Synthesis of Fluorine-Containing Acrylate Copolymer and Application as Resins on Dyed Polyester Microfiber Fabric

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Received 16 May 2007; accepted 1 October 2007
DOI 10.1002/app.27723
Published online 29 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The two resins of fluorine-containing acrylate are synthesized by atom transfer radical polymerization. The raw materials used are hexafluorobutyl mathacrylate and dodecafluoroheptyl methacrylate. The FTIR, ^{1}HNMR, and ^{19}FNMR are used to characterize copolymer structures. The application as resins on dyed polyester microfiber fabric is investigated. Shade darkening effect of the resins is discussed by color yield (K/S), rates of the color yield increase (I%), and the color differences (ΔE). The polymers containing perfluorine groups have excellent shade darkening effect on dyed polyester microfiber fabric. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1778–1782, 2008

Key words: fluoropolymers; resins; synthesis; thin film

INTRODUCTION

Many properties of a material are dependent on the surface structure and the chemical composition of the outermost surface layer.[1–5] Fluorinated polymer are well known as low surface energy materials, which have been proposed for coating of substrates such as textiles, papers, leather, wood, etc.[6,7] On the other hand, the polymers containing perfluorocarbon groups have low index of reflectance. The materials of low index reflectance have wide application in the color fields.[8,9] The polyester microfibers have very large fiber surface because of the fiber of linear density of less than 1 dtex.[10,11] The physical and mechanical properties of these various microfibers are quite different from those of conventional fibers.[12] It is difficult that the polyester microfiber fabrics are deeply dyed because of light reflection. In our recent works, the silicone polymer modified with amino and hydroxy groups has been synthesized. The modified polyorganosiloxane has shade darkening effect on dyed microfiber polyester fabric. The polymers containing perfluorocarbon groups may have lower index of reflectance than the polyorganosiloxane. The polymers containing perfluorocarbon groups as resins have been used to polyester fabrics. The resins could form thin film of low reflectance index on dyed microfiber polyester fabric.

In this article, the two resins of fluorine-containing acrylate were synthesized. The raw materials used were hexafluorobutyl mathacrylate and dodecafluoroheptyl methacrylate. The IR, ^{1}HNMR, and ^{19}FNMR were used to characterize copolymer structures. Shade darkening effect of the resins and the colorimetric data of dyed microfiber were also discussed.

EXPERIMENTAL

Materials

The hexafluorobutyl mathacrylate and dodecafluoroheptyl methacrylate were obtained from Xuegia Fluorine-silicone Chemical Plant, Haerbin, China. The butyl acrylate and cationic surfactant 1831 were obtained from Shanghai Handa Chemical Company, Shanghai, China. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

Disperse Yellow *S*-4RL (CI Disperse Yellow 30) and Disperse Red GS (CI Disperse Red 153) were obtained from Zhejiang Jihua Dyestuff Chemical Company, Hangzhou, China. Disperse Blue 2BLN (CI Disperse Blue 56) were obtained from Zhejiang Longsheng Group, Shangyu, China. Scoured polyester microfiber fabrics (warp: 75 dtex/24 F, weft: 77 dtex/300 F) were obtained from Zhejiang Jinqiu Textile Company, Shaoxing, China.

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TABLE I
Some Properties of the Copolymers

Polymers	Appearance	Polymer content (%)	Viscosity (cp)	Surface energy (mN/m)
HB	Translucent emulsion	20	2399.0	28.61
DB	Translucent emulsion	20	1795.2	31.72

Polymerization and characterization of fluorine-containing polymer

Polymerization of hexafluorobutyl mathacrylate

The cationic surfactant 1831 10 g was first dissolved in the 150 mL of water. The hexafluorobutyl mathacrylate 20 g and butyl acrylate 20 g were added in the emulsion and sufficiently mixed with stirring at room temperature. 0.05 g $(NH_4)_2S_2O_8$ were used as the initiator. The reaction mixture was stirred for 8 h under a nitrogen atmosphere at 85°C. The mixture was cooled to room temperature. The product was a stable aqueous latex dispersion of the acrylate ester. The polymer was called HB. The solid polymer for characterization could be recovered by coagulating with methanol. The solid polymer obtained was washed by methanol and finally dried *in vacuo* before measurements.

