OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 8, No. 7-8, July – August 2014, p. 685 - 688

Polymer dispersions containing thermochromic system

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Present study refers to the analysis of the matrix polarity effect on polymer dispersions containing crystal violet lactone thermochromic complex. Thus, the synthesis by miniemulsion polymerization of blue colored latexes based on different monomer types using polyvinyl alcohol as colloid, was followed. The obtained coloured latexes were characterized and their thermochromic behavior was verified.

(Received December 22, 2013; accepted July 10, 2014)

Keywords: Dye, Polarity, Dispersions

1. Introduction

An important domain in polymer science is the preparation of polymer micro and nanoparticles in aqueous dispersion. Evidently, the principal motivation is driven by the environmental issues. The distinct aspect of monomer droplet nucleation permits miniemulsion polymerization to be a powerful tool to synthesize polymer nanocapsules with organic and inorganic compounds inside [1, 2]. Dye dispersion, drug delivery systems, catalysis are the most common areas of application of the obtained materials [3, 4, 5]. Thermochromic dyes which show reversible color change by temperature have been of great interest in textiles and smart coatings. Among dyes, organic complexes which change color within life-environment temperature range are increasingly important. These dyes found application in toys industry, temperature indicators for plastic and printing inks, for paints, etc. [6].

We aimed to prepare colored latexes with high dye content by miniemulsion polymerization. Present study uses a crystal violet lactone thermochromic complex which contains crystal violet lactone, bisphenol A and a fatty alcohol C14. The dissociation of the C-O bond in the lactone ring (in the presence of a proton donor) results in the formation of a crystal violet cation [6-13]. This process makes CVL suitable in photosensitive and thermochromic coatings [14-16].

In order to study the CVL influence on the polymer matrix, several monomers: styrene, butylacrylate, methylmetacrylate, vinyl acetate, acrylonitrile, were used. The final systems were characterized by Dynamic light scattering (DLS), contact angle and Electron Scanning Microscopy (ESEM) analyses.

2. Experimental

Materials

The monomers (styrene, butylacrylate, methylmetacrylate, vinylacetate, acrylonitrile), were purified by distillation under reduced pressure before use. Divinylbenzene (Aldrich) and benzoyl peroxide (Merck) were used as supplied. CVL complex was synthesized previously [17].

Distilled water was used as dispersion media.

Procedures

The latexes were obtained by using a three neck glass flask with round bottom, immersed in a thermostat ultrasonic bath. A reflux refrigerator, a mechanical stirrer and nitrogen degassing tube, were connected to the glass flask. Firstly, a dispersion of surfactant (1% polyvynilalcohol in water) in water was prepared. The dispersion was kept under temperature (60^oC) and nitrogen bubbling for 30 minutes. Secondly, the CVL complex was melted at 50^oC and then the mixture of monomer (styrene, butylacrylate, methylmetacrylate, vinylacetate, acrylonitrile and styrene-butylacrylate) + divinylbenzene + initiator (benzoyl peroxide), was added dropwise. Next, the system was added to the surfactant dispersion. The polymerization reaction was carried out at 70^oC under nitrogen, mechanical stirring and ultrasonication. After 5 hours the systems were cooled and the latexes were collected for analyses. A small amount of latexes were deposed on a polyethylene foil for water evaporation, which was done at room temperature for several days. Another amount of dispersed systems was collected in glass vials for stability evaluation. The thermochromic behavior was observed by deposing the latex on a glass tile.

Table 1. Samples number correlated with the reference monomer.

No.	Monomers	Blank sample	Colored Sample
1	Styrene	18	11
2	Butylacrylate	19	12
3	Methylmetacrylate	20	13
4	Vinylacetate	16	14
5	Acrylonitrile	17	15
6	Styrene-Butylacrylate	21	22

Measurements

Particles hydrodynamic diameters were determined by Dynamic Light Scattering (DLS) with Zetasizer Nano ZS, ZEN3600, produced by Malvern International Ltd. The samples were dispersed in water, ultrasonicated 10 min (ultrasound bath) and then analyzed (0.1 ml sample/25 ml water).

The diluted latex samples were cast on aluminum stubs and copper grids and were investigated by scanning electron microscopy (SEM-FEI Quanta 200).

Contact angles between the films and water were determined using a CAM 200 Contact Angle Tensiometer instrument from KSV Instruments equipped with a digital camera that was connected to a PC. Distilled water was used as the liquid for the contact angle measurements. The contact angles were calculated from drop images after the shape accentuation, radius and string reading were determined.

3. Results and discussion

Tetradecanol from the thermochromic complex is playing the hydrophobe role so we can state that a miniemulsion polymerization process takes place [18].

