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# Studies on ethoxylated phenolic resin

## Part I. SURFACE CHARACTERISTICS AND PROPERTIES OF COATINGS ON METAL

**Summary** — Phenolic resins such as resol or novolac phenol-formaldehyde (PF) ones have been synthesized and etherified with poly(ethylene glycol) (PEG) with different molecular weights (1000, 1500, 4000). The solution behaviors in aqueous medium of the prepared resol and novolac phenol-formaldehyde ethoxylated resins, as nonionic polymeric surfactants with different hydrophilic chains lengths, have been interpreted. Surface and interfacial tension measurements as well as emulsifying power and foaming properties of the tested nonionic polymeric surfactants were studied. The critical micelle concentration (*CMC*) and the value of free surface energy reached at this concentration $\gamma_{CMC}$ were also measured. Coatings on metal, made of the investigated phenolic ethoxylated resins, were prepared and evaluated as varnishes. This study indicated that the free surface energy of the prepared nonionic polymeric surfactants as well as the ease of formation of aggregates increase with PEG hydrophilic chain length increasing. Also, it was found that coating compositions based on resol PF ethoxylated resins with PEG-4000 offer chain flexibility and excellent coating properties.

**Key words**: resol or novolac phenol-formaldehyde resins, ethoxylation, nonionic polymeric surfactants, surface properties, coatings on metals, mechanical properties.

Water-soluble polymers are reported to be useful for many applications like dispersing agents [1—4], flocculants [5—8], emulsifiers [9], chelating agents [10], foaming or defoaming agents [11]. All these applications are based on the unique properties of these classes of polymers, where both hydrophilic and hydrophobic components are present in a single system.

The water solubility of a polymer depends largely on a sufficient number of hydrophilic functional groups placed along the polymer backbone chain or in the side chains. Solution properties and ultimate performances of water soluble polymers are determined by the specific structural characteristics of the solvated macromolecular backbone chain.

When a water-soluble polymer dissolves in water, its polymeric chain generally gets well extended [12], but some of the polymers can also form aggregates depending on the interaction between hydrophilic and lipophilic moieties present in their backbone chains [13—15].

When a lipophilic polymer backbone is ended with sufficient number of hydrophilic functional groups, the polymer becomes water soluble. These types of polymers can be regarded as polymeric surfactants and in solution they are expected to be bi-folded-surfactants as well as water-soluble polymers.

Measurement of free surface energy as a function of concentration is one of the common tools to study solution properties of surface-active materials [16].

Several types of synthetic graft copolymers with hydrophilic side chains grafted onto a hydrophobic backbone arouse one's considerable interest in copolymers with poly(ethylene glycol) tails [17]. These types of polymers are found to be effective as steric stabilizers for various kinds of dispersions [18].

Ethoxylated or ethoxylated and propoxylated phenol-formaldehyde resins, particularly of the novolac type, are a class of products that have found use as steric stabilizers in the coatings [17].

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The past objectives concerning water-borne coatings, during the early transition from oil based coatings are reviewed and the recent success in achieving these goals by use of hydrophobically-modified, water-soluble polymers is discussed [19].

Polyglycol nonionic surfactants are widely used in industry and consumer products. The applications of these surfactants are numerous [20].

The aim of the present work is to modify the water solubility of two types (resol and novolac) phenol-formaldehyde (PF) resins *via* etherification with hydrophilic functional groups of poly(ethylene glycol) with different molecular weights. The object of this work is to prepare nonionic polymeric surfactants with surface activity and to provide some input on the physical and mechanical properties of the coatings made of them applied as varnishes for metals.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) (PEG) polymers with different molecular weights (1000, 1500 and 4000) were produced by Aldrich Co.

Aqueous formaldehyde (Fo) solution (formalin) and phenol (Ph) were produced by El-Nasr Pharmaceutical Chemicals Co.

All chemicals were used without further purification. Water was distilled from potassium permanganate solution. All experiments were carried out at 23±2 °C.

### Methods

#### Preparation

**— Resol PF resin**

Into a 250 mL three-necked flask, fitted with reflux condenser, stirrer, and thermometer, Ph (47 g), 37 % Fo (63 g) and 40 % aqueous ammonia (2.35 g) were introduced and heated in a water bath for 2 h at 70 °C. The experiment was carried out according to [21].

