Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 76 (2008) 173–178

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Nanocolorants: A novel class of colorants, the preparation and performance characterization

Zhenkun Hu, Minzhao Xue, Qing Zhang, Qiaorong Sheng, Yangang Liu*

School of Chemistry and Chemical Technology, Shanghai Jiaotong University, Shanghai 200240, PR China

Received 24 February 2006; received in revised form 21 April 2006; accepted 9 August 2006
Available online 10 October 2006

Abstract

Anthraquinone-based solvent red, yellow (or green), and blue dyes used as essential ingredients were completely dissolved in styrene miniemulsion system, and a set of nanocolorants were successfully prepared by using a modified miniemulsion polymerization process. In architecture, the obtained nanocolorants belong to a class of nanocomposite entities, in which a fraction of dye molecules are attached with crosslinked macromolecular chains and more dye being embedded in the interior of crosslinked polymer owed to the high hydrophobicity of dyes and phase separation between dye and polymer during the polymerization process. The performance characterization of the obtained nanocolorants indicated that they exhibited excellent chromatic properties attributed to the nanoscale effects of homogeneous nanocolorants, and really achieved superior migration fastness, light fastness, thermal stability, and good processibility. These nanocolorants are very applicable for aqueous ink-jet inks, color resistance, high-performance coloration for polymers, and for electrophotographic toners.

Keywords: Nanocolorants; Modified miniemulsion polymerization; Anthraquinone-based solvent dyes; Performance characterization; Ink-jet inks; Color resists

1. Introduction

In recent years, because of the rapid popularization of digital camera and increasing utility of non-impact digital printers, the market demand for color ink-jet inks and color toners were emerging in multitude [1]. Simultaneously the market expansion of liquid crystal displays (LCDs) made color filter (CF), used as the key part of LCDs, to greatly go up, in which color resists were the crucial material for fabrication of RGB color layer [2]. However, up to now the preparation and application of color ink-jet inks and color resists are still in a dilemma whether to choose dyestuff or organic pigment. As for ink-jet inks, the water-soluble dye-based inks exhibited poor durability, e.g., poor light stability, weak water resistance and insufficient thermal stability, whereas the pigment-based inks had defects like poor image gloss, duller color brilliance, and especially the high cost derived from traditional physical submicronization of pigment particle [3]. And for color resists, which are prepared by the prevailing pigment dispersed method at present still had some drawbacks, e.g., imperfect color saturation and contrast, and the same high cost resulted from submicronization of pigment particle like pigmented inks [2]. Those earlier prepared by dyeing method were too short in life-time due to the poor high-temperature stability and light fastness of the used dyes, but could obtain more excellent color saturation, contrast, and larger color gamut than other methods [2].

Nanocolorants were regarded as a new class of colorants which could get out of dilemma between dyestuffs and organic pigments [3–6]. In nature nanocolorants are a class of nanocomposites which recombine dye acted as an essential ingredient and suitable polymeric matrix, and its performance target is to integrate excellent chromatic properties and good processibility of dyestuffs and good durability of organic pigments. Early two

---

* Corresponding author. Tel.: +86 21 54743270; fax: +86 21 54745602.
E-mail address: ygliu@sjtu.edu.cn (Y. Liu).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.08.026

approaches were briefly reported to prepare nanocolorants. Barashkov and Liu packaged the water-soluble fluorescent dye into submicron polymer particle by a conventional emulsion polymerization, which was called dye-packaging technology (DPT) [3], and Boehm and co-workers prepared the colorants applied for coloration of plastics, cosmetics, etc. via miniemulsion polymerization [4,5]. But the particle homogeneity [6], light fastness, high-temperature stability, and migration fastness of their products were still suspectable. It was well known that miniemulsion polymerization can provide many advantages for the preparation of nanoparticles [7−11]. In a highly stable miniemulsion system, the nucleation of polymerization can only take place in the monodispersive minidroplets which contained the dispersed inorganic or dissolved organic essential ingredients for the nanohybrid formation, which makes the situation very close to a 1:1 copying procedure of minidroplets to nanoparticles; thus the minidroplets really acted as the independent nanoreactors. Recently Takasu et al. prepared nanosized colored latex by miniemulsion polymerization [12,13], and the colored lattices with polyurea shell were prepared by applying interfacial polycondensation reaction to the miniemulsion polymerization process [14].

