Preparation of Macro-RAFT Copolymer and its Application in Pigment Dispersion for Inkjet Inks

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Abstract

By employing Reversible Addition-Fragmentation chain Transfer (RAFT)-controlled polymerization, amphipathic random copolymers were prepared. The hydrophobic monomer used was styrene (St), and hydrophilic one maleic anhydride (MA). The resulting copolymers were characterized by Fourier transform infrared spectroscopy (FT-IR). Molecular weight and distributions were determined using gel permeation chromatography (GPC). Macro-RAFT copolymers had the clear advantage of carrying living ends, which allow further chain extension via the addition of desired monomers at controlled rates.

With hydrophobic and hydrophilic units, the macro-RAFT copolymers have the potential ability to disperse pigment. Organic phthalocyanine blue pigment (P.B.15:3) was dispersed with the macro-RAFT copolymers by vigorously stirring and ultrasonic processing. The properties (particle size, polydispersity index) of pigment dispersions were measured. It was shown that the particle size and distribution (PDI) has relationship with ultrasonication time and the amounts of macro-RAFT copolymers. The results showed that the particle size and PDI of pigment dispersions dispersed with macro-RAFT copolymer were smaller than that of dispersed with sodium dodecyl sulfate (SDS).

Introduction

Textile inkjet printing has demonstrated super properties over the traditional printing methods because of its higher pattern resolution, little pollution, and rapid response to the frequent shift of cloth fashion. Pigmented water-based ink has much more superiority than dyed ink due to higher light and wash fastness, suitable for all kinds of fibers and fabrics, shorter printing procedure[1]. However, most of organic pigments with low polarity always tend to be aggregation or coagulation and were hard to be wetted and dispersed in aqueous media. The dispersant plays an important role in preparing pigment dispersion for inkjet inks.

Polymeric dispersants have proven to have good properties in stabilizing pigments in aqueous media. These polymers have hydrophobic chains, which would attach to organic pigment surface by Van Der Waals force, and hydrophilic chains, which would build a voluminous shell around particles and intensify the charges on the surface [2]. Recently, many works on the polymeric dispersants have been done, for examples diblock polymers[3] and graft polymers[4]. In our group, copolymers such as poly(Styrene-Maleic Anhydride), poly(Maleic anhydride-Methyl methacrylate) were synthesized as polymeric dispersants for organic pigment dispersion[5-7]. It was shown that hydrolyzate of PSMA can be used as effective polymeric dispersant for pigment dispersion. The pigment dispersion had small particle size and good stability, and suitable for preparing pigmented water-based inkjet inks.

As one of the controlled/living radical polymerizations (CLRP), reversible addition-fragmentation chain transfer (RAFT) polymerization has prominent advantages that include the good compatibility with a wide range of monomers and facile experimental conditions that are similar to conventional radical polymerization[8]. By employing RAFT-controlled polymerization, random copolymers can be readily prepared. Moreover, the macro-RAFT copolymers thus synthesized have the advantage of carrying living ends, which allow further chain extension via addition of desired monomers at controlled rate[9].

In present work, macro-RAFT copolymers of styrene and maleic anhydride were prepared by employing reversible addition-fragmentation chain transfer controlled polymerization. The copolymers were characterized by FT-IR and GPC analysis. The application of macro-RAFT copolymers for pigment dispersion preparation was evaluated.

Experimental

Reagents

Water was distilled and deionized before use. The organic phthalocyanine blue pigment (P.B.15:3, Figure 1), a gift from Changzhou North American Chemical Group, was used as supplied. Carbon disulfide, 1-dodecanethiol, tetrabutyl ammonium bromide, hexane, acetone, 2-bromopropanoic acid, from Sinopharm Chemical Reagent Co., LtdS were used as received. The monomers styrene and maleic anhydride (Sinopharm Chemical Reagent Co., LtdS) were distilled under vacuum and kept refrigerated until use. The initiator 2, 2'-azobisisobutylo nitrile (AIBN) was purified by recrystallization from ethanol.