**— Novolac PF resin**

Into a 250 mL three-necked flask, fitted with reflux condenser, stirrer, and thermometer, Ph (65 g), 37 % Fo (46 g), water (7.5 mL) and oxalic acid dihydrate (1 g) were introduced and heated under reflux in on oil bath for 1.5 h at 90—110 °C. The experiment was carried out according to [21].

**— Resol and novolac PF ethoxylated resins**

Into a 250 mL three-necked flask, fitted with reflux condenser, stirrer, and thermometer, Dean-Stark traps, resol PF (3.5 g) or novolac PF (4.5 g) in benzene as a medium, was mixed with PEG [30, 45, 120 g (resol) or 40, 75, 200 g (novolac) showing different molecular weights 1000, 1500, 4000, respectively]. Hydrochloric acid (1 drop) was added as a catalyst. The reaction mixture was then refluxed till the amount of water, theoretically calculated, was removed.

Finally, excess of benzene was removed by rotatory evaporator under reduced pressure to obtain resol PF ethoxylated resins (symbols $R_1$, $R_2$, $R_3$) and novolac PF ethoxylated resins (symbols $N_1$, $N_2$, $N_3$). The experiment was carried out according to the method described in [22, 23]. Symbols of the samples and their initial compositions are given in Table 1.

**T a b l e 1. Samples of ethoxylated resol and novolac PF resins**

| PF resins | Symbols | PEG (weight in g) |
|---|---|---|
| Resol (3.5 g) | $R_1$ | 1000 (30) |
| | $R_2$ | 1500 (45) |
| | $R_3$ | 4000 (120) |
| Novolac (4.5 g) | $N_1$ | 1000 (40) |
| | $N_2$ | 1500 (75) |
| | $N_3$ | 4000 (200) |

**— Coated samples**

Coatings were prepared by dissolving of the prepared samples PF ($R_1$, $R_2$, $R_3$ or $N_1$, $N_2$, $N_3$) in ethanol (1 g/100 mL solvent). Cured samples with *p*-toluene sulfonic acid (PTSA) as a curing agent (1 wt. % of the resin content) were also prepared. Coatings based on pure PF resin — resol (R) or novolac (N) — with or without curing agent were prepared for comparison. The mixture was stirred till a homogeneous solution was obtained. The solution was sprayed on metallic plates and kept in the open air at 23±2 °C for 3 h to evaporate the solvent. Finally the coated samples were thermally cured in an air oven at 150—170 °C for the optimum curing time determination (see Table 5).

#### Characterization of the prepared PF resins

The hydroxyl number was determined according to the method described in [21]. The molecular weight and molecular weight distribution *MWD* were determined by means of a Waters 600 gel permeation chromatography (GPC) equipped with four ultra styragel HR chromatographic columns of 7.8 mm I.DX 300 mm with pore diameters $10^5$, $10^4$, 500 and 100 Å, connected in series, and differential refractometer (type M 2410) as a detec-

**T a b l e 2. Characteristics of the prepared phenolic resins**

| Phenolic resin | Color | pH*) | Specific viscosity*) | Specific gravity*) | OH number | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| Resol PF resin | yellow liquid | 12 | 650 | 1.05 | 3.3 | 283 | 1.038 |
| Novolac PF resin | orange liquid | 6 | 770 | 1.63 | 4.0 | 380 | 1.026 |

*) At temp. 20 °C.

tor. GPC measurements were carried out in toluene of HPLC grade as a mobile phase with a rate of elution of 0.4 mL/min at 35 °C. The calculations were reported relative to monodisperse polystyrene standards and were performed using Millennium 32 chromatography Manager with Gel-Permeation application software. Characteristics of the prepared phenolic resins is given in Table 2.

### Surface properties of the prepared resol and novolac PF ethoxylated resins

— **Free surface and interfacial energy**

Free surface and interfacial energies measurements of the prepared surfactants were made at room temperature (23±2 °C) with Du Nouy tensiometer (Kruss Type 8451) using distilled water solution of 0.1 % by weight concentration [24]. Free surface energy of distilled water used was 73 mJ/m$^2$ and free interfacial energy between medicinal paraffin oil and distilled water was 56.2 mJ/m$^2$. Surfactant solutions were aged for 2 h before the measurements. Three readings were made on each sample to determine any change with time and to obtain an average value [25].