Polymerization of dodecafluoroheptyl methacrylate

The polymer of dodecafluoroheptyl methacrylate was synthesized in the manner described earlier for the polymerization of hexafluorobutyl mathacrylate. The polymer was called DB. The solid polymer for characterization could be recovered by coagulating with methanol.

Measurements of FTIR, ^{19}FNMR ^{1}HNMR, and surface tension

The IR was recorded on a Nexus-670 (Nicolet, Boston, MA). The ^{19}FNMR and ^{1}HNMR spectra were recorded on a Bruker AV 400 (Bruker, Faellanden, Switzerland). The surface tensions of the polymers were determined using DCA322 Surface Tension Meter (Therno Cahn).

Dyeing

The dyeing solutions were prepared by using 3% (owf) of dyes based on weight of fabric. The fabrics were dyed in an IR dyeing machine (PYROTEC-2000), the liquor ratio being 1 : 10. Fabrics were immersed in the dye bath at room temperature, and the temperature was increased to 130°C at a rate of 1°C/min. Dyeing was carried out at this temperature for 60 min. After dyeing, the dyed samples were treated for 15 min in 0.5 g/L sodium hydrosulfite and 1.0 g/L sodium carbonate solution at 75°C. Then, all the samples were rinsed with water until the rinsing water was clear and dried.

After treatment

The dyed samples were padded with the solutions of certain concentration polymers to give 80% wet pick-up. The dry temperature and time were 95°C and 3 min, respectively. The cure temperature was 180°C, and cure time was 1 min. To compare, the dyed samples without polymer were cured under the same conditions.

Color yield analysis

The color yield (K/S) of the dyed fabric was determined by Datacolor SP600^{+} spectrophotometer. The tristimulus values of dyed samples were measured in the visible region of the spectrum 360–700 nm.

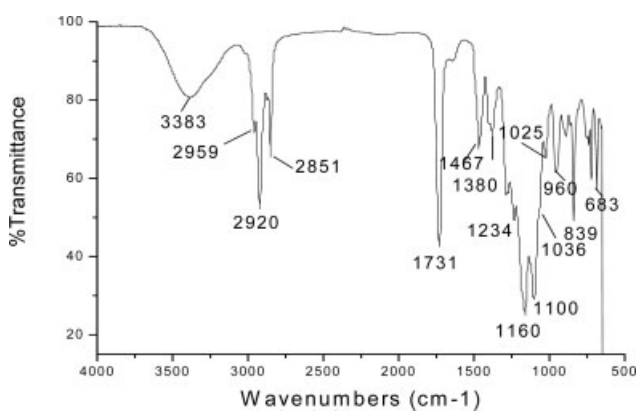

Figure 1 FTIR spectrum of polymer HB.

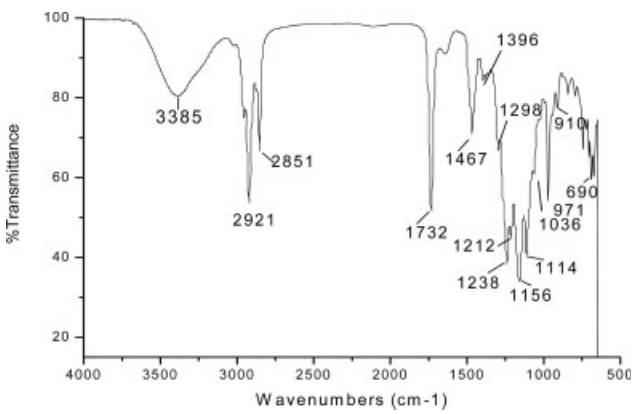

Figure 2 FTIR spectrum of polymer DB.