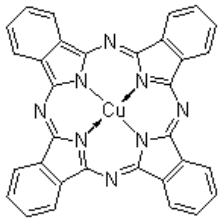

Figure 1. *Structure of organic phthalocyanine blue pigment.*

Synthesis of RFAT agent

The RAFT agent 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl} propanoic acid (Figure 3) was synthesized as follows[10]. A 40% NaOH solution (4.00 g, containing 1.60 g, 40 mmol of NaOH) was added to a stirred mixture of 1-dodecanethiol (8.08 g, 40 mmol) and water (60 mL). Then acetone (20 mL) and a tetrabutyl

ammonium bromide solution (6.4g, containing 1.28 g, 4 mmol of tetrabutyl ammonium bromide) was added, and the resulting clear solution was stirred for 30 min, then cooled to near room temperature and treated with carbon disulfide (3.42 g, 45 mmol) to give a clear orange solution. This was stirred for another 30 min, then cooled in an ice bath to an internal temperature of <10°C. 2-bromopropanoic acid (6.273 g, 41 mmol) was then added at a rate that the temperature did not exceed 30°C followed by 40% NaOH (4.1g, 410 mmol), also kept the temperature did not exceed 30°C. When the exotherm had stopped, the ice bath was removed and 60 mL water was added. The orange solution was stirred at ambient temperature for 24h, then diluted with water (20 mL) and stirred and cooled in an ice bath while HCl was added at a rate which kept the temperature <10°C. A yellow oil separated, and stirring of the mixture was continued until the oil solidified. The solid was collected by suction filtration, washed with cold water, and dried under reduced pressure. The crude sample was recrystallized from hexane with gentle stirring to give bright yellow microcrystals. IR (KBr): 2954.51, 2954.51, 2919.82, 2851.84, 1707.31, 1450.20, 1421.40, 1298.36, 1209.87, 1097.55, 1043.42, 980.40, 913.68, 825.59, 722.54, 649.94 cm^{-1} (Figure 2).

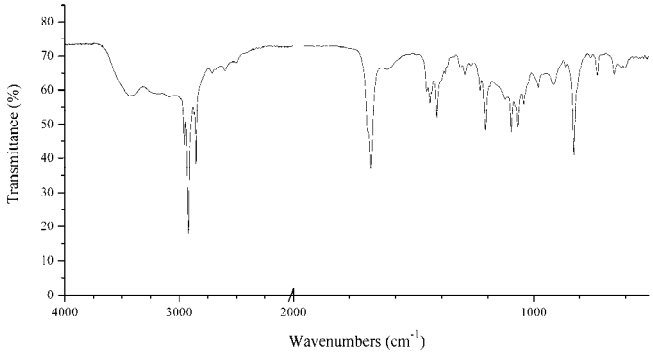

Figure 2. *FT-IR spectrum of RAFT agent*

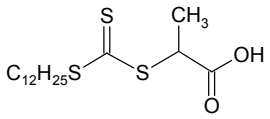

Figure 3. *Structure of RAFT agent 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl} propanoic acid*

Formation of macro-RAFT copolymers

The RAFT agents were reacted with styrene and maleic anhydride in the presence of initiator to give a macro-RAFT copolymer. A solution of RAFT agent (0.75g) and 2, 2'-azobisisobutyronitrile (0.15g), styrene (9.37g), and maleic anhydride (5.88g) was prepared in dioxane (50g) in a 250 mL round-bottomed flask. This was sparged with nitrogen for 10 min and stirred slightly. Then the flask was heated to 70°C and maintained for 5h under constant stirring. While the reaction solution was transferred to water, synthesized polymers were precipitated.

Pigment dispersion

Pigment dispersion was normally carried out by mechanical milling or ultrasonication. The aim of these process was to apply external force to break up pigment aggregates to small particles. During the dispersion process, dispersants adsorbed onto the surface of pigment particles to prevent particles agglomerating.

A solution containing macro-RAFT copolymer, water and sodium hydroxide was prepared in 50 mL beaker. To this solution P.B.15:3 was added, mixed and then dispersed with a JY98-3D Ultrasonic Pulverizer (Scientz company) at 800 W (1s pulse on/4s pulse off) for 10 min. During the ultrasonication process, the dispersion was cooled in a water bath.

Measurements

FT-IR spectra

Fourier transform infrared (FT-IR) spectra were recorded on a NICOLET NEXUS 470 spectrometer (Thermo Fisher Scientific Inc., America) with a DTGS detector. The dried samples mixed with KBr were compressed into a disc for FT-IR scanning. The measurement was performed with 32 runs scanning and the resolution of 2 cm^{-1}.

GPC analysis

Molecular weight and distributions were determined using gel permeation chromatography (GPC). Analyses were carried out using a Waters 1515 HPLC system fitted with a series of HP PLgel MIXED-C columns (3×10^{-6}L and 5×10^{-6}L). Molecular weight was determined from Waters 2414 refractive index data analyzed with Waters Breeze GPC software, with all molecular weights being relative to polystyrene standards.