— **Emulsifying power**

Surfactant solution (0.1 g/L, 10 mL) and paraffin oil (1 mol) were mixed in a measuring cylinder. After vigorous shaking (20 times) the tube was allowed to stand till any separation of two phases appeared.

Emulsifying power or emulsifying time (in sec) was determined according to the method described in [26, 27].

— **Foaming properties**

Surfactant solution (0.1 g/L, 100 mL) was placed in a measuring cylinder. After vigorous shaking (10 times), foam production was measured as the foam height (in mL) initially produced and foam stability was measured as the foam height after 3 min. Foaming properties were measured according to the method described in [28].

— **Determination of critical micelle concentration (*CMC*)**

*CMC* of the prepared surfactants was determined by free surface energy method [29]. In this method the values of free surface energies obtained for various concentrations of aqueous solutions of the prepared surfactants (from $1 \cdot 10^{-5}$ to $2 \cdot 10^{-1}$ m/L) were plotted *vs.* the logarithm of the corresponding concentrations.

### Adhesion and mechanical tests

Mechanical tests of the prepared samples of coatings on metal surface (with film thickness approximately 1.4—1.5 μm) were carried out. The thickness of the prepared film samples was measured according to ASTM D4138-94 "Standard Test Methods for Measurement of Dry Film Thickness of Protective Coating Systems by Destructive Means".

— **Adhesion by tape test**

A lattice pattern with either six or eleven cuts in each direction was made in the film to the substrate. Pressure sensitive tape was applied over the lattice and then removed. Adhesion properties of the prepared coatings can be evaluated according to test method B of ASTM D3359-95 "Standard Test Methods for Measuring Adhesion by Tape Test".

— **Impact test**

The coatings under test were applied to suitable thin metal panels. After the coatings have cured, a standard load (1.8 kg) was dropped from 1 m distance to indent the surface what deformed the coating and the substrate. Gradual increasing of the distance let determine the point at which failure usually occurs according to ASTM D2794-93 "Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)". This procedure can be applied as a "pass/fail" test by determining of cracking caused by impacts.

— **Mandrel bend test (elongation)**

The coating materials under test were applied at uniform thickness *ca.* 1.4—1.5 μm, onto the panels of metal sheet. After drying and curing the coated panels were bent over cylindrical mandrels of various diameters and elongation of the films were determined according to test method B of ASTM D522-93a "Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings".

— **Scratch hardness by pencil test**

A coated panel was placed on a firm horizontal surface. The pencil was hold firmly against the film at a 45° angle and pushed a way from the operator in 6.5 mm stroke. The process was started with the hardest pencil and continued down the scale of hardness (6H 5H 4H 3H 2H H F HB B 2B 3B 4B 5B 6B) to the pencil that will not scratch the film according to ASTM D3263-92a "Standard Test Methods for Film Hardness by Pencil Test".

## RESULTS AND DISCUSSION

### Surface properties

The data given in Table 3 indicate that free surface and interfacial energies of the prepared polymeric surfactants increase when the hydrophilic branch length increases. This can be attributed to the fact that polymeric

**Table 3. Surface properties of the prepared resol and novolac PF ethoxylated resins**

| Sample No | Free surface energy mJ/m$^2$ | Free interfacial energy, mJ/m$^2$ | Emulsifying power, sec | Foaming mL |
|---|---|---|---|---|
| $R_1$ | 49.0 | 14.0 | 720.92 | 20 |
| $R_2$ | 51.0 | 19.0 | 25.30 | 10 |
| $R_3$ | 56.0 | 15.0 | 240.00 | 10 |
| $N_1$ | 53.0 | 15.5 | 600.00 | 10 |
| $N_2$ | 55.0 | 18.0 | 262.69 | 20 |
| $N_3$ | 56.5 | 20.5 | 701.00 | 30 |

surfactants with low molecular weight and long hydrophilic chain tend to desorb from the interface and dissolve in the aqueous phase forming micelles at low concentration [17].

It is clear from Table 3 that all prepared nonionic polymeric surfactants show adequate emulsifying power towards paraffin oil.

Table 3 indicates, also that all prepared nonionic polymeric surfactants show not only low foaming (measured by the height of the foam initially produced) but also low stability indicated by the height of the foam after 3 min. These low foaming effects are probably due to the presence of many hydrophilic groups which cause a considerable increase in area per molecule and produce less cohesive forces at the surface [30, 31].