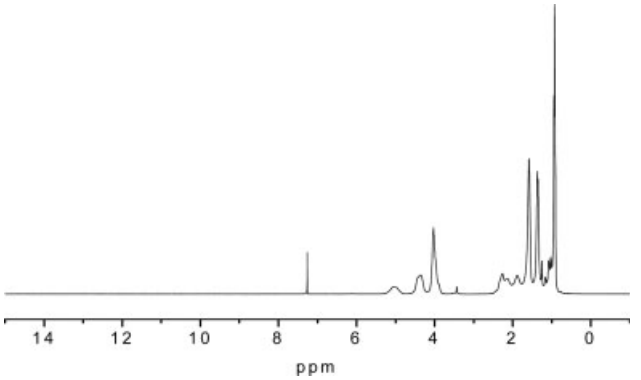

Figure 3 ^{1}HNMR spectrum of polymer HB.

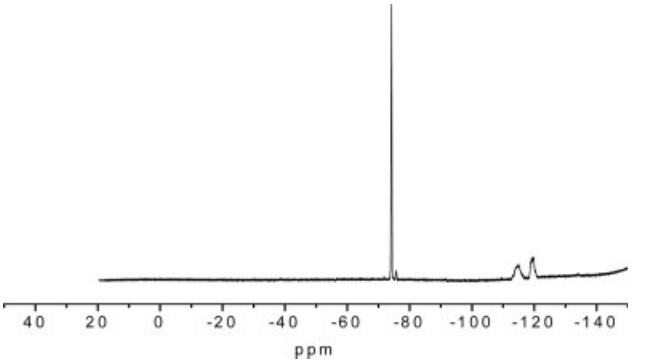

Figure 5 ^{19}FNMR spectrum of polymer HB.

The reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of dyed fabrics by the Kubelka–Munk Equation. The color differences (ΔE) were calculated using the measured values of CIELAB [eq. (1)].

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (1)$$

where ΔL, Δa, and Δb are the difference in the color parameters after and before treat with the polymer.

The color yield increase ($\Delta K/S$) and the rates of the color yield increase ($I\%$) were calculated using eqs. (2) and (3), respectively.

$$\Delta K/S = (K/S)_1 - (K/S)_0 \quad (2)$$

$$I\% = \left[\frac{\Delta(K/S)}{(K/S)_0}\right] \quad (3)$$

where $(K/S)_1$ and $(K/S)_0$ represent K/S of dyed fabrics after and before treat with polymer, respectively.

RESULTS AND DISCUSSION

Synthesis of fluorine-containing polymer

The polymers containing perfluorocarbon have many specific properties by virtue of its good water repellency, lubricity, high flexibility, excellent thermal stability, and low reflecance index. To keep high flexibility of fabrics treated with the polymer resin, the raw materials used were hexafluorobutyl mathacrylate and dodecafluoroheptyl methacrylate, respectively. Polymerizations of fluoromonomer and butyl acrylate are shown in Scheme 1. Some properties of the copolymers are given in Table I. The surface tensions of the polymers show that HB and DB had high surface activity because of fluorocarbon groups. The IR spectra of samples HB and DB see Figures 1 and 2, respectively. In the FTIR spectra, the sharp bands at 1160 cm^{-1} and 1156 cm^{-1} are the typical signal of C—F group.

NMR spectra of polymers

The ^{1}HNMR spectra of polymers HB and DB are given in Figures 3 and 4, respectively. In Figure 3, signal for —CFH— is found at 7.26 ppm. The proton peaks COO—CH_2—CF_2— appear at 4.97–5.50. The signals for —CH_2— and CH_3— are found at 4.02–4.41 and 0.87–1.16, respectively. The proton peaks of the polymer DB are similar to the polymer HB. The ^{19}FNMR spectra of polymers HB and DB are shown in Figures 5 and 6, respectively. The ^{19}F signals for —CF_3 and —CF_2— are found at −74.21 and −119.83 ppm

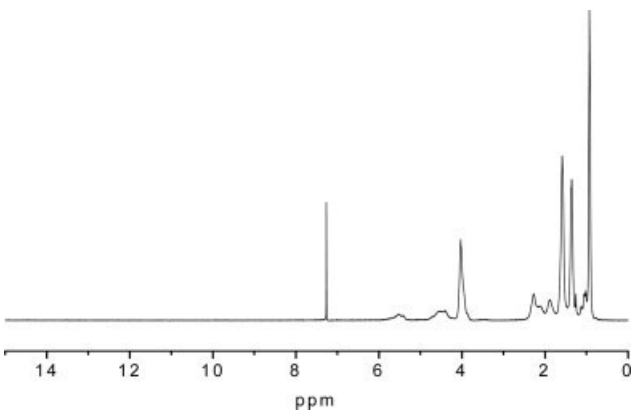

Figure 4 ^{1}HNMR spectrum of polymer DB.

