

# Studies of the self-organization phenomena in polymer materials

G. STRAT<sup>a\*</sup>, S. GURLUI<sup>b</sup>, M. STRAT<sup>b</sup>, A. FARCAS<sup>c</sup>, S. STRATULAT<sup>d</sup>

<sup>a</sup>*Gh. Asachi Technical University of Iasi, Romania*

<sup>b</sup>*Al. I. Cuza University of Iasi, Romania*

<sup>c</sup>*P. Poni Institute of Macromolecular Chemistry, Iasi, Romania*

<sup>d</sup>*GR.T. Popa University of Iasi, Romania*

The main motivation for this paper is to analyse the platform of photoreactive compounds through the study of some diazo-polymers and new polyurethane ionomers with stilbene, base Schiff and pyrene pendants covalently attached to polymers to evaluate and eventually improve the sensitivity of the resulting materials. The experiments suggest applications in optoelectronics in which a low-power compact laser source can be used to encode information that will be transferred to a polymer film assisted by a strong incoherent light source.

(Received September 1, 2008; accepted October 30, 2008)

*Keywords:* Pyrene, Nano-aggregate, Film, Self-organization, Fluorescence

## 1. Introduction

The incorporating of a trans-stilbene chromophore and pyrene chromophore in the polymeric chains proved to be a useful tool for developing of polymer properties such as liquid crystalline (LC) behavior, nonlinear optics (NLO) response, and electroluminescent effect or to investigate some biomembranes. Given the broad spectrum of properties of polyurethanes and some biopolymers and implicitly their applications in various fields including biomedical area, a series of ionic or non-ionic polymers bearing stilbene or pyrene groups anchored in the hard segments of the polyurethane and cholesterol-bearing polymethacrylate backbones have been studied. The incorporating of a trans-stilbene chromophore in a fatty acid and phospholipids chains have been found to exhibit sharp changes in absorption and fluorescence spectra upon self-assembly in Langmuir-Blodgett films and aqueous dispersion. The spectral changes are readily associated with aggregates in which there is a strong noncovalent interaction between trans-stilbene chromophore

Polymers with photochromic azobenzene moieties are very promising materials for reversible optical data storage, optical processing, as "command layers" for the alignment of liquid crystals, or the photochemically driven formation of surface relief gratings.

## 2. Results

### 2.1. The formation of cholesterol-bearing polymethacrylate aggregates in solutions

It is known that amphiphilic derivatives of cholesterol form various types of molecular assemblies in aqueous solutions such as lyotropic liquid-crystalline phases, liposomes, micelles and ordered monolayers [1-2]. The formation of these molecular assemblies is mainly due to

hydrophobic molecular associations (short and long distance molecular interactions). An interesting aspect of such polymer-bound mesogens is that lyotropic mesophases may be formed in solution, owing to the micro phase separation of polymers in a selective solvent, a good solvent for mesogenic groups and a poor solvent for the polymer chain, or vice versa. However, such solvent-induced micro phase separation of side-chain LC polymers may yield nanometer-scale mesophases that are too small to be optically observed by commonly used polarizing microscopes. This binary solvent mixture, e. g. a nonpolar solvent and a polar or weakly polar solvent, shows a critical concentration of one of solvent, such as the solvate, in our case a copolymer of cholesteryl 6-(methacryloyloxy)hexanoate and a small amount of (1-pyrenylmethyl) 6-(methacryloyloxy)hexanoate (Py-C5-MA) to form molecular aggregates [poly(Chol-C5-MA/Py-C5-MA)].

A study of computer modeling implies that ester groups in the side chains of the polymers in nonpolar solvents tend to form clusters due to dipole-dipole interactions, thus each ester group avoiding direct contact with solvents. Because an ester group is linked to pyrene via a methylene group, pyrene labels tend to be situated near the ester cluster, although pyrene rings are mostly incorporated in Chol stacks. Thus, the pyrene labels would experience a microenvironment more polar than the bulk solvent phase. This explains the observation that the  $I_3/I_1$  ratio for the Chol-containing copolymer in n-hexane is significantly smaller than that for the monomer (see Figure 1, Figure 2 and Figure 3).

