

# The interaction of liotrope liquid crystals with divinylbenzene- maleic anhydride copolymers particles

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The preparation of copolymer particles by alternating copolymerization of divinylbenzene with maleic anhydride and the obtaining of silver hybrids and discoid liquid crystals (LC)-DVB-MA composites are reported. The dispersions containing the copolymer particles were characterized by DLS, pursuing the mixtures stability and the particles interactions. The ternary DVB-MA-MEMNPEO<sub>4</sub> copolymers segregate the largest quantity of LLC and they have the highest degree of particles association after water dilution. The dried particles were observed by SEM. The comparative study of particle dimension, with and without Ag<sup>0</sup>, distinguishes the fact that the metal hybrids spread in smaller particles both with and without LLC.

(Received February 22, 2010; accepted April 11, 2010)

**Keywords:** Liquid crystals, silica, Layered silicates, Silver hybrids

## 1. Introduction

Several attractive lyotropic liquid crystals (LLC) systems have been put into evidence due to a high degree of surfactant self-organization in water at certain concentrations [1-8].

These LLC present selective interactions with partners of different polarity, optical and electrical anisotropy, and the modification of the fluidity in different temperature ranges. The presence of a co-surfactant allows the obtaining of different structures as discotic (ND) or calamitic (NC) phases that can modify the orientation of supplementary dispersed particles[5-8].

For these reasons recent studies have shown the possibility of dispersing in LLC different systems such as: biodegradable polymers or monomers [9], different polymer structures [10], carbon nanotubes [11], silica particles [12], metal nanoparticles [13], polymeric nanoparticles [14]. In the polymer case, the stability of the final obtained systems is much improved by steric repulsion between the surfactant that induces the formation of the LLC, and the macromolecular chain [10]. This is why we present in this paper the study of dispersions of carboxyl group particle neutralized with ammonia in LLC formed by sodium dodecyl sulfate (SDS), decanol (C10OH) and water [4-8,14]. These particles were obtained by alternating copolymerization of divinylbenzene (DVB) with maleic anhydride (MA). Polymeric dispersions were neutralized with ammonia while few of them were covered with Ag<sup>0</sup> particles, obtained by the reaction of AgNO<sub>3</sub> with NaBH<sub>4</sub> [15].

## 2. Experimental

### 2.1 Materials

The divinylbenzene (Aldrich), maleic anhydride (Fluka) were purified by distillation and by sublimation.

Heptane (C<sub>7</sub>) (Merck), methyl ethyl ketone (MEK) (Reactivul), sodium dodecyl sulfate (Fluka), decanol (Merck), silver nitrate (Fluka), sodium borohydride (Fluka), azoizobutyronitrile (AIBN) (Fluka) and sodium montmorillonite (ClNa) (Southern Clay Prod. Inc.) were used without further purifications.

### 2.2 A- Preparation of polymeric particles

The copolymerization of DVB-MA was accomplished in similar conditions as in [15]. We used 60ml C<sub>7</sub>, 40ml MEK, and a mixture of 4g DVB, 4g MA and 0.2g AIBN that were introduced in a round bottomed flask equipped with mechanical stirring (350rot/min), condenser and thermometer. The mixture was homogenized under stirring, than it was purged with nitrogen and heated to 70°C. This temperature is maintained for 4 hours. 0.2g AIBN were added after 2 hours from the beginning of the heating for a better conversion. In the case of using ClNa or nonylphenol etoxilated with 4 moles ethylene oxide (MEMNPEO<sub>4</sub>) maleic monoester, 1g was dispersed in the initial reaction in an ultrasonic bath for 30 min. The whole compound is transferred in polyethylene recipes after polymerization for the solvents evaporation.

### 2.3 B- Preparation of silver hybrids

We used 0.8 g copolymer DVB-MA that were dispersed in a round bottomed flask, previously described, into 59 g water and 1ml 25% NH<sub>4</sub>OH mixture. It is stirred for 15 minutes and it is ultrasonically treated for another 15 minutes. 0.1168 g AgNO<sub>3</sub> dissolved in 10ml water are added to the mixture in this way. The whole dispersion is maintained under stirring 3 hours at room temperature. After this droplets of 0.104 g NaBH<sub>4</sub> dissolved in 10ml water are added. The samples used in this paper are presented in Table 1.

## 2.4 C- Preparation of the systems LLC - CVB-MA copolymers

A discotic LLC mixture was made for the obtaining of these systems. Its composition is SDS (2.82 g) water (6.61 g) and C10OH (0.57 g). 0.2g DVB-MA copolymer prepared according to A and B methods previously mentioned are added under magnetic stirring. The tight closed samples are left without stirring and are analyzed.