Particle size and its distribution

The particle size was measured at 25°C using a Malvern Instrument NANO-ZS 90 at a fixed scattering angle of 90°. The dispersion was diluted with distilled water before measuring. Dynamic light scattering (DLS) measurements give a Z-average size, which is intensity mean of the particle diameter, and the polydispersity index (PDI), which provides information about the width of the particle size distribution.

Results and Discussion

Preparation of macro-RAFT copolymers

A trithiocarbonate RAFT agent with a dodecylsulfanyl Z group (Figure 3) was used to prepare macro-RAFT copolymers.

It was shown from figure 4 that styrene and maleic anhydride copolymerized by RAFT controlled polymerization. The wave numbers 1454cm^{-1}, 1495cm^{-1}, 1602cm^{-1} were in-plane stretching vibration of –C=C– in benzene; There were symmetric and asymmetric stretching vibration of C=O in wave numbers of 1778 and 1856cm^{-1}, and the absorption intensity of 1856cm^{-1} was weaker than that of 1778cm^{-1}, which was the remarkable characteristic of cyclic anhydrides (5 membered rings). It can be seen from these absorption bands that there were styrene and maleic anhydride units in synthesized copolymers.

It was proven from the FT-IR spectrum that styrene and maleic anhydride copolymerized according to RAFT controlled/ living radical polymerization using the trithiocarbonate RAFT agent. In FT-IR spectra, there were some differences of absorption intensity in some bands between macro-RAFT copolymer and PSMA (polystyrene-co-maleic anhydride). The relative absorption

intensities of macro-RAFT copolymer in wave numbers 2922cm^{-1} and 1778 cm^{-1} were much stronger than that of PSMA. The wave numbers 2922cm^{-1} and 1778 cm^{-1} were stretching vibrations of C-H in –CH_2– and C-O in -C=O, respectively. So, it was undoubtedly that the RAFT agent with dodecyl and carboxyl groups copolymerized with styrene and maleic anhydride according to RAFT controlled/living radical polymerization process.

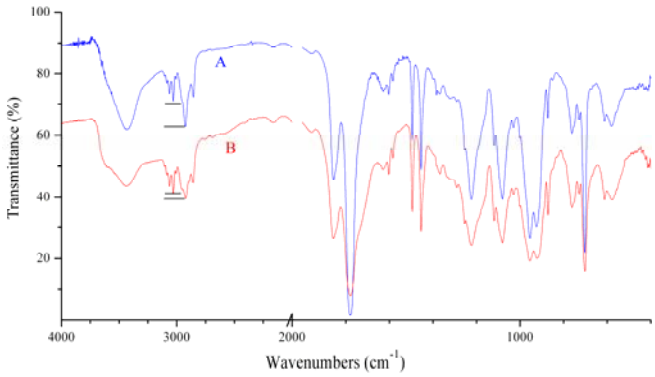

Figure 4. *FT-IR spectrum of polymers (A: macro-RAFT copolymer, B: PSMA)*

Table 1. Molecular weight and distributions of copolymers

RAFT (%)[a]	Mn	Mw	Polydispersity
0	152410	233339	1.50
1.0	75551	107029	1.42
2.5	60561	79693	1.32
5.0	42518	55134	1.30
7.5	33296	43010	1.29
10	18936	21806	1.15

[a] The amounts of RAFT agent were weight fraction relative to monomers.

The average molecular weight and its distributions (polydispersity) of copolymers were shown in table1. The average molecular weight and its distributions of macro-RAFT copolymers were smaller than that of PSMA. Furthermore, they decreased with the amount of RAFT agent increasing. The smaller distributions of molecular weight than that of traditional radical polymerizations showed the character of RAFT polymerizations.

From above analyses of FT-IR and molecular weight of copolymers, it can be concluded that in present of RAFT agent, styrene and maleic anhydride copolymerized according to reversible addition-fragmentation chain transfer controlled/living radical polymerization.

Pigment dispersion

Ultrasonication time

Pigment dispersed with hydrolyzed macro-RAFT copolymers was evaluated. There were styrene and maleic anhydride units in macro-RAFT copolymers. The styrene hydrophobic region especially the benzene can interact with organic pigment. The hydrophilic maleic acid or its salt hydrolyzed from maleic anhydride could provide the dispersion stability depending on steric and electrostatic repulsions.