Relative intensities of the vibronic bands of pyrene fluorescence are known to show a significant dependence on the microenvironmental polarity around pyrene. The ratio of the third to the first vibronic bands ( $I_3/I_1$ ) in fluorescence spectra of pyrene reflects the polarity in local media where pyrene exists, i.e.,  $I_3/I_1$  ratio being larger in less polar media. Therefore, the  $I_3/I_1$  ratio can be used to discuss environmental effects on pyrene fluorescence. The

ratios of  $I_3/I_1$  for the pyrenyl monomer and the copolymers are plotted in Figure 2 against the  $F(n)$  of solvents employed.

The function of  $F(n)$  has the form:

$F(n) = n^2 - 1 / 2n^2 + 1$ , where  $n$ , represent the refractivity index for wavelength 589.3nm. This functions take into consideration the dispersion interactions.

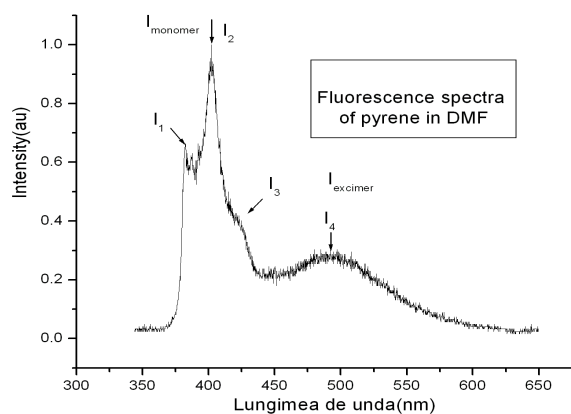


Fig. 1. Fluorescence spectra of pyrene in DMF.

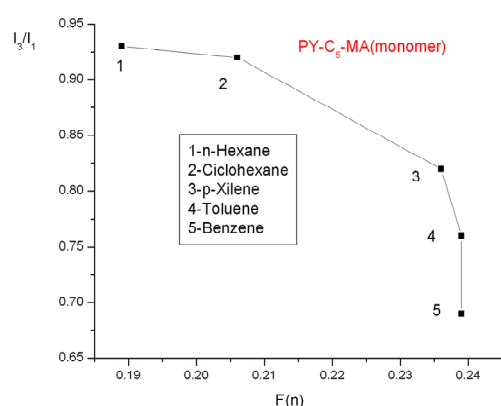


Fig. 2. The dependence of  $I_3/I_1$  versus  $F(n)$  for Py-C5-MA.

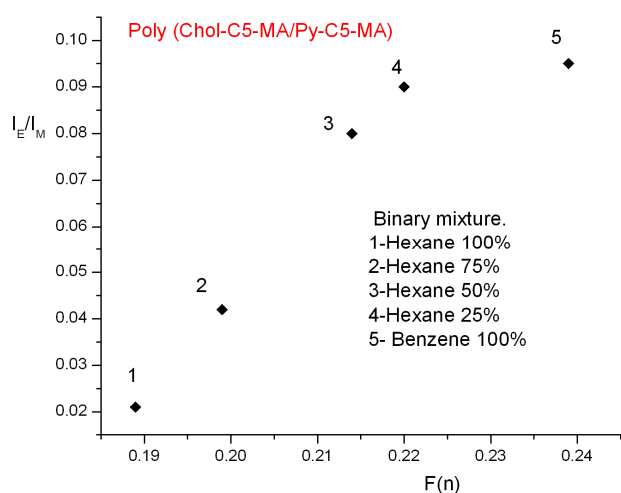


Fig. 3.  $I_E/I_M$  versus  $F(n)$  for poly(Chol-C5-MA/Py-C5-MA) in binary mixture n-hexane / benzene.