## 2.5 Measurements

The monomers conversions in DVB-MA copolymerization were gravimetrically assigned and they were over 98% in all cases. Particles dimensions and Zeta potential were measured with a Zetasizer Nano ZS ZEN 3600 (Malvern) by dynamic light scattering (DLS). 1 g from the samples previously described (C method) was diluted with 9ml water for these measurements. Droplets from the same diluted samples were dried on conductive stubs for SEM analyses. A FEI Quanta 200 microscope was used for these analyses.

## 3. Results and discussion

The previous studies distinguished the limited stability of the 1%wt. dispersions containing 1.4  $\mu\text{m}$  polymeric particles and LLC. The LLC shape ordered systems were  $N_D$  and  $N_c$  type, formed by SDS,  $C_{10}OH$  and water [4-8].

We used particles formed by DVB-MA copolymers, where we tried to modify the LLC interaction capacity, and we studied the parameters contributions in the system stability. This modification was done by particles inclusion in a layered silicate (sodium montmorillonite), by ternary copolymerization with MEMNPEO<sub>4</sub> and by Ag<sup>0</sup> particles deposition on previous particles (Table 1).

These mixtures were steadied for 1-2 days. A strong segregation of the systems presented in Table 1. was

observed after 3 days. All the system is separated in a bottom batch, where the particles with a fraction of LLC are sedimented, and an upper clear batch. Meanwhile the system used as LLC was homogeneously maintained, with no phase separation. The volumetric quantity of the lower separated phase is correlated with the polymer particles in an interesting mode. The maximum quantity deposited in the lower batch was observed for DVB-MA unmodified copolymers. The samples C<sub>1</sub> and C<sub>5</sub> (Table 1.) depose a layer on 70% of the total initial volume of the mixture. The samples containing stratified silicate, C<sub>3</sub> and C<sub>7</sub> (Table 1.) depose about 30% of the initial volume. The thinner lower batch (around 25%) was observed for the samples formed by the ternary copolymers, DVB-MA-MEMNPEO<sub>4</sub> (C<sub>2</sub>, C<sub>6</sub> from Table 1). The presence of the reactive comonomer ensures a better interaction between its own particles, establishing a clearer segregation without a marked association with the LLC system.

The weight of the separated LLC mixture, not integrated between polymer particles, varies in next order: DVB-MA-MEMNPEO<sub>4</sub> copolymer > DVB-MA-CiNa copolymer > DVB-MA copolymer. Thus, the distinguished order proves the fact that the best interaction with LLC is shown by unmodified copolymers DVB-MA. A very interesting event is the Ag<sup>0</sup> particles deposition on the used copolymers surface does not strongly affect the LLC system interaction. These results demonstrate the fact that the metallic particles do not cover the whole copolymer surface.

We analyzed the samples from the Tab.1 immediately after processing with respect of particle dimensions and zeta potential to establish a part of the parameters that induce the stability of the systems formed by polymeric particles and LLC. For these analyses the samples were diluted in water. The results are presented in Table 1 and Figs. 1 and 2. We included for comparison the particles dimensions and zeta potential of the aqueous particles dispersions without LLC constituents.

Table 1. The modification of particle dimensions ( $D_i$ ,  $D$ ) and  $\zeta$ -potential ( $\zeta_i$ ,  $\zeta$ ) in accordance with the synthesis conditions.

| Sample nr.     | Addition (0,29/10gN <sub>D</sub> )                               | $D_i$ (nm) | $D$ (nm) | $\zeta_i$ (mV) | $\zeta$ (mV) |
|----------------|------------------------------------------------------------------|------------|----------|----------------|--------------|
| C <sub>1</sub> | D <sub>24</sub> cop. MA-DVB                                      | 853        | 1014     | -31.1          | -54.7        |
| C <sub>2</sub> | D <sub>23</sub> cop. MA-DVB + MEMNPEO <sub>4</sub>               | 1920       | 3811     | -39.4          | -91.9        |
| C <sub>3</sub> | D <sub>25</sub> cop. MA-DVB + CiNa                               | 1480       | 2866     | -35.5          | -105         |
| C <sub>4</sub> | D <sub>28</sub> cop. MA-DVB + MEMC <sub>12</sub> EO <sub>4</sub> | -          | 2110     | -              | -77.6        |
| C <sub>5</sub> | D <sub>24</sub> + Ag                                             | 172        | 220      | -29.3          | -56.8        |
| C <sub>6</sub> | D <sub>23</sub> + Ag MEMNPEO <sub>4</sub>                        | 2540       | 2085     | -28.3          | -71.5        |
| C <sub>7</sub> | D <sub>25</sub> + Ag CiNa                                        | 249        | 177      | -30.1          | -63.5        |
| N <sub>D</sub> |                                                                  |            | 602.8    |                | -75.6        |

(i index for the dispersions without ND component; no index for the dispersions with ND component).