In this paper, a modified miniemulsion polymerization process was reported to prepare a set of nanocolorants based on the architecture which we originally designed as follows, and the practical performances of the obtained nanocolorants were well characterized. Because the dyes incorporated into the nanocolorants combined with the polymer by non-covalent interaction, in order to realize the performance target of nanocolorants, several key issues must be solved, i.e., how to realize the homogeneity of nanoscale particle for generating sufficient color brilliance and depth, how to achieve the recombinational integrity between dye and polymer to obtain superior migration fastness and thermal stability, and how to really obtain satisfying photostability. First of all, it was crucial to select optimum dyestuffs. The basic requirements of dyes to be suitable for the introduction into minidroplets are high hydropobicity, high solubility in monomer, large absorption coefficient, and small radical transfer coefficient [12]. In this case highly hydrophobic anthraquinone-based solvent dyes were used, so the used dyes themselves just acted as good hydrophobes to prevent the minidroplets from Ostwald ripening [15]. The amount of hydrophobic dyes dissolved in styrene played an important role in the phase separation between polymer and dye during the polymerization process [16]. For the small dye loading, the intermolecular interaction of dyes is weak due to the relatively large intermolecular distance, thus it is difficult to obtain complete phase separation. As a result, the dye molecule is likely to be, respectively, having affinity to macromolecular chains. Along with the increasing amount of dye, the enhanced intermolecular interaction of dye and hydrophobicity facilitate the phase separation. Thereby, besides a fraction of dye being affinitied with polymeric chains, the more dye forms the separated dye-phase and tends to embed in the polymeric core, finally to be encapsulated by the outer polymer.

Secondly, to achieve integrated morphology of nanocolorants and to promote the preserving fastness of dye in polymeric matrix, on the basis of water-insoluble nonpolar styrene, it is very important to introduce a proper amount of polar monomers. In this case, we introduced polar methyl methacrylate (MMA) and polar glycol dimethacrylate (GDMA) which also acted as a crosslinker. Due to the incomplete surfactant molecules coverage for minidroplets [17], the polar monomers in minidroplets tend to concentrate in oil/water interface region because of their higher hydrophilicity and in order to further lower the interfacial energy, simultaneously the high hydrophobic dyes were impelled into the inner region of minidroplet. Accordingly, it facilitated the crosslinked polar polymer to mainly locate on the outer layer of nanoparticle and made the dye to embed in the interior of nanoparticle during the polymerization process; also the nanocolorant particles obtained a modified polarity and surface property at last. In addition, to enhance the preserving fastness of dye in polymeric matrix as well as the heat-durability of matrix polymer, the moderate crosslinking density for polymer is indispensable. Because the crosslinking can lead the more compact polymeric exterior and greatly reduce the free volume of the polymer, the dye molecular migration from polymeric matrix will be sharply controlled. In addition to GDMA being used as crosslinker, a proper amount of divinylbenzene (DVB) was added.