The pigment dispersions were produced by ultrasonication of mixture of pigment, hydrolyzed macro-RAFT copolymers and water. Ultrasonic waves of high intensity ultrasound generate cavitations in liquids. The cavitations can be used in liquids for many processes, e.g. for mixing and blending, deagglomeration, milling and cell disintegration. In ultrasonication process, pigment aggregates were broken up to small particles because of ultrasonic cavitations. With time prolong, the particle size of pigment was smaller, and the particle size distribution (polydispersity index, PDI) decreased. With about 5min ultrasonication, the particle size almost did not change, and PDI increased slightly. Except of deagglomerztion, the effect of ultrasonic cavitation was to generate heat. With time prolong, the heat generation made the temperature of dispersions rising. In higher temperature, the smaller particles may interaction with each other, which made the particle size and PDI increased. Therefore, in the ultrasonic dispersing process, the temperature must be kept lower and too long process was not expected.

Table 2. Effect of ultrosonication time on pigment dispersion

Time (min)	Particle size (nm)	PDI
1	190.7	0.375
2	170.4	0.214
3	166.8	0.230
4	169.1	0.207
5	165.9	0.217
7	164.8	0.225
9	162.4	0.211

[a] St/MA=3:2(mol/mol), RAFT agent 7.5% (to monomer), AIBN 10% (to monomer), copolymer 10% (to pigment).

Amount of macro-RAFT copolymers

It revealed from table 3 that particle size of pigment dispersions reduced first and then increased, with increasing the amount of macro-RAFT copolymers. The variation of particle size distribution (PDI) was similar to that of particle size. The smaller particle size of pigment, the surface areas were larger, and also higher surface energy. The smaller particles were tending to interact to each other to decrease surface energy. Therefore, there were much more amounts of copolymers required to adsorb on the surface of particles preventing aggregations among particles.

However, too many amounts of copolymers were not desirable. When the amount of copolymers was too high, a part of copolymers would disperse in the water which could increase the viscosity of dispersion, thus led to lower dispersing efficiency. Moreover, copolymers dispersed in water might bridge two or more particles to large aggregates.

Table 3. Effect of amount of macro-RAFT copolymers on pigment dispersions

Copylymers (w %)[a]	Particle size(nm)	PDI
3	175.2	0.234
5	156.8	0.228
7	154.8	0.219
10	172.6	0.313
20	169.7	0.292

[a] The amounts of copolymers were weight fraction relative to pigment. Copolymers: St/MA=3:2(mol/mol), RAFT agent 2.5% (to monomer), AIBN 10% (to monomer).

Compared with traditional dispersant

In preparation of pigment dispersion, traditional dispersants were small molecule surfactants. But, the disperse efficiency of these surfactants was not effective compared with polymeric dispersants. Table 4 showed the particle size and PDI of pigment dispersions dispersed with synthesized copolymer and surfactant (SDS, sodium dodecyl sulfate). The particle size and PDI of pigment dispersion dispersed with macro-RAFT copolymer were smaller than that of dispersed with SDS. There were a lot of benzene rings in the copolymers, which could interact with hydrophobic surface of pigment particles. And, there were repulsions among the carboxyl and carboxylic ions in the chains, which made the small pigment particles stable. However, for the surfactant SDS there were less hydrophobic adsorption and ionic repulsion.

Table 4. Pigment dispersions dispersed with different dispersant

Dispersants	Particle size(nm)	PDI
copolymer[a]	170.3	0.251
SDS	228.7	0.381

[a] St/MA=3:2(mol/mol), AIBN 1%(w/w, to monomer), RAFT 7.5%(w/w, to monomer)

Conclusions

Macro-RAFT copolymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) controlled/living radical polymerization. The copolymers were characterized by FT-IR spectra and molecular weight analyses.

The macro-RAFT copolymers, with hydrophobic and hydrophilic units, have the potential ability to disperse pigment. Organic phthalocyanine blue pigment (P.B.15:3) was dispersed with them by vigorously stirring and ultrasonic processing. The properties of pigment dispersions (particle size, polydispersity index) were measured. It was shown that the particle size and distribution (PDI) has relationship with ultrasonication time and the amounts of macro-RAFT copolymers. With prolong of ultrasonication time the particle size and PDI reduced first and then increased slightly. When the amounts of copolymers were too low or high, the particle size and PDI were larger. The particle size and PDI of pigment dispersion dispersed with macro-RAFT copolymer were smaller than that of dispersed with sodium dodecyl sulfate (SDS).

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Author Biography

Professor K. J. Fang received his Ph.D. in textile chemistry from China Textile University (1993). His research interest recently focuses on the development of nano-scale pigment dispersions and pigment inks, and pretreatment process of fabrics for inkjet printing. He has published one book about and 90 papers on textile chemistry and eco-technologies of textiles.