The comparative study of particle dimensions, with and without Ag<sup>0</sup>, distinguishes the fact that the metal hybrids spread in smaller particles both with and without LLC. These results demonstrate the fact that the polymer

particles are formed starting from smaller particles that are dispersed in elementary particles after Ag<sup>0</sup> doping.

The dimensions for ternary DVB-MA-MEMNPEO<sub>4</sub> copolymers (samples C<sub>2</sub>, C<sub>6</sub>) are higher in all cases. As we have already mentioned, all these copolymers introduced

2%wt in the LLC ternary system cause a higher segregation, thus removing 75% from the system forming  $N_D$  after three weeks.

The ternary system  $N_D$  is perfect stable even after three weeks. This (Sample O in Fig. 1) is aggregated in approximately 600nm microdomains by water diluting (1/9). These aggregates are negatively charged and they have  $-75.6\text{mV}$  zeta potential (Table 1, Fig. 2).

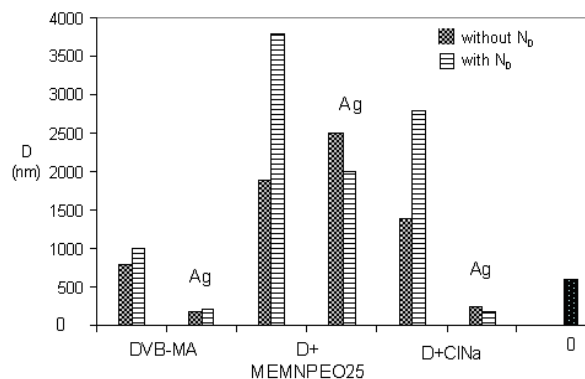


Fig. 1. The modification of the copolymer particles mean diameter.

Zeta potential value is lower than  $-75.6\text{mV}$  for the systems containing  $\text{Ag}^0$  particles. Zeta potential is higher in no  $\text{Ag}^0$  copolymers cases, when the particles are modified with  $\text{MEMNPEO}_4$  (sample 2) or sodium montmorillonite (sample 3).

The fact that all the  $\text{Ag}^0$  doped samples have a lower value of zeta potential demonstrates that a part of negative charges, most of them deriving from  $\text{COO}^-$  groups of MA structural units, are neutralized by metal particles interactions.

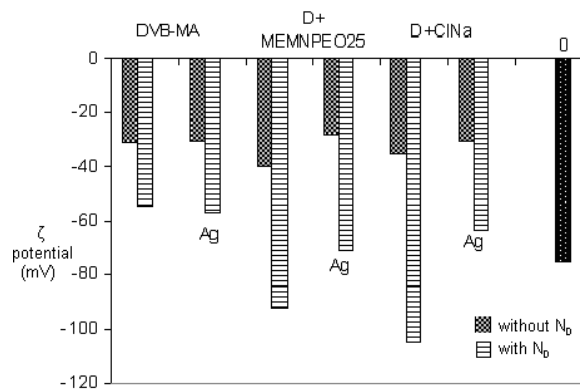


Fig. 2. The decreasing of  $\zeta$ -potential for the systems containing  $\text{Ag}^0$  particles.

The comparative zeta potential data of the water-dispersed copolymers with the copolymers mixed with  $N_D$  system demonstrates that the presence of the SDS increases the particles negative charges. This increment of negative charge can be an evidence of the interactions of particles – LLC forming system.