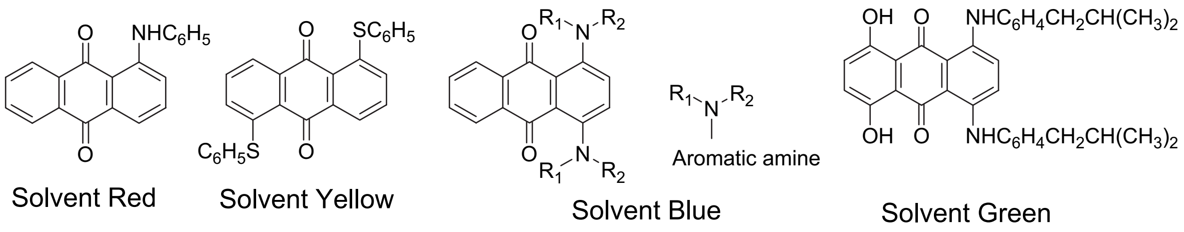
Finally, to really ensure the enhancement of light stability of both matrix polymer and dye, we introduced the well compatible light stabilizer into minidroplets, especially the introduction of copolymerizable light stabilizer, e.g., reactive hindered amine light stabilizer (r-HALS) into the system, which is supposed to make nanocolorants to structurally achieve photostability [13,18,19].

2. Experimental section

2.1. Preparation of nanocolorants

Anthraquinone-based solvent red, yellow, blue and green dyes (technical grade, Aolunda Co. Ltd and Bayer Corp.) were used as the essential material, the molecular structure of which are shown in Scheme 1.

The deionized water (50 g) solution of sodium dodecyl sulfate (SDS, analytical grade, based on water 20 mM) and sodium bicarbonate ($NaHCO_3$, analytical grade) was added to styrene (10 g) solution comprising 1.5 g MMA, 1.0 g DVB and GDMA (technical grade, Shanghai Chemistry Reagent Co.), 0.8−2.0 g completely dissolved dyes, 0.15 g predissolved polystyrene ($M_w = 50{,}000$, Shanghai Chemistry Reagent Co.), and reactive light stabilizer (HALS-13, Clariant Corp.), and then quickly stirred at room temperature for 20 min. The resultant macroemulsion was miniemulsified with an ultrasonic homogenizer (ZhiSun Instrument Co., JYD-650), operated at 400−500 W for 15 min under ice cooling, and finally obtained a miniemulsion. The miniemulsion was transferred into a flask equipped with an agitator, a thermometer, a reflux condenser, and a nitrogen tube. The system was purged with nitrogen for 10 min and heated to 60 °C under nitrogen flow, simultaneously stirring by paddle stirrer at



Scheme 1. Molecular structure of the used dyes.

200 rpm. The reaction was initiated by the injection of a water solution of potassium persulfate (KPS) at 60 °C, and then kept polymerization at 65 °C for 4 h. The polymerization conversion was determined by a gas chromatography (GC, FULI Analytical Instrument Co., GC9790), until no monomer could be detected.

2.2. Analysis and performance characterization

Samples dispersed in deionized water were transferred to copper grids and left to dry for transmission electron microscopy (TEM, JEOL JEM-2010) and field emission TEM (JEOL JEM-2100F). Samples properly diluted in high-purity water were studied with a photon correlation spectrum (PCS, Malvern Zetasizer 3000HSA) to obtain the particle size and size distribution. UV–vis absorption was studied using a UV–vis spectrometer (Lambda-20, Perkin Elmer). For the thermogravimetric analysis, the used apparatus was a TGA-7 from Perkin Elmer. The ζ potential was measured using a Zetasizer Nano ZS (Malvern Instruments), and the samples were prepared by the same procedure as those of PCS.

2.2.1. Preparation of color films on paper and light fastness test

The dyes predissolved in a proper amount of ethanol and then blended with transparent water-varnish to obtain coating system with 0.3 wt% dye content, whereas the nanocolorant (dye/polymer = 0.8, 1.2, 1.5 g/12.5 g represented loading of red, yellow, and blue dyes, respectively) dispersions were directly blended with the same varnish to obtain coating system with the same dye content based on total recipe. Finally the color films with definite thickness were prepared by coating the coating systems on the printing paper using a Bar-coater and then dried. The color films were irradiated by a Xenon lamp for 120 h under the condition, i.e., 30,000 lux light illumination, 6 ± 1 cm distance between samples and light source, 60 °C, and 50% relative humidity. Before and after light irradiation, the color difference (ΔE) of each sample was directly obtained by a benchtop colorimeter (HunterLab Co., ColorQuest® XE).