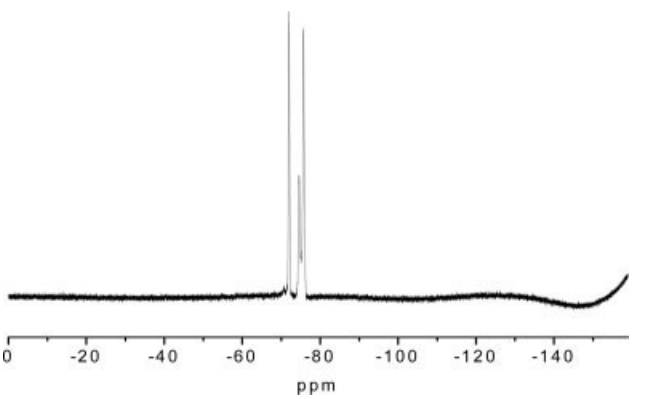

Figure 6 ^{19}FNMR spectrum of polymer DB.

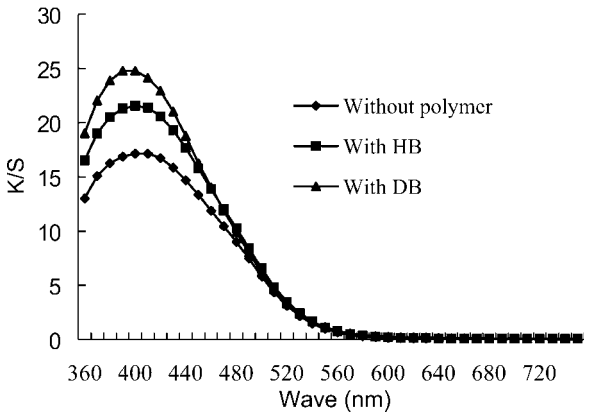

Figure 7 K/*S* curves of yellow fabric before and after treat with the polymers.

in the Figure 5. ^{19}FNMR spectrum of the polymer DB shows that signals for —CF_3 (—$CH(CF_3)_2$ and —CF_2CF_3) appear at −74.57 to −75.72. The signal for —CF_2 is found at −71.98 ppm.

Surface shade darkening effect of perfluoropolymers HB and DB on the dyed microfiber fabric

To investigate the surface shade darkening effect of polymers containing fluorocarbon groups, Disperse Yellow *S*-4RL, Disperse Red GS, and Disperse Blue 2BLN were used for the fabric. The dyed samples were padded with the solutions of polymers HB and DB, respectively. The *K/S* curves of dyed fabric before and after treat with the polymers are shown in Figures 7–9. It is clear that the color yields (*K/S*) of dyed fabric treated had significant increase using all three disperse dyes in the visible region of the spectrum. Compared with the sample with HB, the dyed fabrics treated with DB showed a noticeable depth shade. It shows that the polymer of dodecafluoroheptyl methacrylate had better shade darkening effect on dyed polyester microfiber fabric than

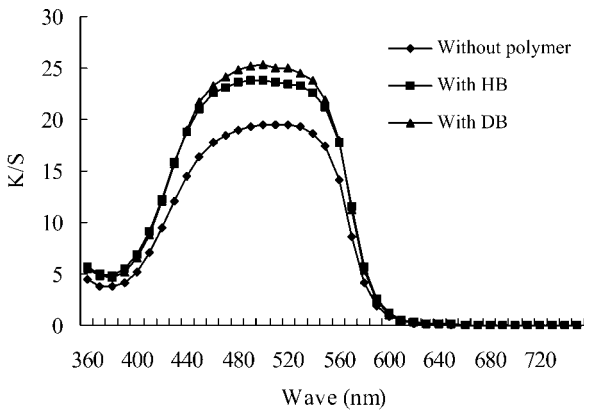

Figure 8 K/*S* curves of red fabric before and after treat with the polymers.