Fig. 3 depicts the plots of the  $I_E/I_M$  ratios ( $I_E$ -intensity of excimer band;  $I_M$ - intensity of monomer band) for the Chol-containing copolymers as a function of  $F(n)$  in a solvent mixed of n-hexane and benzene. In the case of the Chol containing copolymer, the  $I_E/I_M$  ratio remains practically constant in the range 0.22–0.24 values of  $F(n)$  and then it decreases in the range 0.22–0.19. These observations suggest that Chol groups in the copolymer would form aggregates in a nanometer scale in the n-hexane/benzene mixed solvent at a n-hexane content higher than ~ 40 wt %, and pyrene labels are incorporated in the stacks in the monomer form.

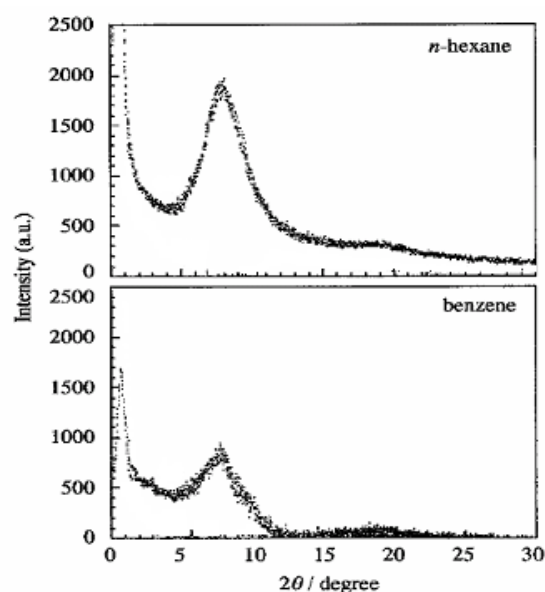


Fig. 4. The XRD patterns for poly(Chol-C5-MA/Py-C5-MA) in solutions.

Fig. 4 shows wide-angle X-ray diffraction patterns for the Chol copolymer in concentrated n-hexane and benzene solutions (10 wt %); (see Figure 2 from the paper [3]). The Chol-containing copolymer shows a sharp diffraction peak at  $7.7^\circ$  in n-hexane, which corresponds to a spacing of 5.3 Å. The analyze of the diffraction patterns for this copolymer implies that the pendant Chol groups in the Chol-containing copolymer form nano-aggregate structures with a 5.3 Å spacing in an n-hexane solution.

## 2. 2. Diazobenzene polymers in foils and tablets. Photochromic properties

New copolyethers and polyesters based on chloromethyl oxetane and phenol mixtures presenting properties of a liquid crystal (LC) have been studied [4-5]. Their thermotropic properties are favoured by the presence of diazobenzene and phenol groups within the polymer structure. The diazobenzene groups in the polymer structure confer them characteristics with important application in optics and optoelectronics. The priority in

our study is the polyesters and polyethers including in their molecular structure the diazobenzene groups placed along the polymeric chain.

We have some results of the study of a series of polyethers and polyesters based on chloromethyl oxetane embedded in polymer matrices of polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA) type. These polymers have been studied both in solid state as thin films deposited on quartz disks and in solution (Figures 5-7). The molecular structures of the studied polymers are given in Scheme 1 [6-7].

