Biosoluble 포함한 양성 Poly(acrylate)s의 합성

강남경 하종욱 박인준 이수복 Shiyuan Cheng
한국화학연구원 재래과학실, 풍백이 대학교 화학재료과학부

Synthesis of Fluorine-Containing Amphoteric Poly(acrylate)s

Na Kyung, Kang¹, Jong-Wook Ha¹, In Jun Park¹*, Soo-Bok Lee¹
¹Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, Taejon 305-606, Korea
Shiyuan Cheng²
²School of Chemistry and Material Science, HuBei University, Wuhan, 430062, P. R. China

Abstract

We report on preparation of novel fluorine-containing amphoteric poly(acrylate)s using hydrophobic macromonomer of perfluoroalkyl group for the soil release agent of the fabrics. The macromonomer was synthesized by radical copolymerization of perfluoroalkylacrylate and methyl methacrylate with a chain-transfer agent with hydroxyl group in order to attenuate solubility in organic solvent and hydrophobic property, and successive acylation with acyl chloride. The amphoteric fluorine-containing graft poly(acrylate) was prepared by radical copolymerization of the macromonomer with hydrophilic monomer of 2-(dimethyl amino)ethyl methacrylate (2-DMAEMA). The design, and the synthetic route, and characterization of the amphoteric graft copolymer of fluorine containing amphoteric poly(acrylate) are described.

1. Introduction

The amphoteric poly(acrylate), which has both of hydrophobic and hydrophilic segments in one molecules, has been attracted particular attentions in coating because it has surface properties of not only water and oil repellency but soil release property of contaminated wet soils on the surface of the polymer. The amphoteric polymer is easy to emulsify in water without additional surfactants ("soap-free"), it has advantages in environmental pollution, fire safety compared with solvent-based poly(acrylate)s (1). Furthermore, the surface of amphoteric polymer does not have surfactants, it is possible to obtain the clean surface polymer particles which can be importantly used in immobilization of functional groups which can be utilized in biochemistry. Although it is very important in water/oil repellent agents and soil release agents, it is difficult to find the work about the amphoteric polymer because of difficulties in synthesis and characterization. When the amphoteric polymer coated on solid surface, the outermost layer of the surface is composed of hydrophobic groups in atmosphere, and the surface has a property of water/oil/soil repellencies. When the environment of the surface is changed to water after the soil is contaminated, the conformation of the functional group is occurred, and the hydrophobic group immersed under interface with the emergence of hydrophilic group, and the soil is removed easily from the surface as shown in Figure 1. In this study, the two-phase amphoteric fluorine-containing graft copolymer was prepared by macromonomer technique. The design concept, synthesis procedure, and the characterization results of the amphoteric polymer will be described.

2. Design of Amphoteric Fluorine-Containing Graft copolymer

It has been known that the chemical structure of soil release agents should have both hydrophilic and hydrophobic segments (2, 3). The typical commercialized product has the structure of random copolymer of perfluoroalkyl acrylate as a hydrophobic monomer and acrylate with long ethylene oxide side chain as a hydrophilic monomer (2). An alternating form of the soil release agent is the oligomer by 3M, which shows the triblock oligomer with perfluoroalkyl acrylate and ethylene oxide (3). But both of them have disadvantages of low performance because of lack of massive concentration of both hydrophilic and hydrophobic groups or difficulties in emulsification which is essential in commercial products.

In order to circumvent these problems, the novel structure of amphoteric polymer which can be used in soil release agents is proposed as shown in Figure 2. The polymer is designed as a graft copolymer to have both of blocky hydrophobic group and hydrophilic groups in order to enrich the surface property at outermost layer. The hydrophobic segment is composed of perfluoroalkyl acrylate and methyl methacrylate to control the solubility and hydrophobic property. As a hydrophobic segment, homopolymer of 2-DMAEMA is chosen because the poly(2-DMAEMA) itself is hydrophilic, and it is possible to emulsify the synthesized polymer by salifying with acids. Therefore the poly(2-DMAEMA) acts as hydrophilic segment of surface in atmosphere and internal surfactant in water.
3. Experimental

**Materials.** Perfluorooalkylethyl acrylate \([F\text{CF}_2]_n\text{CH}_2\text{CH}_2\text{COOCH} = \text{CH}_2\) (FA, Nicca Korea) and methyl methacrylate (MMA) were purified chromatographically over neutral AlO\(_3\), distilled in vacuum from copper(I) chloride, stored under Ar atmosphere at -30 °C. The radical initiator, 2,2'-azobisisobutyronitrile (AIBN), was used after recrystallization from methanol. Triethyl amine was dried by distillation from CaH\(_2\). Acetyl chloride was purified by distillation after distillation from hydroquinone. Acetone was used after drying in molecular sieve 4A. The solvents used in this study were spectrophotometric grade. Millipore-Q water was used throughout the experiments. All other chemicals were used as received.