2.2.2. Preparation of colored PS sheets and migration fastness test

The nanocolorants treated by spray drying and corresponding dyes (0.2 part of each dye vs 1.8 parts of each nanocolorant) were added into 50 parts polystyrene (PS, $M_w = 280{,}000$ g/mol) bulk, and uniformly mixed at 175 °C by Hakke Rheocord System (Rheocorel 90), and then the mixtures were pressed to sheets of 1 cm thickness by using compression moulding machine at 190 °C. The colored PS sheet of 1.0 g was put in the 30 ml capped sample bottle poured with 15 ml absolute ethyl alcohol, and placed in 70 °C calorstat for 60 h. The obtained solution was drawn for UV–vis absorption analysis which can evaluate migration fastness of nanocolorants.

3. Results and discussion

3.1. Analysis by TEM and PCS

Typical TEM images obtained demonstrated that the morphology of nanocolorants is homogeneous spherical nanoparticle with a uniform surface, as shown in Fig. 1. Under the

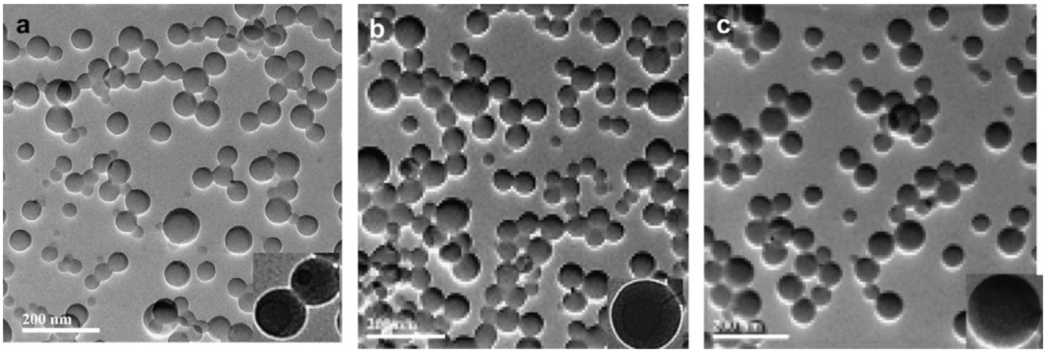


Fig. 1. TEM images of nanocolorants: (a) red, (b) yellow, (c) blue nanocolorant (scale bar 200 nm). Insets: enlarged images by field emission TEM image. Dye/polymer = 0.9, 1.2, 1.5 g/12.5 g represented loading of red, yellow, and blue dyes, respectively.

condition of enough dye loading, the phase separation between polymer and dye would generate the polymerization process. By field emission TEM it could be shown that the separated dye-phase, i.e., the darker domain was embedded in the cross-linked polymer matrix.

By using photon correlation spectra (PCS), we could exactly obtain the particle size and size distribution of nanocolorants. As shown in Fig. 2, the average particle size was below 100 nm which is identical with TEM result, and the polydispersity index (PDI) indicated that the size distributions of nanocolorants are unimodal. However, the PDI of red nanocolorant (dye/polymer = 1.0 g/12.5 g) was relatively wide, which resulted from the poorer solubility of Solvent Red in styrene. The saturated concentration of Solvent Red dissolved in 10 g styrene was 1.0 g, so some dye aggregate would be expelled out from the polymeric matrix due to the dye/polymer phase separation in the polymerization process, which led the PDI to increase.