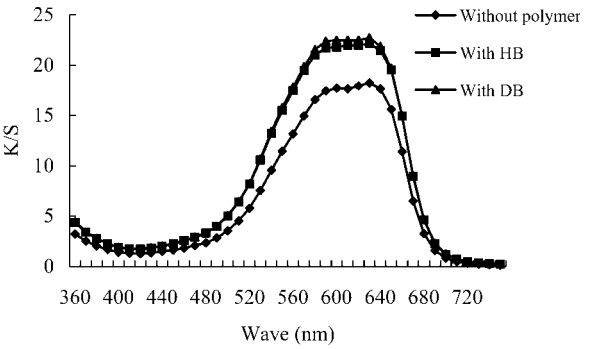

Figure 9 K/*S* curves of blue fabric before and after treat with the polymers.

the polymer of hexafluorobutyl mathacrylate as resin.

Colorimetric data of the dyed fabrics

The colorimetric data of the dyed fabric was important parameters. The color parameters *L*, *a*, *b*, were calculated by the tristimulus values *X*, *Y*, and *Z*. *L* refers to brightness–darkness, with values from 100 to 0 representing white to black. The *a* values run from negative (green) to positive (red). The *b* values run from negative (blue) to positive (yellow).

Colorimetric data of dyed fabric before and after treat with polymers are summarized in Tables II–IV, respectively. The results in Table II–IV show that *K/S* values of all dyed fabrics remarkably increased after treated with the polymers. The rates of the color yield increase (*I*%) of all dyed samples with three dyes after treated with polymer exceeded 20%. *L* values of dyed fabrics show that all *L* values decreased after dyed fabrics were treated with the polymers HB and DB. This means that the color of dyed fabric became dark. The results show that the resins of the polymer containing perfluorine groups had excellent shade darkening effect on dyed polyester microfiber

TABLE II
Colorimetric Data of Dyed Yellow Fabric

	L	*a*	*b*	*K/S*	Δ*K/S*	*I*%	Δ*E*
Without polymer	62.39	31.73	67.29	17.13			
With HB	58.18	28.9	66.51	21.56	4.43	25.90	2.94
With DB	57.87	28.15	65.61	24.78	7.65	44.68	5.1

TABLE III
Colorimetric Data of Dyed Red Fabric

	L	*a*	*b*	*K/S*	Δ*K/S*	*I*%	Δ*E*
Without polymer	36.60	54.98	33.71	19.42			
With HB	37.05	55.60	34.52	23.88	4.46	22.95	1.44
With DB	36.89	55.90	33.95	25.34	5.32	26.58	1.77

TABLE IV
Colorimetric Data of Dyed Blue Fabric

	L	*a*	*b*	*K/S*	Δ*K/S*	*I*%	Δ*E*
Without polymer	26.62	8.09	−36.90	18.23			
With HB	24.75	7.78	−36.66	22.14	3.91	21.44	2.6
With DB	24.28	7.46	−35.31	22.71	4.46	24.47	2.20

fabric. The color differences (Δ*E*) increased after dyed samples were treated with the HB and DB.

CONCLUSIONS

The two polymers containing perfluorocarbon were synthesized by atom transfer radical polymerization. FTIR and ^{1}HNMR and ^{19}FNMR spectroscopy provided information regarding structure, conformation of the polymers. The two copolymers were used as resins on the dyed microfiber fabrics. The color yields (K/S) of dyed samples treated with the polymers had remarkable increase in the visible region of the spectrum. Colorimetric data of dyed fabric show that the polymer containing perfluorocarbon had excellent shade darkening effect on dyed polyester microfiber fabric. The polymer of DB had better shade darkening effect than HB.

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