Preparation of Fluoroacrylate Nanocopolymer by Miniemulsion Polymerization Used in Textile Finishing

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ABSTRACT: Latex based on fluoroacrylate (TAN) and other comonomers was prepared via miniemulsion polymerization in the presence of stearyl trimethyl ammonium chloride (STAC) and 2, 2′-azobis (2-amidinopropane) dihydrochloride (ABAP) as a water soluble initiator. Light transmittance studies demonstrated that the light transmittance of prepared emulsions increases with the amount of TAN, STAC, cosolvent DPM, and hydrophobe DM. Given suitable reaction temperature and quantities of TAN, STAC, DPM, and DM, a copolymer emulsion of fluoroacylate with a particle size of 50 nm was produced. The water repellency tested on polyester fabrics displayed greater effectiveness than that of commercial products with higher fluorine content. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1466–1472, 2004

Key words: fluoroacrylate; nanocopolymer; miniemulsion; light transmittance; hydrophobe; water repellency

INTRODUCTION

Fluorine-containing copolymers are prepared by emulsion polymerization to produce latex with fluorinated surfaces to reduce surface free energy on numerous systems.[1–8] The incorporation of perfluoro alkyl moieties (-$(CF_2)_nF$) into organic polymers significantly changes the properties of polymeric materials, such as wettability. The equation describing surface tension was given by Young,[9]

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}$$

where γ_L, γ_S, and γ_{SL} refer to interfacial tension at liquid/air interface (γ_L), solid/air interface (γ_S), and solid/liquid (γ_{SL}) interfaces, respectively. θ denotes the contact angle of a liquid droplet resting on the solid surface. Fluorochemical surfaces, due to their low surface free energy (tension), yield a large contact angle in commonly available materials. The successful application of perfluoro alkyl-containing polymers in thermostable materials coatings has been reported.[10,11] Fluorine-containing coatings make textile, paper, and leather surfaces water, oil, and soil repellent because of the markedly reduced surface tension.

In the textile industry, many fabrics have been commercially treated with fluorine-containing polymers that were manufactured through emulsion polymerization. Due to the high price of fluorinated acrylate, water repellent fabric is quite expensive. This work aims to prepare a nanoparticle of fluorine-containing copolymer emulsion.[12] Due to the higher surface area of nanoparticles compared to traditional 300 nm particles of fluoroacrylate copolymer, the nanoemulsion is expected to have better water repellency. Given the same water repellency, lower dosage and lower cost can be achieved using nanoemulsion of perfluoroacrylate copolymer.

EXPERIMENTAL

Materials

All chemicals were used as received without purification. Perfluoro-octyl ethyl acrylate (TAN) was supplied by Du Pont Inc., 3-chloro-2-hydroxy-propyl methacrylate (Topolene M) and cyclohexyl methacrylate (CHMA) by Shin-Nakamura Chemical CO., Ltd. (Wakayama, Japan), 2,2′-azo bis(2-amidinopropane) dihydrochloride (ABAP) by Nippoh Chemical, Ltd., dodecyl mercaptan (DM) by Pennwalt Chemical Ltd., and stearyl trimethyl ammonium chloride (STAC) by Kao Corp. (Taipei, R.O.C.) Double deionized water (DDI water) was used for all experiments.

Three different kinds of fabrics were used for the water repellency test: nylon (Nylon 6), woven polyester, and raised polyester. Raised polyester has been widely used in the textile industry for garment and sports wear. The surface fibers on polyester were raised by the peach skin finishing technique, that is, brushing or sanding to achieve a special silk hand feeling. The raised polyester after water repellent