3.2. UV–vis absorption spectra of nanocolorants

UV–vis absorption spectra were obtained from the dried nanocolorants dispersed in absolute ethanol (0.2 mg/ml) and corresponding dyes dissolved in absolute ethanol (0.05 mg/ml which do not lead to dye molecular stacking) by using absolute ethanol as reference solvent. When compared with the maximum absorption wavelength (λ_{max}) of corresponding dye, λ_{max} of each nanocolorant showed a bit of bathochromic shift as shown in Fig. 3, i.e., λ_{max} 514 nm of red nanocolorant vs λ_{max} 508 nm of dye, λ_{max} 459 nm of yellow nanocolorant vs λ_{max} 447 nm of dye, λ_{max} 631 nm and 585 nm of blue nanocolorant vs λ_{max} 627 nm and 581 nm of dye. Because the anthraquinone-base of dye is a big π-conjugated planar structure, which generates intermolecular π–π interaction and lead to molecular stacking [20]. Therefore, we concluded that the separated dye-phase embedded in polymeric matrix will similarly form molecular stacking, which resulted in the bathochromic shift of λ_{max} [20].

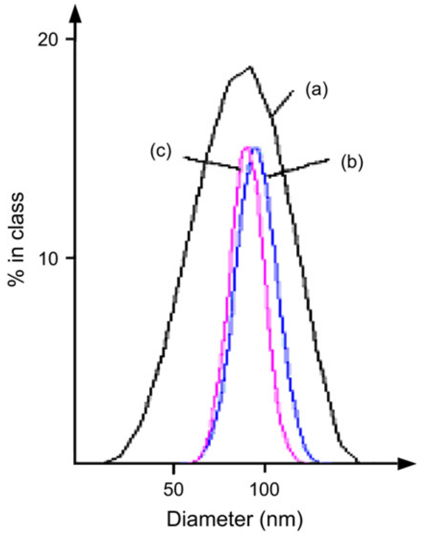


Fig. 2. The size distributions of nanocolorants from PCS: (a) red nanocolorant, Z_{Ave} 82.2 nm, PDI 0.136; (b) yellow nanocolorant, Z_{Ave} 90.8 nm, PDI 0.0243; (c) blue nanocolorant, Z_{Ave} 86.2 nm, PDI 0.0175. Dye/polymer = 1.0, 1.2, 1.5 g/12.5 g represented loading of red, yellow, and blue dyes, respectively.

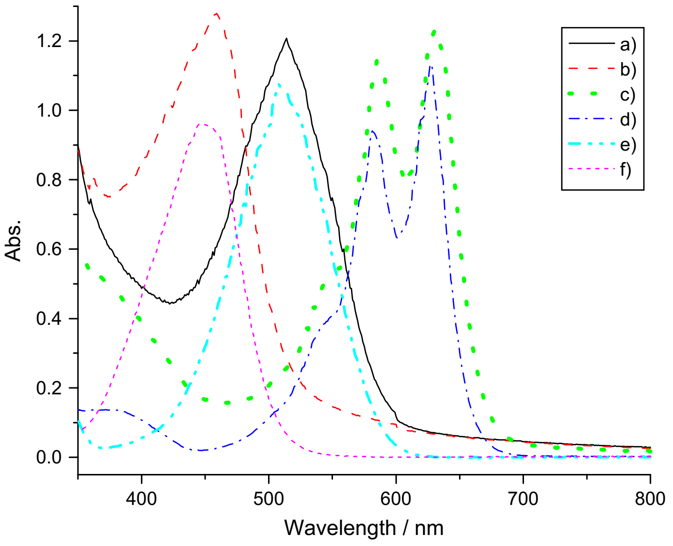


Fig. 3. UV–vis absorption spectra of: (a) red nanocolorant, (b) yellow nanocolorant, (c) blue nanocolorant, (d) blue dye, (e) red dye, and (f) yellow dye. Dye/polymer = 0.9, 1.2, 1.5 g/12.5 g represented loading of red, yellow, and blue dyes, respectively.

3.3. Nanocolorant aqueous dispersions' behavior

As shown in Table 1, each of the obtained nanocolorant aqueous dispersion demonstrated a high surface tension, very low rotary viscosity, high ζ potential and excellent storage stability. These characteristics are very desirable for aqueous ink-jet inks application.