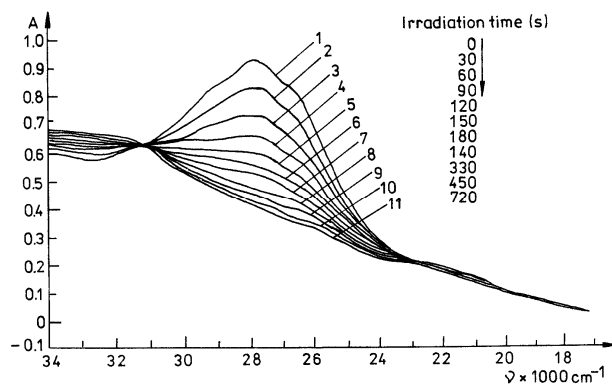
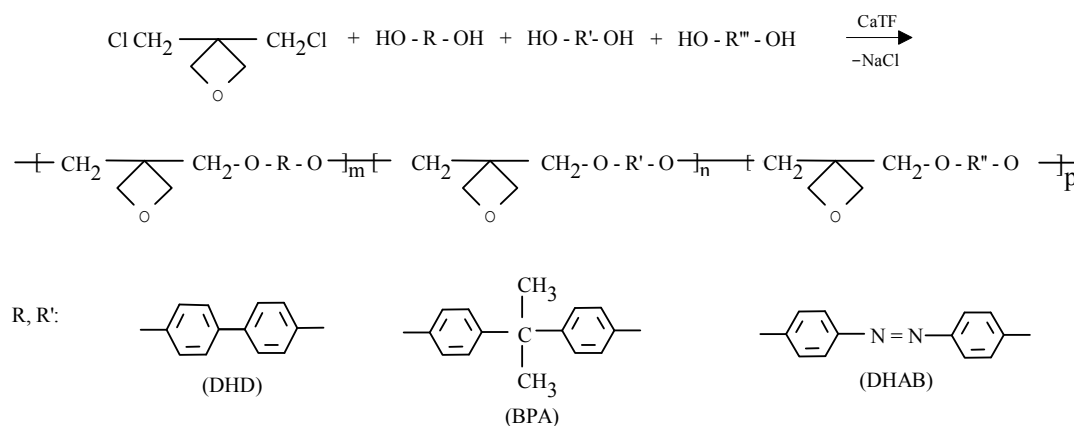


Fig. 5. Electronic absorption spectra of sample 1068 dissolved in PMMA matrix.

Table 1. Some characteristic of the synthesised copolyethers.

Sample number	Copolymer composition	(CH <sub>2</sub> ) <sub>n</sub>	M <sub>n</sub>
1 1202	DHAB/BPA/DHD = 3.8/2/1	3	1,900
2 1205	DHAB/BPA = 3.2/1	4	2,000
3 1206	DHAB/BPA = 1.1/1	5	2,200
4 1287	DHAB/DHD = 3.7/1	8	1,800
5 1297	DHAB/BPA = 2.8/1	9	1,400
6 1068	DHAB/BPA/DHD = 3.9/2/1	4	2,200



Scheme 1

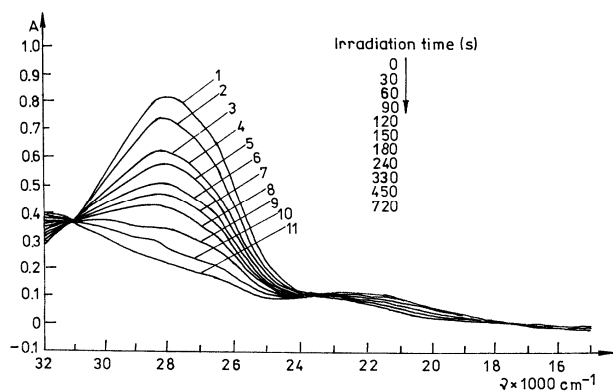


Fig. 6. Electronic absorption spectra of sample 1068 dissolved in chloroform.

As already specified, a general characteristic of the compounds studied in this work is that the azobenzene groups belonging to the polymer chain are aligned along the polymer chain structure. The photochromic effect appears as the result of molecular strain in diazobenzene units. Considering all these, it is more difficult to induce a deformation in the polymer chain as compared to other polymer structures, where the azobenzene units also belonging to the polymer structure, yet being perpendicular to it.