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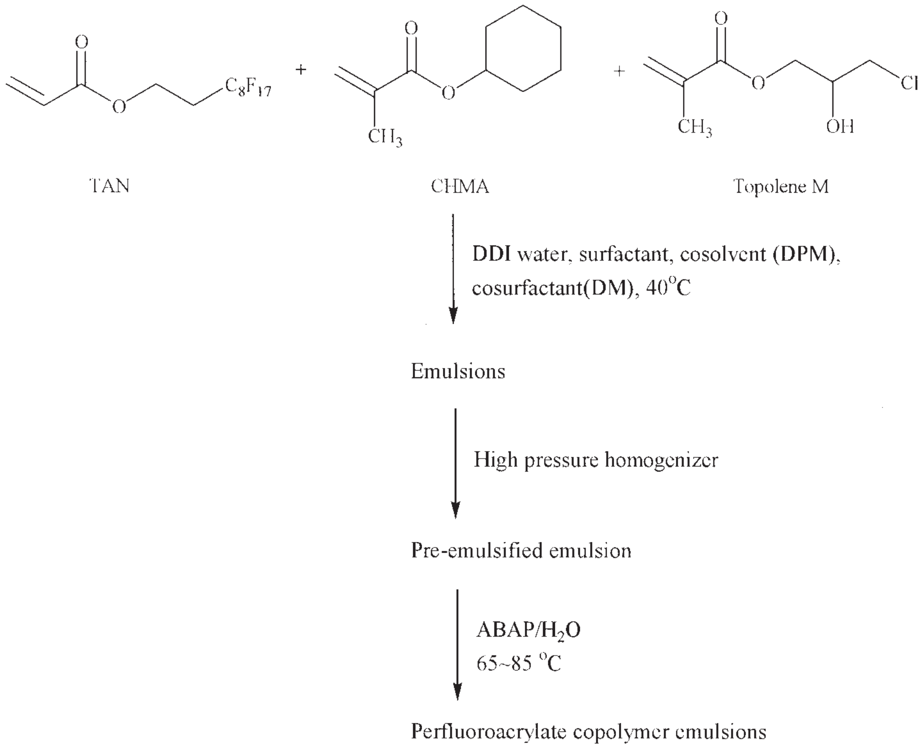

Scheme I Preparation of perfluoroacrylate copolymer emulsions.

treatment is an important material for high grade sports wear.

Preparation of perfluoroacrylate copolymer emulsions

Scheme I illustrates a typical procedure for perfluoroacrylate copolymer emulsions:

The emulsion polymerization was performed as follows: an appropriate amount of premelted TAN, CHMA, Topolene M, DDI water, surfactant, cosolvent (DPM), and cosurfactant (DM), were added into a 500 c.c. beaker and heated to 40°C under magnetic stirring. The amount of water added was varied to maintain a constant total solution weight. After 30 min, the emulsified solution was passed through a high pressure homogenizer twice under 200 kg/cm^2 pressure. The homogenized solution comprised of the pre-emulsified solution was thus obtained, and then transferred to a four-neck flask fitted with a mechanical stirrer, thermometer, nitrogen inlet, and condenser under N_2 purging. The reaction temperature was raised to 75°C, and 0.6 g of ABAP and 10 g of DDI water were added to the solution and stirred vigorously. Subsequently, the mixture was polymerized at 75°C for 12 h. The emulsion thus obtained was cooled to 30°C before being poured out.

Characterization

Conversion

The conversion of the reaction was analyzed using a gas chromatograph (Varian star 3400CX) packed with a capillary column of DB-1. The prepared emulsion then was delivered to the column via injection.

Light transmittance

Analysis was performed using a Shimadzu UV-160A with a light wavelength of 600 nm. The synthesized emulsion was tested to obtain the light transmittance. Five readings were taken from each sample, and the mean values are reported.

Contact angle

For contact angle measurement, the emulsion was coated onto a glass plate pretreated by drying at room temperature for 16 h followed by drying at 110°C for 4 h, and then was analyzed with a Face contact angle meter (CA-D from Kyowa Interface Science Co., Ltd.).

Particle size

The particle size was measured using a light scattering instrument (Malvern Zetasizer 3000HS). All measure-

TABLE I
Correlation Between Particle Size and Light Transmittance

Light transmittance (%)	Particle size (nm)
40.4	44.4
31.3	55.7
27	60.8
17.7	97.3
5	146.3
0.3	280.0

ments were carried out at Chung-Shan Institute of Science and Technology, Taiwan.

Molecular weight

The molecular weight of the prepared polymer was determined by gel permeation chromatography (GPC) using a Waters 410 Instrument. HPLC-grade tetrahydrofuran (THF) served as the eluent.

