinds of photo-responsive polymers containing pendant pyrene [1], 2-itorobenzene [2], and spiropyran [3] groups have been prepared and characterized in more detail. The association behavior of these photo-responsive polymers can be controlled by light-irradiation. In this work a novel approach to the flocculation phenomenon was investigated, i.e. application of light-sensitive polymers. In this case the stimulus that triggers the change of the system behavior is the light energy of a given (often strictly defined) weave length. When such macromolecule is excited by irradiation it may undergo photo-dimerization or photolysis depending on its chemical properties [4,5]. An example of photo-dimerization of cinnamoyl groups is presented in Fig. 1.

The photo-dimerization can occur both inter- and intramolecularly. The cinnamoyl group may be incorporated to form larger structures, enabling the possibility of cross-linking between high molecular weight polymer chains. Such “carrier” will gain light-sensitivity which will be proportional to the molar ratio between light-sensitive and nonsensitive parts of macromolecule.

The proposed mechanism is presented in Fig. 2. If the cinnamoyl groups were incorporated into polyacrylamide chain in small degree, the first stage of the flocculation process should be identical to the classical approach to this phenomenon: the macromolecules are introduced to the suspension and they adsorb onto the surface of solid

particles. At this point an aggregation may occur via bridging mechanism depending on the molecular weight of polymer [6,7]. However, the key mechanism of aggregation should occur when the system will be irradiated using UV light source. The cinnamoyl groups should start to dimerize (Fig. 1) and thus polymer bridges between particles will be created. Such mechanism implies that the flocculation process will not be sensitive to the overdose effect. Moreover, it may be successfully used in order to enhance standard flocculation.

2. Experimental section

2.1. Polymers synthesis

2.1.1. Materials

Acrylamide (AAM, 95%), cinnamoyl chloride (95%) from Wako Pure Chemical, and *N*-(2-aminoethyl)methacrylamide hydrochloride (AEMA, 95%) from Polysciences Inc. were used as received without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN, 98.0%) from Wako Pure Chemical was recrystallized from methanol. Water was purified with an ion exchange column system. Other reagents were used as received.

2.1.2. Preparation of polymers

Two random copolymers were synthesized by conventional free radical copolymerization and postreaction in the research, i.e. P(A/

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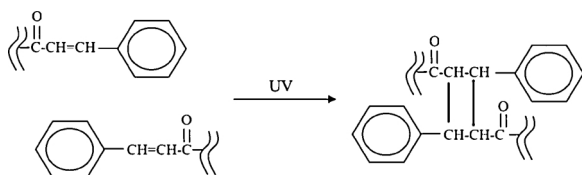


Fig. 1. Photo-dimerization of cinnamoyl groups.

AE21/C1) containing 1 mol% of cinnamoyl group and P(A/AE17/C4) containing 4 mol% of cinamoyl group. The synthesis route of the P(A/AE21/C1) copolymers was as follows (Fig. 3). AAm (1.40 g, 19.7 mmol), AEMA (0.860 g, 5.23 mmol), and AIBN (20.5 mg, 0.125 mmol) were dissolved in water (24.6 mL). The solution was stirred at 60 °C for 24 h. After polymerization, a small amount of the polymerization mixture was measured with ^1H NMR. The conversion was monitored via vinyl protons in monomers, which was 100%. The reaction mixture was dialyzed against pure water for 3 days. The polymer aqueous solution (P(AA/AE22)) was concentrated to be 50 mL. Sodium hydroxide (0.688 g, 17.2 mmol) was added to the aqueous solution. Cinnamoyl chloride (4.36 g, 26.2 mmol) was added to the aqueous solution with stirring at 40 °C. After addition, the reaction was continued for 24 h with no light at 50 °C. Unreacted cinnamoyl chloride was changed to cinnamic acid which is solid and insoluble in water. Therefore, the precipitate of cinnamic acid was removed by filtration. The filtrate was dialyzed against water for 2 days. Photocross-linking group-containing random copolymer (P(A/AE21/C1)) was recovered by a freeze-drying method (1.41 g, 63.6%). The contents of AEMA and cinnamoyl group were 21 and 1 mol%, respectively, estimated by ^1H NMR. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were 5.05×10^5 and 3.21, respectively, estimated by gel-permeation chromatography (GPC). In the case of P(A/AE17/C4) copolymer the contents of AEMA and cinnamoyl group were 17 and 4%mol respectively. M_n and M_w/M_n were 3.20×10^5 and 6.00, respectively.