3.4. Chromatic properties of nanocolorants

To test the chromatic properties of nanocolorants compared with dyes, the color films on paper prepared as described in Section 2 were photographed by a digital camera. The same dye-content nanocolorants (a, d, f) exhibited excellent color properties as seen in Fig. 4, which showed even brighter lightness and higher saturation than that of the corresponding dyes

Table 1
Characteristics of nanocolorant aqueous dispersions (dye/polymer = 0.9, 1.2, 1.5/12.5 g represented loading of red, yellow, and blue dyes, respectively)

Color sample	Surface tension (30 °C, mN/m)	Rotary viscosity (30 °C, cP)	ζ Potential (mV)	Storage stability
Red	54.1	1.1	−55.1	E
Yellow	54.3	1.0	−53.9	E
Blue	60.2	1.2	−57.8	E

Storage stability evaluated as E, i.e., dispersed very well without agglomerate, settled for 60 days at 30 °C.

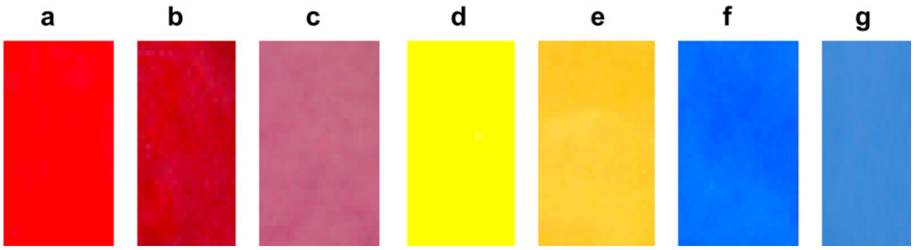


Fig. 4. Digital photographs of the color films prepared by using nanocolorants and corresponding dyes: (a) red nanocolorant, (b) red dye, (c) uncrosslinked red nanocolorant, (d) yellow nanocolorant, (e) yellow dye, (f) blue nanocolorant, and (g) blue dye.

(b, e, g). Herein, we considered that the dye incorporated into a nanocolorant particle performs the function similar to that of chromophore group in a dye molecule due to the nanoscale effects of homogeneous nanocolorants. Moreover, the smaller particle size, the stronger color depth owing to its descending light reflection index. But the uncrosslinked colorant showed a weak color depth and dull saturation as in Fig. 4 (c) due to the dye migration from the polymeric matrix as well as the formation of some agglomerates in which mixed dye migrated from polymeric matrix with latex particles. Therefore, we could achieve equivalent or slightly higher color saturation and lightness by using lower loading of relatively expensive dyes.

3.5. Migration fastness of nanocolorants

We specially designed an experiment as described in Section 2 to evaluate the migration fastness of nanocolorants, in which the both migration fastness of nanocolorant in PS media and preserving fastness of dye in polymeric matrix were included. When the concentration of dye in solution is low enough to obey Beer's Law, the lower UV–vis absorption peak indicates that the amount of colorant migrated out from the media is smaller. In Fig. 5, it is shown that the migration fastness of nanocolorants in PS media is markedly improved than that of the corresponding dyes, which just indirectly reflected that the preserving fastness of dye in polymeric matrix is superior. Whereas the uncrosslinked colorant exhibited a poorer migration fastness due to the inferior preserving fastness of dye in polymeric matrix.