Water repellency

The water repellency was assessed by the spray test of the American Association of Textile Chemists and Colorists (AATCC) test method 22–2001. Five readings were taken from each sample, and the mean values are reported.

Homogenizer

The mixed emulsion was twice passed through a high pressure homogenizer (Rannie and Gaulin Homogenizers APV 1000) at 200 kg/cm^2.

RESULTS AND DISCUSSION

The particle size of the polymer emulsions is determined by many factors, including cosolvent, surfactant, cosurfactant, and reaction temperature. The first part of this work examines the influence of these factors on the particle size by comparing the light transmittance of their corresponding emulsions. The water repellencies of these emulsions when applied to a textile were evaluated and compared.

Correlation between light transmittance and particle size

Nanoparticle size is known to correlate strongly with light transmittance. Greater light transmittance of the emulsions indicates smaller size of the nanoparticles contained. Table I lists the correlation between particle size and light transmittance. As expected, the analytical results indicate a good correlation between light transmittance and particle size. Notably, the particles are nano-sized when the light transmittance exceeds 17.7%.

Light transmittance of the emulsions with different cosolvents

Due to the low hydrophilicity and high density of TAN (specific gravity of 1.6 at 40°C), the polymer emulsion of fluorinated acrylate is unstable. The stability of polymer emulsion can be enhanced by adding cosolvent. Moreover, the incorporation of cosolvent also reduces the particle size of the emulsion.[13,14] Linemann et al.[13] have conducted some research using acetone as a cosolvent in the emulsion polymerization of fluorinated acrylate. Their findings suggest that higher emulsion stability and smaller particle size from emulsion polymerization can be achieved by adding cosolvent. This work examined the effect of various cosolvents on the system of perfluoroacrylate copolymer emulsion by measuring the light transmittance of the emulsions. Table II shows the light transmittance of the emulsions prepared with different cosolvents. All the emulsions listed in Table II were prepared under the conditions as described below the table. The measurement results show that dipropylene glycol monomethyl ether (DPM) gives maximum light transmittance of 38.3%. Similar results are also obtained by using 3-methoxy butanol and hexylene glycol, which are more expensive than DPM. Obviously, those cosolvents with higher light transmittance solu-

TABLE II
Light Transmittance of the Emulsions Prepared with Different Cosolvents

Test no.	Cosolvent	Light transmittance (%) λ = 600nm
101	Acetone	32.5
102	Amyl alcohol	4.9
103	3-Methoxy 3-methyl butanol	36.8
104	Hexyl alcohol	11.2
105	Butyl alcohol	9.2
106	Dipropylene glycol	28.5
107	2-Ethyl hexanol	1.0
108	Dipropylene glycol monomethyl ether (DPM)	38.3
109	Ethylene glycol	23.0
110	Hexylene glycol	37.0
111	Propylene glycol	27.0
112	1,4-Butane diol	26.4
113	Dipropylene glycol monomethyl ether acetate	32.5
114	Diethylene glycol monobutyl ether acetate	27.0
115	Diacetone alcohol	30.4
116	None	20.8

Pre-emulsion : TAN 16 g, CHMA 20 g, Topolene M 4 g, DDI water 346.9 g, STAC 2.8 g, DM 0.3 g, cosolvent 10 g, total weight of pre-emulsion solution : 400 g.

TABLE III
Light Transmittance of the Emulsions Prepared with Different Amounts of Cosolvent DPM

Test no.	DPM (% to monomer)	Light transmittance (%)
117	0	20.8
118	25	29.7
119	50	38.4
120	75	41.8

Pre-emulsion : TAN 16 g, CHMA 20 g, Topolene M 4 g, STAC 2.8 g, DM 0.3 g, DPM : 0 (117), 10 g (118), 20 g (119), 30 g (120), DDI water is varied to keep the total weight 400 g.

bilize the monomer and reduce the droplet size of micelle more than cosolvents with lower light transmittance. The smaller droplet size of a micelle then yields smaller particles in the polymer emulsion.[13,15] Note that some of the cosolvents, such as amyl alcohol, butyl alcohol, and 2-ethyl alcohol, give lower light transmittance than those prepared without cosolvents. Moreover, the monohydroxyl alcohols, due to their poor ability to solubilize the monomer and decrease the droplet size of micelle, give lower light transmittance than those without cosolvent.