The final latexes were homogenous. Only PSt, P(St-BuA), PACN and PVAc gave blue colored liquid latexes but all the latexes when deposed produced blue colored films. An indirect method to prove the dye encapsulation and also the thermochromic behavior was to depose the latex on a glass tile, dry it and analyze it before and after exposing above the dye melting temperature (Fig. 1). When heating all the blue samples became white (Fig. 1, B), and when cooling the samples returned to the blue color (Fig. 1, C and D). Thus, all the dye-polymer films are thermochromic. If all the dye was encapsulated the polymer film remains blue after cooling, if not, the dye melts and flows at the bottom part of the glass tile, the film remaining colorless. From the pictures it can be observed that a small quantity of dye melts and flows at the bottom part of glass tile but still the remained film became blue when cooling (Fig. 1, C and D). Therefore, very probably, only a partial encapsulation was accomplished.

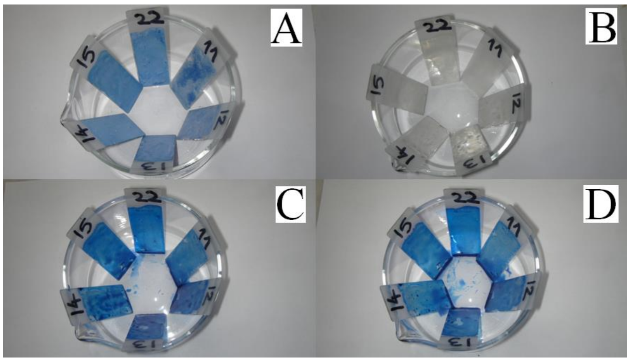

Fig. 1. Thermochromic systems (11 dye-PSt; 12 dye-PBuA; 13 dye-PMMA; 14 dye-PVAc; 15 dye-PACN; 22 dye-P(St-BuA)) deposed on glass tiles at: A-room temperature; B-60 ^{o}C; C-room temperature, after 1 h at 60^{o}C; D-room temperature, after 2 h at 60^{o}C.

Table 1 summarizes the medium hydrodynamic diameter (D) obtained by DLS for blank and colored samples at 20 and 50^{o}C. As it can be observed, for the latexes obtained in the presence of dye, the medium hydrodynamic diameters increased in all the cases in comparison with blank latexes. This could be a consequence of dye encapsulation, as observed by other researchers [18-22]. Also, we can observe the influence of monomer polarity on the latex sizes. As polarity grows from styrene to acrylonitrile, the latex size increases the hydrophobic dye being more compatible to the unpolar monomers, as expected. For the majority of the samples we obtained one particle generation, the distribution being narrow in the case of colored sample and broader for the blank latexes (Fig. 1 and 2).

Table 2. The medium hydrodynamic diameter obtained for the blank and colored samples.

Reference Monomer	Blank sample	D (nm) 25^{o}C	D (nm) 50^{o}C	Colored sample	D (nm) 25^{o}C	D (nm) 50^{o}C
St	**18**	176.8	170.5	**11**	715.3	332
BuA	**19**	320	291.5	**12**	932	336.2
MMA	**20**	221	200	**13**	4865	616
VAc	**16**	211.8	301.6	**14**	2288	488.3
ACN	**17**	245.3	217.1	**15**	5090	447.2
St-BuA	**21**	233.8	237.2	**22**	597.7	376.8

As the dye melts beyond 50°C, we measured the medium hydrodynamic diameter at this temperature for all the samples. No significant change was observed between the diameters obtained for the blank latexes. In the case of the colored latexes the diameter at 50°C decreased compared with the diameter obtained at low temperature. Still, the diameters are bigger compared to the blank samples.

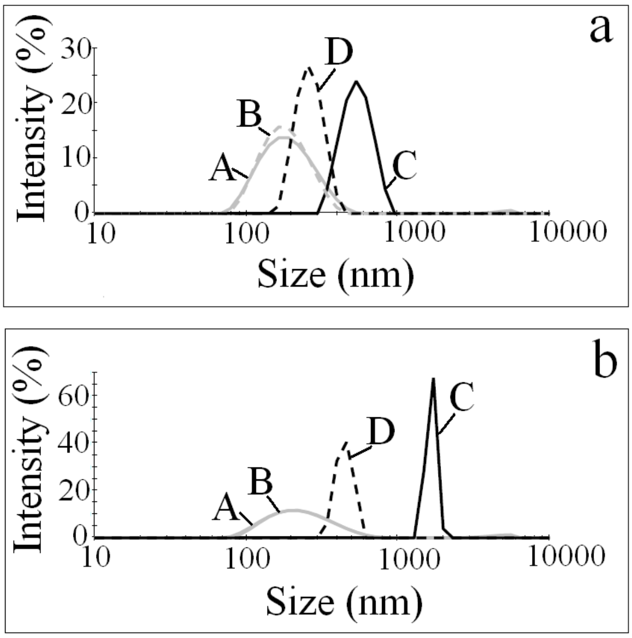

Fig. 2. Distribution by intensity for: a) PSt latexes; b) PMMA latexes (A- blank latex 20°C; B-blank latex 50°C; C-colored latex 20°C; D-colored latex 50°C).