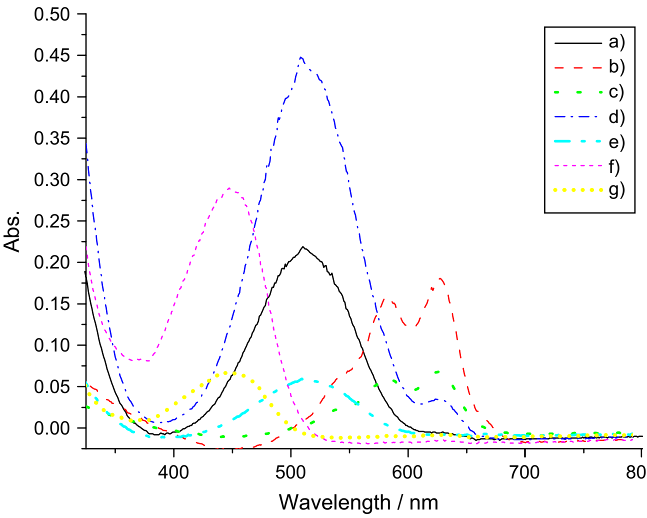


Fig. 5. UV–vis absorption spectra to evaluate the migration fastness of nanocolorants and corresponding dyes: (a) uncrosslinked red colorant, (b) blue dye, (c) blue nanocolorant, (d) red dye, (e) red nanocolorant, (f) yellow dye, and (g) yellow nanocolorant.

3.6. Light fastness of nanocolorants

The light fastness of the nanocolorants was evaluated by an irradiation experiment on color films as shown in Section 2, simultaneously compared with that of the corresponding dyes. The larger the ΔE, the weaker the light fastness of color sample [3].

As listed in Table 2, the light fastness of nanocolorants are much better than that of the corresponding dyes. The great enhancement of photostability was owed to the covalently bound light stabilizer and polymeric matrix which can insulate the ambient oxygen and other harmful chemicals.

3.7. Thermal behavior of nanocolorants

Through thermogravimetric analysis (TGA), the thermal behavior of nanocolorants could be obtained. Herein, we illustrated the thermal behavior of blue nanocolorant, which is quite similar to that of red, yellow and green nanocolorants. The space length of crosslinked macromolecular chains will increase as well as the affinity between dye molecule and macromolecule will weaken along with the increasing temperature. When the temperature rises to a certain extent, the dye molecule affinitied with macromolecular chain will first be broken away from the polymeric matrix. From Fig. 6, it could

Table 2
Light fastness of the films coated on printing paper using nanocolorants and the corresponding dyes

Color sample	ΔE
Red dye	10.04
Red nanocolorant	2.73
Yellow dye	3.83
Yellow nanocolorant	0.71
Blue dye	13.92
Blue nanocolorant	3.56

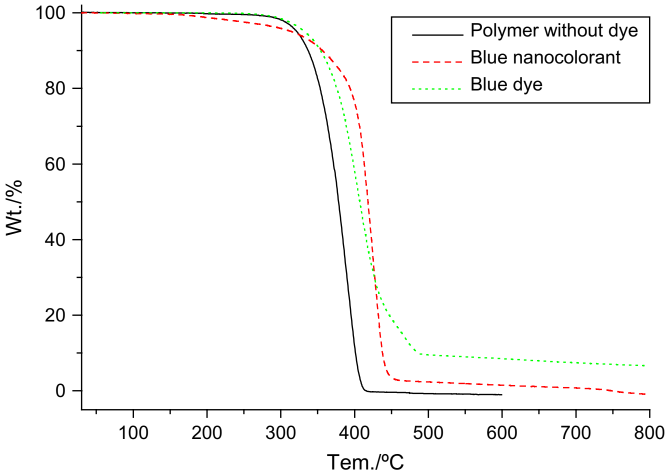


Fig. 6. TGA of the blue nanocolorant (dye/polymer = 1.5 g/12.5 g) and corresponding dyes operated at 15 °C/min.

be concluded that the starting temperature of dye disengaged from blue nanocolorant matrix is about 175 °C.

Along with the further increase of temperature, the clustered dye-phase embedded in interior of crosslinked polymer would also be gradually escaped and sublimated. Moreover, the heat resistance of nanocolorants can be more improved by optimizing the formulation of reaction system. Therefore, it was also indicated that the obtained nanocolorants have sufficient thermal stability for practical applications.