Light transmittance of the emulsions with different amounts of cosolvent (DPM)

Besides the cosolvent type, the quantity of cosolvent used also affects emulsion particle size. The effect of cosolvent quantity was further studied using the best cosolvent identified in the previous section, DPM. Table III shows the light transmittance of the emulsions prepared with different amounts of cosolvent DPM. Clearly, the light transmittances of emulsions increase with the amount of cosolvent DPM. The cosolvent DPM solubilizes the monomer, and also decreases the micelle size, resulting in the higher light transmittance. The particle size of the polymer emulsion is related to the micelle droplet size. Katharina et al.[15] found that the minidroplet growth is slower than the polymerization rate, and a situation closely approximating a 1 : 1 copying of the monomer droplets to polymer particles occurred, freezing the critically stabilized state in the miniemulsion polymerization. The identical size, before and after polymerization, was also confirmed by SANS (Small Angle Neutron Scattering) measurement.[16] These studies generally concluded that decreasing the micelle droplet size is an important factor in preparing smaller particle polymer emulsion. Note, however, that an alternative explanation is that the increase in light transmittance with cosolvent concentration does not result from the smaller particle size but rather results from a more diluted emulsion.

Light transmittance of the emulsions with different amounts of cationic surfactant (STAC)

The cationic type of surfactant is the most important factor among hundreds of different surfactants that have been used to produce fluoroacrylate emulsion.[17,18] Because of the high density and hydrophobic property of fluoroacrylate, the use of suitable surfactants is important for maintaining emulsion stability. Especially, stearyl trimethyl ammonium chloride (STAC), due to its high emulsification efficiency, provided a cationic surfactant with excellent emulsion stability in this work. No precipitation was noted on the glass reactor following reaction. The emulsion is fairly stable and exhibits a precipitation free shelf life exceeding one month. On the other hand, the combination of STAC with nonionic surfactants or the use of other surfactants (such as ethoxylated lauryl alcohol) caused precipitation upon emulsion preparation.

Table IV lists the correlation of light transmittance of the emulsions prepared using different STAC content. The higher STAC content produces emulsions with higher light transmittance. The miniemulsion droplets size is controlled via the quantity of surfactant relative to the monomer.[19] The lower surfactant concentration in the aqueous phase of a miniemulsion eliminates micelle nucleation. The probability of particle nucleation by direct oligoradical entry into monomer droplets is related to particle nucleation by homogeneous and micelle nucleation.

Light transmittance of the emulsions containing different ratios of cationic/nonionic surfactants

Some commercial products have combined cationic and nonionic surfactants in preparing perfluoroacrylate copolymer emulsion.[20,21] Such a combination is claimed to achieve improved water repellency. This work uses a nonionic surfactant (ethoxylated oleyl alcohol) in combination with cationic surfactant (STAC) to prepare fluoroacrylate copolymers. Table V reveals that the emulsion prepared using more non-

TABLE IV
Light Transmittance of the Emulsion Prepared with Different Amount of STAC

Test no.	STAC (% to monomer)	Light transmittance (%)
121	3.5	11.5
122	5.6	31.3
123	7.0	37.4
124	8.4	42.3
125	10.2	50.7

Pre-emulsion: TAN 16 g, CHMA 20 g, Topolene M 4 g, DM 0.3 g, DPM 10 g, STAC 1.4 g (121), 2.24 g (122), 2.8 g (123), 3.36 g (124) 4.08 g (125), DDI water is varied to keep the total weight: 400 g.

TABLE V
Light Transmittance of the Emulsions Prepared with Different Ratio of Cationic/Nonionic Emulsifiers

Test no.	STAC/EOA	Light transmittance (%)
140	3/0	38.4
141	2/1	22.6
142	1/2	8.6

EOA: Ethoxylated oleyl alcohol (nonionic emulsifier) Pre-emulsion : TAN 16 g, CHMA 20 g, Topolene M 4g, DM 0.3 g, DPM 10 g, DDI water 347 g, STAC/EOA : 2.7 g/0 g (140) 1.8 g/0.9 g (141), 0.9 g/1.8 g (142), total weight 400 g.