Figures 1 and 2 represent the variation of free surface energy of the investigated surfactants *versus* the logarithm of surfactant concentration (-log c). The curves decline indicating that free surface energy decreases sharply when the surfactant concentration increases up to a certain concentration, then remain nearly constant with slight decrease or increase.

The concentration at which the slope starts to change or become nearly constant marks the location of the critical micelle concentration *CMC* value. At this concentration, the surfactant begins to aggregate in the bulk phase forming a sort of cluster known as micelle. At this moment their hydrophilic moieties are oriented this way that contact with the aqueous phase while the hydrophobic moieties are tucked into the interior of the aggregate [32]. The value of free surface energy reached at this concentration is defined as $\gamma_{CMC}$. The values of both *CMC* and $\gamma_{CMC}$ are collected in Table 4. The values of *CMC* of the prepared nonionic polymeric surfactants decrease with increasing molecular weight of poly(ethylene glycol) used as a hydrophilic species.

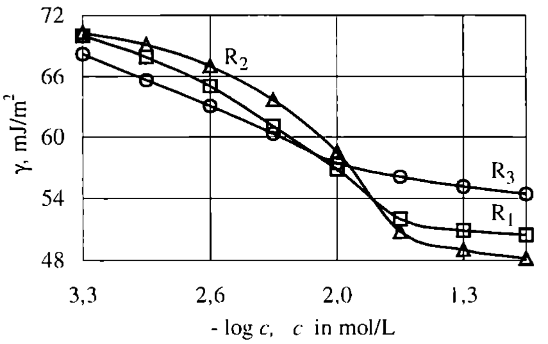

*Fig. 1. Dependence of free surface energy (γ) on logarithm of concentration (- log c) of resol PF ethoxylated resin; for symbols see Table 1*

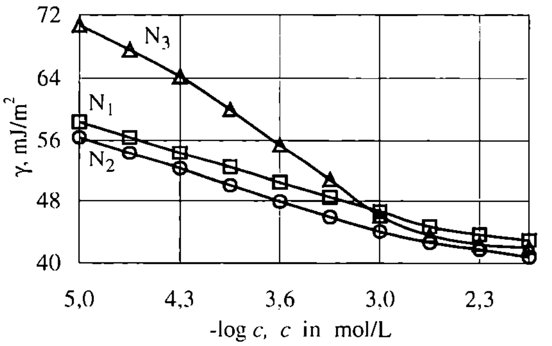

*Fig. 2. Dependence of free surface energy (γ) on logarithm of concentration (- log c) of novolac PF ethoxylated resin; for symbols see Table 1*

**Table 4. *CMC* and $\gamma_{CMC}$ values of resol and novolac PF ethoxylated resins**

| Surfactant | *CMC* · $10^{-2}$, mol/L | $\gamma_{CMC}$, mJ/m$^2$ |
|---|---|---|
| $R_1$ | 3.000 | 50.000 |
| $R_2$ | 2.500 | 50.100 |
| $R_3$ | 1.000 | 57.170 |
| $N_1$ | 0.190 | 45.000 |
| $N_2$ | 0.125 | 43.750 |
| $N_3$ | 0.100 | 45.625 |

It was found that the efficiency of the aggregation process depends on the content and nature of the hydrophobic groups and their distribution along the chain [33—35]. Thus throughout the present work it was expected that the hydrophobic parts of the backbone accumulate at the center of the structure and are oriented towards the interior, while the hydrophilic poly(ethylene glycol) grafts are oriented towards the aqueous phase. This rearrangement would minimize the exposure of the polymer backbone to the aqueous phase and leads to a decrease in *CMC* value.

## Adhesion and mechanical properties

All results concerning adhesion and mechanical properties of the coatings on metal are given in Table 5.

### Adhesion

5B (according to ASTM D3359-95) indicates not removable area while in 4B, 3B, 2B and 1B less than 5.5—15, 15—35, 35—65 and greater than 65 % of the area is removed, respectively.

All prepared coated samples based on R or N PF ethoxylated resins and cured with PTSA show better adhesion properties as compared with those cured without PTSA.