**Synthesis of Hydrophobic Macromonomer (F-macromer) and Amphoteric Fluorine-Containing Poly(acrylate)s (AFP).** Synthesis of hydroxy group terminated hydrophobic macromonomer (FOH) was performed by adding 30 g of FA (0.0579 g/mol), 10 g of MMA (0.1 g mol), 0.4 g of AIBN (0.0024 g/mol), 2-mercaptoethanol (ME) (0.0157 g/mol, [ME]/[monomers]=0.1), and 120 mL of tetrahydrofuran into a 250 mL Pyrex reactor. After degassing by repeated freeze-thaw cycles, thermal radical polymerization was done in a thermostat (accuracy ±0.1 °C) with stirring at temperature of 60 °C with Ar atmosphere. The conversion of reaction was detected by analysis of un-reacted FA and MMA by gas chromatography (Donam DS 6200). Reaction was terminated at conversion about 50 % of FA by adding reaction mixture into large amounts of n-hexane. Purified FOH was obtained after re-precipitation three times from n-hexane and drying under vacuum. The F-macromer having an acryloxy functional group at one end was prepared by acylation of FOH with AC. Acylation of FOH was done by dropping 10 % excess of AC on the FOH solution (FOH/THF=1/1, w/w) for 30 min and ageing for 24 h at room temperature. The reaction solution was precipitated in n-hexane after neutralization with N(Et)\(_3\) and filtration with Celite. Purified F-macromer was obtained by precipitation and drying at room temperature under vacuum.

Synthesis of amphoteric fluorine-containing polymer were done by radical solvent polymerization. Radical solvent polymerization was done by adding 10 g of F-macromer, 10 g of 2- DMAEMA, 0.5 g of AIBN, and 20 mL of acetone into 100 mL of Pyrex reactor. After degassing by repeated freeze-thaw cycles, thermal radical polymerization was done in a thermostat (accuracy ±0.1 °C) with stirring at temperature of 60 °C with Ar atmosphere. Reaction was terminated after 3 days with a conversion about 90 % of 2- DMAEM by adding reaction mixture into large amounts of n-hexane. The synthesized polymer was purified by re-precipitation three times from hot methanol and drying under vacuum.

**Bulk Characterization.** Molecular weights were measured by gel permeation chromatography (GPC) of Waters R-401 ALC/GPC with RI detector, and polystrene as a standard. NMR spectra were recorded on a Bruker AMX 500 with CDCl\(_3\). Transmission FTIR spectra of films cast onto KBr was recorded on a Bio-rad FTS-40 at a resolution of 2cm\(^{-1}\). DSC traces was measured on a DuPont 2100 at a scan rate of 10 Kmin\(^{-1}\).

4. Results

**Synthesis of FOH and F-macromer.** The FOH were prepared by radical copolymerization of FA and MMA with ME. FA was chosen due to extremely hydrophobic property of perfluorooalkyl group(3-5). ME was used in order to induce a hydroxyl group in one end of FOH, and to control M\(_n\) of FOH (6). F-macromer have number average molecular weights (M\(_n\)) about 3,400 by GPC. \(^1\)H-NMR spectrum of F-macromer was shown in Figure 3. The presence of double bonds (CH=CH\(_2\), 5.86-6.49 ppm) shows the successful synthesis of F-macromer, and composition could be obtained from methylene (-CH\(_2\)CF\(_2\_), 4.3 ppm) and methyl protons (-COOCH\(_3\), 3.6 ppm) originated from FA and MMA, respectively. The M\(_n\) of the F-macromer was ca. 8,000, composition of FA was 76 % by weight. The T\(_g\) of the F-macromer was 16 °C (Figure 4) because of high content of low T\(_g\) PFA (ca. 40 °C) and relatively small molecular weight of the F-macromer.

**Synthesis of Amphoteric Graft Copolymer.** F-macromer were copolymerized with hydrophilic monomers of 2-DMAEMA to prepare amphoteric poly(acrylate). During the initial period of the reaction the reactant solution is homogeneous because the F-macromer and homopolymer of p(2-DMAEMA) are soluble in acetone. But the polymer was precipitated as the reaction proceeds due to the increment of hydrophobic property of the polymer. The resultant reaction solution was purified by washing from acetone three times, and purified fluorine-containing two-phase graft copolymer was obtained. Figure 5 shows the IR traces of F-macromer, homopolymer of hydrophilic p(2-DMAEMA), and the graft copolymer. The IR traces shows that the amphoteric copolymer was synthesized successfully, and the polymer has the characteristic peaks of both hydrophobic F-macromer and hydrophilic polymer of p(2-DMAEMA).

5. Conclusions and Future work

The novel amphoteric poly(acrylate) was prepared by macromonomer technique and radical copolymerization. The amphoteric polymer has both of strong hydrophobic and hydrophilic properties. The synthesized polymer can be the good candidate for the main component of soil release agent. The emulsion properties and the surface conformation of the functional groups at the interface with the environment will be report in future.
6. Acknowledgment

This work is supported financially by the Korea Ministry of Science and Technology under the International Cowork Program.

References
4. Dae-Hwan Jung, In Jun Park, Young Kook Choi, Soo-Bok Lee, Hyung Sang Park, and Juergen Ruche, 

![Diagram](image)

Fig 1. Schematic diagram for Fluorine-Containing amphoteric Poly(acrylate)s synthesis.

![Diagram](image)

Fig 2. Schematic diagram for novel structure of amphoteric polymer
Fig 3. $^1$H-NMR spectrum of F-macromer.

Fig 4. DSC of F-macromer.

Fig 5. IR trace of F-macromer, p(2-DMAEMA) and Amphoteric polymer.