TABLE VII
Light Transmittance of the Emulsions Prepared with Different Amounts of Dodecyl Mercaptan (DM)

Test no.	DM (% to monomer)	Light transmittance (%)	M.W ($\times 10^4$)
130	0	20.3	30
131	0.75	38.2	11.4
132	1.5	38.4	3.5
133	2.25	40.3	3

Pre-emulsion : TAN 16 g, CHMA 20 g, Topolene M 4 g, DPM 10 g, STAC 2.8 g, DM : 0 g (130), 0.3 g (131), 0.6 g (132), 1.0 g (133), DDI water is varied to keep total weight: 400 g.

ionic emulsifiers produces lower light transmittance. Significant variation in particle size can be achieved by varying the amount and type of surfactant.[14] Owing to their lower efficiency, nonionic surfactants have lower emulsion stability than the ionic surfactant. This difference occurs because a considerably higher weight fraction of nonionic surfactant is required to obtain similar particles to those produced using ionic surfactants.[15] The results of the present experiments demonstrated that substitution of cationic surfactant with a nonionic surfactant increased the particle size of the emulsion due to the lower efficiency of the nonionic surfactant. Similar results have also been reported by Bechthold et al.[17]

Light transmittance of different amounts of fluoroacrylate (TAN)

This section presents the results from applying three different monomers: TAN, CHMA, and Topolene M as listed in Table VI. Higher percentage of fluoroacrylate (TAN) is known to produce lower surface energy, thus improving the water repellency of the treated fabric, even given higher material costs. In this study on the increase in TAN dosage, the light transmittance of emulsion also increases. Emulsification, leading to decreased micelle droplet size, is easily achieved by increasing TAN percentage.

TABLE VI
Light Transmittance of the Emulsions Prepared with Different Amounts of Fluoroacrylate (TAN)

Test no.	TAN (% to monomer)	Light transmittance (%)
126	30	28.5
127	40	38.4
128	50	40.2
129	60	44.4

Pre-emulsion : Topolene M 4 g, DM 0.3 g, DPM 10 g, STAC 2.8 g, DDI water 346.9 g, TAN/CHMA : 12 g/24 g (126), 16 g/20 g (127), 20 g/16 g (128), 24 g/12 g (129), total weight 400 g.

Light transmittance of the emulsion with different amounts of cosurfactant (DM)

Droplets in homogeneous miniemulsions must be prepared using high shear devices, for example, ultrasonication or high pressure homogenizers, to obtain smaller droplets with equal Laplace pressure or smaller than osmotic pressure following homogenization. Dodecyl mercaptan (DM) serves as a chain transferring reagent and hydrophobe (cosurfactant) of the miniemulsion.[15]

Following the homogenization, minidroplets are quite unstable and can be further grown by Ostwald ripening[22] or collisions. The suppression of both processes is needed to formulate a stable miniemulsion. The addition of cosurfactant (hydrophobe) can suppress the Ostwald ripening effect and obtain a stable miniemulsion. From Table VII, a big difference in light transmittance exists between No. 130 and No. 131. Adding the hydrophobe gives a stable miniemulsion with smaller particle size. Increasing the quantity of cosurfactant does not significantly increase the light transmittance, consistent with the general conclusion in the study of Katharina.[15] The molecular weight (MW), measured by GPC, showed that DM addition remarkably decreases the MW due to its chain transfer effect. Therefore, the reduced emulsions light transmittance on DM addition may also be explained by the decrease of MW and hydrophobe effect.

Light transmittance of the emulsions with different reaction temperatures

In many polymer emulsion systems, temperature is crucial for conversion and other phenomena. Three different temperatures were used in this study. Table VIII reveals that the light transmittance of the emulsions prepared at 65°C is lower than for those prepared at 75°C or 85°C. Moreover, gas chromatography analysis shows that the conversion averages over 99% despite no direct correlation between temperature and conversion being apparent. The higher light transmittance and smaller micelle droplets observed at higher

TABLE VIII
Light Transmittance of the Emulsion Prepared with Different Reaction Temperatures

Test no.	Reaction temperature (°C)	Light transmittance (%)	Conversion (%)
137	65	38.3	99.01
138	75	48.2	99.03
139	85	49.8	99.08

Pre-emulsion : TAN 16 g, CHMA 20 g, Topolene M 4 g, DM 0.3 g, DPM 10 g, STAC 2.8 g, DDI water 346.9 g, total weight 400 g.

temperature may result from the easy solubilization of the monomer.