4. Conclusions

In conclusion, based on the architecture of nanocolorants that we originally designed, a set of red, yellow (or green), and blue nanocolorants with monodispersive particle size less than 100 nm were successfully prepared by using a modified miniemulsion polymerization process, which holds the advantages, such as facilitation and availability, low-cost, and environment-friendly, etc. The obtained nanocolorants exhibited excellent color saturation, lightness and strong color depth owed to the nanoscale effects of homogeneous nanocolorants. By dissolving primary color dyes in the minidroplet, the full-tone nanocolorants will be easily obtained according to additive color matching. They really achieved superior migration fastness, light fastness, thermal stability, and good processibility, and their aqueous dispersions can be easily made to high-quality color ink-jet inks, and be used in color resists. Furthermore, through spray drying and simple post-treatment they will be turned to ultrafine color toners suitable for electrophotographic process and for high-performance coloration of polymers. Accordingly we suggest that the structural concept of nanocolorant should be applied to develop some advanced optoelectronic functional materials, e.g., electronic inks for electrophoretic display [21], light-stable solid laser dyes [22], etc.

Acknowledgments

We are grateful to Dr. Yanfei Liu in Ciba Specialty Chemicals for helpful discussions, and thank for the help of TEM Laboratory of Instrumental Analysis Center in Shanghai Jiaotong University.

References

[1] Biry S, Sieber W. In: Final program and proceedings of IS and T's NIP20: international conference on digital printing technologies. Salt Lake City, UT, United States; 2004. p. 763–8.
[2] Sabnis RW. Displays 1999;20:119.
[3] Barashkov NN, Liu RH. In: International conference on digital printing technologies 2001. Fort Lauderdale, United States; 2001. p. 878–80.
[4] Clemens T, Boehm AJ, Sabine KB. In: The San Francisco meeting, Polymer Preprints, Division of Polymer Chemistry, vol. 41(1), San Francisco, CA, USA; 2000. p. 24–5.
[5] Boehm AJ, Alban G, Koch O. In: The 61st annual technical conference (ANTEC 2003), vol. 2. Nashville, TN, United States; 2003. p. 2419–22.
[6] Boehm AJ, Sabine KB, Peter R. Prog Colloid Polym Sci 1999;113:121.
[7] Landfester K. Top Curr Chem 2003;227:75.
[8] Landfester K. Adv Mater 2001;13:765.
[9] Landfester K, Montenegro R, Scherf U, Guntner R, Asawapirom U, Patil S, et al. Adv Mater 2002;14:651.
[10] Tiarks F, Landfester K, Antonietti M. Langmuir 2001;17:908.
[11] Anderson CD, Sudol ED, El-Aasser MS. Macromolecules 2002;35:574.
[12] Takasu M, Shiroya T, Takeshita K, Sakamoto M, Kawaguchi H. Colloid Polym Sci 2003;282:119.
[13] Takasu M, Shiroya T, Takeshita K, Sakamoto M, Kawaguchi H. Colloid Polym Sci 2004;282:740.
[14] Takasu M, Kawaguchi H. Colloid Polym Sci 2005;283:805.
[15] Chern CS, Chen TJ, Liou YC. Polymer 1998;39:3767.
[16] Jang J, Oh JH. Adv Mater 2003;15:977.
[17] Landfester K. Macromol Rapid Commun 2001;22:896.
[18] Haacke G, Longordo E, Andrawes FF, Campbell BH. Prog Org Coat 1998;34:75.
[19] Liu XX, Yang JW, Chen YL. Polym Adv Technol 2002;13:247.
[20] Kim JH, Matsuoka M, Fukunishi K. Dyes Pigments 1998;40:21.
[21] Yu DG, An JH, Bae JY, Jung DJ, Kim S, Ahn SD, et al. Chem Mater 2004;16:4693.
[22] Kalogeras IM, Neagu ER, Vassilikou-Dova A. Macromolecules 2004;37:1042.