2.1.3. Characterization of polymers

^1H NMR spectra were obtained with a Bruker DRX-500 spectrometer operating at 500.13 MHz. GPC measurements for cationic polymer were performed using a Jasco RI-2031 Plus refractive index detector

equipped with a Jasco PU-8020 pump and a ShodexOHpak SB-804 HQ column (exclusion limit $\sim 10^7$) working at 40 °C under a flow rate of 0.6 mL/min. A 0.3-M Na_2SO_4 aqueous solution containing a 0.5-M acetic acid was used as eluent. The values of M_n and M_w/M_n were calibrated with standard poly(2-vinylpyridine) samples. Attenuated total reflection-infrared (ATR-IR) spectra were obtained using a Jasco FT/IR-4200 spectrometer with a Jasco ATR-PRO450S base kit. UV-vis absorption spectra were recorded using a Jasco V-530 UV/Vis spectrophotometer.

Photo-dimerization was conducted using an Asahi Spectra MAX-300 instrument equipped with a 300-W Xe lamp at > 250 nm with 20 mW/cm 2 . The polymer aqueous solution was irradiated with UV-light at polymer concentration of 0.5 g/L. To monitor the photo-reaction of the cinnamoyl groups in the polymer aqueous solution, changes in the absorption spectra of the polymer film were monitored.

2.2. Flocculation experiments

In experiments a model suspension of calcium carbonate in reverse osmosis (RO) water (purity of $0.06 \mu\text{S}\cdot\text{cm}^{-1}$) was used. The final solids concentration in suspension was equal to $12 \text{ g}\cdot\text{dm}^{-3}$. The zeta potential of the suspension was measured using Malvern Nano-Z equipment. It was equal to (-22.2) mV. Before experiment, an appropriate mass of polymer was weighted using an analytical balance and transferred to a small flask. Then, RO water was added and the solution was mixed for 1 h. The final concentration of polymer solution was equal to 1 mg/mL.

The experiments were performed using two different laboratory setups. In the first case a thermostated vessel equipped with four baffles and magnetic stirrer (1000 RPM) (Fig. 4) was used. The UV light source (OSRAM ULTRA-VITALUX 300 W lamp) was placed 300 mm above the suspension level. In the second case, the light source (Philips PL-S 9 W/12) was placed in a quartz tube immersed in the suspension (Fig. 5).

When the suspension was prepared it was mixed for ten minutes in order to achieve a steady state. Then the polymer was injected and the time was measured. The samples were taken using a Pasteur pipette with a wide end and transferred into a laser particle sizer (Fritsch Analysette 22). The samples were analyzed every 10 min after polymer injection, however no more than five samples per experiment were taken. The experiments were repeated until three independent

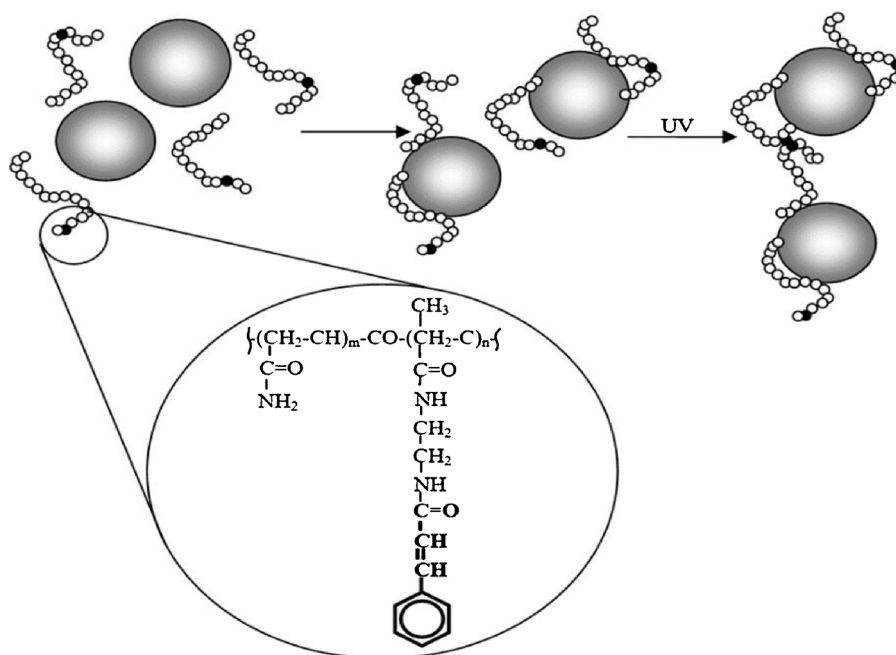


Fig. 2. Mechanism of light-sensitive flocculation.

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