Water repellency of our products on nylon and polyester fabrics

The above results can be used to derive the optimal conditions for emulsion preparation. To examine the water repellency of the emulsions when applied to textiles, some samples were prepared using various recipes (Table IX). The products developed here were also compared with commercial products: A (Jintexguard FEN) and B (Jintexguard FPC). The water repellency tests were conducted on nylon, woven polyester, and raised polyesters. The samples were prepared by padding 2% test emulsions in water, following by drying and curing at 170°C for 2 min. The water repellency test results met the AATCC standard method, and the results are listed in Table X. Several conclusions can be derived from the results shown in Tables IX and X:

1. Increasing the percentage of fluorine in the emulsion is associated with higher contact angle and better water repellency on nylon (Nos. 145, 146, and 147).

TABLE IX
Light Transmittance of the Emulsions Prepared with Different Combinations

Test no.	TAN (%)	DPM (%)	DM (%)	STAC (%)/ EOA (%)	Light transmittance
143	40	50	1.5	7/0	38.4
144	40	70	1.5	7/0	39.1
145	30	70	1.5	4.9/2.1	28.0
146	40	70	1.5	4.9/2.1	32.6
147	50	70	1.5	4.9/2.1	37.1
A	40	—	—	—	0.3
B	50	—	—	—	0.3

A (Jintexguard FEN) and B (Jintexguard FPC) are commercial samples for comparison. TAN, DPM, DM, and STAC/EOA percentage are based on total weight of monomer.

TABLE X
Water Repellency Test Results

Test no.	Contact angle of water	Water repellency on nylon	Water repellency on polyester (woven)	Water repellency on polyester (raised)
143	112	80^+	80^+	90^+
144	115	90^-	90	90^+
145	108	80^-	80^+	80
146	112	80	80^+	80^+
147	113	80^+	90	80^+
A	90	90^-	80	70
B	112	90	90^-	90^-

2. Increasing the quantity of DPM is associated with higher contact angle and better water repellency on nylon and woven polyester (Nos. 143 and 144).
3. With the same fluorine content but different surfactant, cationic surfactant produces better contact angle and water repellency on three fabrics (Nos. 144 and 146).
4. Comparing No. 144 with commercial products A and B reveals that No. 144 has higher contact angle and higher water repellency on two kinds of polyester fabrics, but has slightly lower water repellency on nylon. Notably, the water repellency of No. 144 on polyester is even better than that of commercial product B, which possesses higher fluorine content. Thus, a lower dosage of No. 144 is required than of product A to achieve the same performance, thus reducing finishing costs.

CONCLUSIONS

Miniemulsion polymerization in the presence of cosolvent and cationic emulsifiers such as STAC affords stable and nano-sized latex of fluoroacrylate copolymer. Many factors influence the particle size of the miniemulsion. This work reaches the following conclusions:

- Good correlation exists between particle size and light transmittance of the emulsion, with particle size decreasing with increasing light transmittance.
- Some of the cosolvents, such as DPM, 3-methoxy 3-methyl butanol, and hexylene glycol, reduce the particle size of the emulsion.
- Emulsion with smaller particle sizes can be obtained with increasing amount of cosolvent DPM.
- Emulsion with smaller particle sizes can be obtained with increasing amount of emulsifier STAC.

- Emulsion with smaller particle sizes can be obtained with increasing amount of TAN (fluorinated acrylate).
- Emulsion with smaller particle sizes can be obtained using a small amount of hydrophobe DM.
- Emulsions with even a smaller particle size can be obtained at a reaction temperature exceeding 75°C.
- The use of a combination of nonionic emulsifiers with STAC reduces light transmittance. The emulsion particle size increases with the amount of nonionic emulsifiers used.
- With a suitable combination of monomer, surfactant, cosolvent, and hydrophobe, a stable nanosized miniemulsion (No. 144) with better water repellency than commercial products for use on polyesters can be obtained.

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