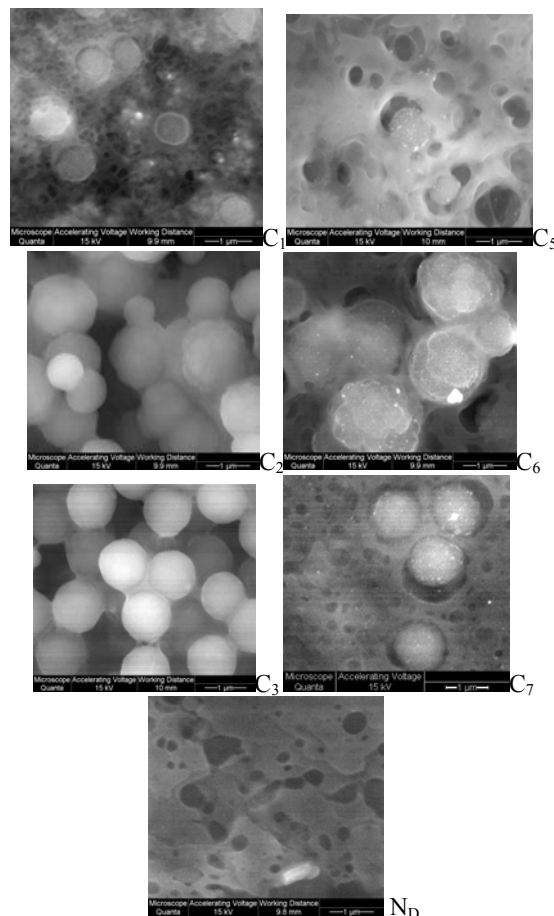


Fig. 3. SEM pictures of the samples from Table 1.

Table 1 data are confirmed by SEM images (Fig. 3) of diluted and dried particles respectively. Due to  $\text{SDS} - \text{C}_{10}\text{OH}$  interactions, the  $N_D$  system without water is presented like heterogeneous connections. The aggregation state of initials copolymers ( $C_1, C_2, C_3$  samples) is higher than the  $\text{Ag}^0$  hybrids ( $C_5, C_6, C_7$  samples).

#### 4. Conclusions

The time stability of the obtained systems by mixing the DVB-MA copolymers (2%wt.) and LLC obtained from  $\text{SDS}, \text{C}_{10}\text{OH}$  and water, is time limited. The unmodified polymers show the best stability.

The ternary DVB-MA-MEMNPEO<sub>4</sub> copolymers segregate the largest quantity of LLC and they have the highest degree of association of particles after water dilution.

The dispersed copolymers in LLC don't modify the time stability in  $\text{Ag}^0$  hybrids. These copolymers show smaller particle dimensions and a reduced zeta-potential by water dilution. The DLS data regarding particle dimensions after water dilution are studied by SEM analyses.

### Acknowledgements

The authors wish to thank the Romanian Ministry of Education and Research UEFISCSU (Executive Agency for Higher Education and Research Funding), project PNII ID\_123 for funding this study.

### References

- [1] M. Bourrel, R. C. Schecher, *Microemulsions and Related Systems*, Marcek Dekker Inc., N.Y., Basel, 1988.
- [2] St. Friberg, P. Neoghi, *Surfactant-Based Separation Processes*, Eds. J.F. Scamehorn, J.H. Harwell, Marcel Dekker Inc., N.Y., Basel, 120, 1989.
- [3] L. Richard, G. J. Tiddy, S. Casey, *Coll. Polym. Sci.* **31**, 286 (2008).
- [4] L. Q. Amaral, M. E. M. Helene, D. R. Bittencourt, R. Itri, *J. Phys. Chem.* **91**, 5987 (1987).
- [5] L. Q. Amaral, M. E. M. Helene, *J. Phys. Chem.* **92**, 6057 (1988).
- [6] P. O. Quist, B. Halle, J. Furo, *J. Chem. Phys.* **96**, 3875 (1992).
- [7] L. Q. Amaral, O. S. Filho, G. Taddei, M. Vila-Romeu, *Langmuir* **13**, 5016 (1997).
- [8] O. S. Filho, R. Itri, L. Q. Amaral, *J. Phys. Chem.* **B104**, 959 (2000).
- [9] J. D. Clapper, C. A. Guymon, *Macromolecules* **40**, 7951 (2007).
- [10] K. A. Simon, J. Sejval, R. B. Gerecht, Z. Z. Luk, *Langmuir* **23**, 1453 (2007).
- [11] W. Jiang, B. Yu, W. Liu, J. Hao, *Langmuir* **23**, 8549 (2007).
- [12] M. Hara, S. Magano, N. Hizroshita, T. Seki, *Langmuir* **23**, 12350 (2007).
- [13] P. S. Kumar, S. K. Pal, S. Kumar, V. Lakshminarayanan, *Langmuir* **23**, 3445 (2007).
- [14] Ph. Poulin, N. Frances, O. Mondain-Monval, *Phys. Rev.* **E59**, 4384 (1999).
- [15] S. Gavrilu, M. Lungu, F. Grigore, D. Donescu, M. Ghiurea, *J. Optoelectron. Adv. Mater.* **10**, 3247 (2008).

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