Therefore, only a part of dye was encapsulated, the other part co-existing in the latex system.

SEM pictures showed particle dimensions in good agreement with DLS analyses. For the samples obtained in the presence of the colored complex, the morphology of the films changes, the pictures being hard to obtain because of the low melting temperatures of the samples. The most concludent images were obtained for polystyrene samples.

Water contact angle of the final systems synthesized in the presence of the colored complex showed differences in comparison with the neat samples. From the results it was observed that the colored films possessed enhanced roughness against blank samples. After exposing the glass tiles on the temperature 60°C for 2 h, the water contact angles were higher than those measured for the initial films, being around the values determined for the neat latexes. The colored complex in excess was removed from the tile, only those encapsulated remained in the film.

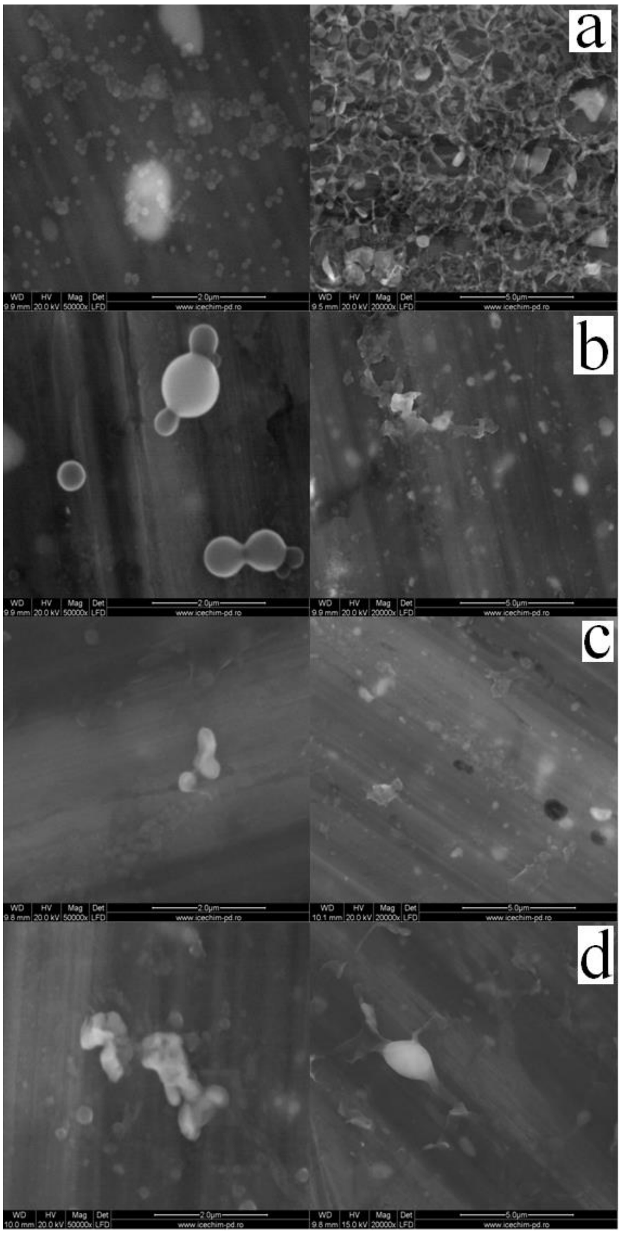

Fig. 3. SEM images obtained for the final systems with styrene (a), butylacrylate (b), vinyl acetate (c) and acrylonitrile (d), for the neat samples (left) and those obtained in the presence of the colored complex (right).

Table 3. Water contact angle (CA) determined for the neat and colored samples.

Reference Monomer	Blank sample	CA	Colored sample	CA	CA (after 2h at 60^{o}C)
St	**18**	73.4	**11**	24.6	68.3
BuA	**19**	65.1	**12**	24	69.6
MMA	**20**	65.5	**13**	28.8	65.7
AcV	**16**	52.1	**14**	51.4	63.3
ACN	**17**	65.3	**15**	39.5	66.8
St-BuA	**21**	47.2	**22**	40.4	69.4
			Col A	**59.7**	

4. Conclusions

Homogenous aqueous polymeric dispersion containing thermochromic systems based on monomers with different polarities, were sythesised. For all synthesized samples were obtained dried blue films regardless of the monomer used in synthesis.

The colored complex is only partially encapsulated, the other part coexisting in the final system. The colored complex influences the size and morphology of the final latexes and water contact angle of the films obtained. Analyzes confirmed the partial encapsulation of the blue complex and the necessity for further investigations.

Acknowledgment

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI, project number 3.2-1391.

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