Ethoxylated coatings samples based on PEG showing the highest molecular weight (*i.e.* PEG 4000) and cured with the above mentioned curing agent show excellent adhesive properties as compared with those based on PEG 1500 or 1000. This can be attributed to the fact that PEG 4000 is more flexible hydrophilic species than PEG 1500 and 1000. This evidences the hydrophilic branch

**Table 5. Adhesion and mechanical properties of the coatings on metal (film thickness *ca.* 1.4—1.5 µm)*)**

| Pure PF resins 1 g | Phenolic ethoxylated resins | Curing process at 150—170 °C | | Properties | | | |
|---|---|---|---|---|---|---|---|
| | | agent type | time min | adhesion | impact resistance*) | elongation % | scratch hardness |
| R | — | — | 10 | 1B | P | 4.40 | F |
| R | — | PTSA | 5 | 2B | F | 3.30 | H |
| | $R_1$ | — | 120 | 2B | P | 6.75 | B |
| | $R_1$ | PTSA | 60 | 3B | P | 4.40 | HB |
| | $R_2$ | — | 180 | 3B | P | 9.00 | 3B |
| | $R_2$ | PTSA | 150 | 4B | P | 6.57 | 2B |
| | $R_3$ | — | 270 | 4B | P | 28.00 | 5B |
| | $R_3$ | PTSA | 240 | 5B | P | 14.00 | 4B |
| N | — | — | 10 | 0B | F | 3.30 | 3H |
| N | — | PTSA | 5 | 0B | F | 0.00 | 4H |
| | $N_1$ | — | 120 | 1B | F | 4.40 | H |
| | $N_1$ | PTSA | 60 | 2B | F | 3.30 | 2H |
| | $N_2$ | — | 180 | 2B | P | 6.75 | HB |
| | $N_2$ | PTSA | 150 | 3B | P | 4.40 | F |
| | $N_3$ | — | 270 | 3B | P | 9.00 | 2B |
| | $N_3$ | PTSA | 240 | 4B | P | 6.75 | B |

*) P — passing, F — failing, for other symbols see text.

length in the synthesized nonionic polymeric surfactants affects the adhesion properties of the samples of coatings.

Samples of cured resol PF coatings improve adhesion properties in comparison with those based on cured novolac PF ones. This is due to the increased number of hydroxy methylated groups in resol PF resin structure [21].

### Impact resistance

Almost all samples of the prepared coatings based on resol or novolac PF ethoxylated resins pass the impact test (P) as compared with non-ethoxylated ones (pure PF resins). This can be attributed to the fact that the presence of oxyethylene units $(\text{-CH}_2\text{-CH}_2\text{-O-})_n$ in PEG with different molecular weights increases the flexibility of the coatings which in turn increases their cracking resistance.

Samples of coatings films based on pure resol PF resin pass the impact test as compared with those based on pure novolac PF resin. This is due to the increased number of methylene bridges per molecule of R PF resin [21, 36, 37].

Both R and N PF coatings films samples cured with PTSA are brittle coatings due to their structural rigidity after curing [37].

### Elongation

Effects of ethoxylation and number of oxyethylene groups in PEG chain on elongation are very similar to their effects on impact resistance and can be similarly interpreted.

### Scratch hardness

All prepared coatings samples based on R or N PF ethoxylated resins show higher softness on the hardness scale as compared with non-ethoxylated ones.

Increasing number of oxyethylene groups in PEG species causes an increase in the flexibility of ethoxylated coating films in accordance with hardness scale as follows: 5B > 3B > B for the coating based on resol PF ethoxylated resins while 2B > HB > H for the coatings based on novolac PF ethoxylated resins with PEG 4000, 1500 and 1000, respectively.

All ethoxylated and non-ethoxylated samples of coatings cured with PTSA show some greater hardness on the hardness scale as compared with the samples cured without curing agent.

## CONCLUSIONS

From the study of the surface properties of the surfactants prepared by us we can conclude as follows: Free surface energies of resol or novolac PF ethoxylated resins increase with hydrophilic chain length increasing, the ease of formation of micelles is in accordance with increasing of the hydrophilicity.

From the study of the adhesion and mechanical properties of the prepared film coatings based on the synthesized nonionic polymeric surfactants it is clear that these properties vary with the hydrophilic chain length as well as the hydrophobic type (R or N). Coating compositions based on resol PF ethoxylated resins with PEG 4000 offer the best chain flexibility and excellent coating properties and can be used as varnishes for metals.

## REFERENCES

1. Mather R. R.: *Colloids Surf.* 1989, **37**, 131.
2. Muroi S.: *Shokubai* 1983, **56**, 36.
3. Grant R. L.: *Paper Technol.* 1962, **3**, 539.
4. Kuo P. L., Chang T. C., Lu L. M.: *J. Appl. Polym. Sci.* 1992, **44**, 859.
5. Dixon J. K., Lamer V. K., Li C., Messinger S., Linford H. B.: *J. Colloid Interface Sci.* 1967, **23**, 465.
6. Walles W. E.: *J. Colloid Interface Sci.* 1968, **27**, 797.
7. Anthony A. J., King P. H., Randall F. W.: *J. Appl. Polym. Sci.* 1975, **19**, 37.
8. Clark A. Q., Herrington T. M., Petzold J. C.: *Colloids Surf.* 1990, **44**, 247.
9. Kuo P. L., Chen C. J.: *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 99.
10. Kobayashi S., Suh K. D., Shirokua Y.: *Macromolecules* 1989, **22**, 2363.
11. Kuo P. L., Cheng V., Chen C. L.: *J. Appl. Polym. Sci.* 1999, **71**, 805.
12. Turro N. J., Arora K. S.: *Polymer* 1986, **27**, 783.

13. Chu D. Y., Thomas J. R.: *Macromolecules* 1989, **17**, 2132.
14. Price C.: *Pure Appl. Chem.* 1983, **55**, 1563.
15. Kuo P. L., Hung M. N.: *J. Appl. Polym. Sci.* 1993, **48**, 1571.
16. Rosen M. J.: "Surfactants and Interfacial Phenomena", John Willey & Sons Inc., New York 1978.
17. Jonsson B., Lindman B., Holmberg K., Kronberg B.: "Surfactants and Polymers in Aqueous Solution", John Willey & Sons Ltd., New York 1998.
18. Zaki N., Al Sabagh A.: *Tenside Surfactants, Detergents* 1997, **34**(1), 12.
19. Edward G. J.: "Proceedings of the IS and T-Annual Conference Soc. Imaging Sci. Technol", Springfield, VA, USA 1996, p. 531.
20. Edans M. W., Nace V. M., Knoell J. C.: *Polym. Mat. Sci. Eng.* 1993, **69**, 551.
21. Braun D., Cherdron H., Ritter H.: "Polymer Synthesis: Theory and Practice Fundamentals, Methods, Experiments", 3rd ed., Springer-Verlag, Berlin—Heidelberg—New York 2001.
22. Liston T. R.: *J. Am. Chem. Soc.* 1938, **60**, 1264.
23. Ismail D. A., Negm N. A.: *J. Faculty Educ. Ain Shams Univ.* 2001, No. 26.
24. Findlay A.: "Practical Physical Chemistry", 6th ed., Longmans Pub., 1963, p. 92.
25. Hampson J. W., Cornell D. G.: *J. Am. Oil Chem. Soc.* 1996, **73**, 891.
26. Chen K. M., Wang H. R.: *J. Am. Oil Chem. Soc.* 1992, **69**.
27. Eley D. D., Hey M. J., Symonds J. D.: *Colloids Surf.* 1988, **32**, 87.
28. Ross J., Milles G. D.: *Oil Soap* 1941, **18**, 90.
29. Hikota T., Meguro K. J.: *Japanese Chem. Soc.* 1970, **47**, 158.
30. El-Sukkary M. M., El-Dip F., El-Sawy A. A.: *Hungarian J. Ind. Chem.* 1986, **14**, 223.
31. Fineman M. N., Brown G. L., Meyers R. J.: *J. Phys. Chem.* 1952, **56**, 963.
32. West C. C., Harwell J. H.: *Environ. Sci. Technol.* 1992, **26**, 2324.
33. Magng B., Iliopoulos I., Audebert R. in: "Macromolecular Complexes in Chemistry and Biology", Springer-Verlag, Berlin 1994.
34. Wang T. K., Iliopoulos I., Audebert R.: *Polym. Bull.* 1988, **20**, 577.
35. Wang T. K., Iliopoulos I., Audebert R.: *Am. Chem. Soc.* 1989, **30**(2), 377.
36. Brydson J. A. "Plastic Materials", 3rd ed., Newnes-Butterworths, London 1975.
37. Feldman D., Barbalata A.: "Synthetic Polymers. Technology, Properties, Applications", 1st ed., Chapman & Hall, London 1996.

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