Upon UV irradiation (365 nm) of the polymer in THF, the strong  $\pi$ - $\pi^*$  absorbance of the azobenzene group decreases, while the absorbance of the  $n$ - $\pi^*$  transition is increased, due to the E/Z photoisomerization. The kinetics of the photoisomerization and the thermal Z/E isomerization in solution cause isosbestic points at 321 and

431 nm. A steady state is established upon irradiation with 365 nm, characterized by a proportion of about 0.95 of the Z isomer, while the irradiation with visible light of 458 nm establishes an E isomer, reaching dynamic equilibrium. In the dark, the E isomers are rebuilt by thermal Z/E isomerization. The behavior of the photochromic main-chain polymer in solution is identical with that of the related monomeric azobenzene derivative. The UV irradiation results in similar spectral changes as in solution. However, in contrast to solution, isosbestic points are neither observed during the photoisomerization nor during the thermal Z/E isomerization. Therefore, the interpretation of all spectroscopic observations becomes more difficult due to the simultaneous occurrence of photoisomerization, subsequent orientation, and aggregation.

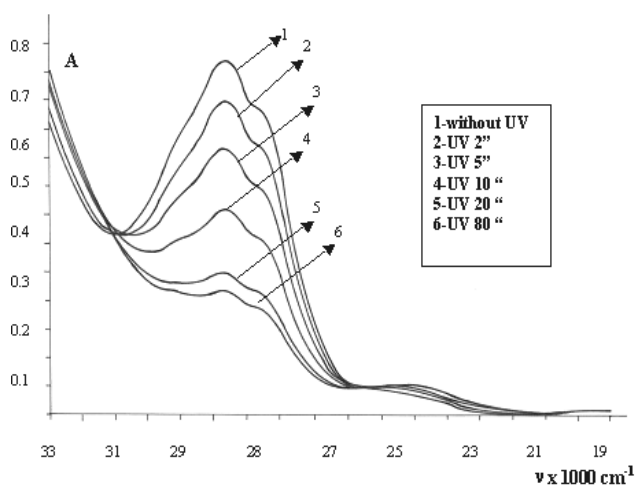


Fig. 7. Electronic absorption spectra of sample 1206+THF.

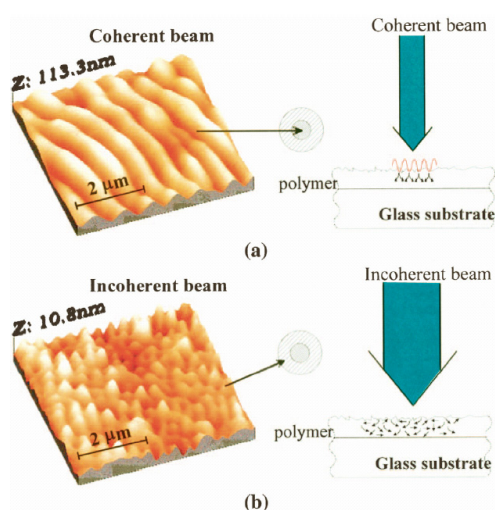


Fig. 8. AFM images of self-patterned surface relief gratings (SRG) structures obtained after 30 mn exposure with a low-power coherent beam and a large power incoherent beam. (a) It scan the SRG in the central part of the coherent beam region [8].

The samples are polymer films made from a photoactive azobenzene derivative containing heterocyclic sulfonamide moieties. 1  $\mu$  m-thick polymer films on glass substrates were spin coated from a tetrahydrofuran solution. Isomerization induces a molecular migration almost parallel to the polarization direction. In particular, when a collimated laser beam impinges onto the polymer surface, light is diffused inside the polymer film in all directions around any microroughness. It will diffract a light amplitude into the film plane. The roughness amplitude is increased. This creates a surface modulation that organizes coherently to diffract the incident laser light out of the polymer film (Figure 8). The modulation amplitude increases with time from its initial value, up to saturation of the diffraction efficiency. Saturation corresponds to the balance between incident and diffracted intensities: more light coupled by diffraction into the polymer film resulting into more light diffracted out of the polymer film.

### 3. Conclusions

1. The existence of the aggregates or dimerized probe in the ground state of the molecule was indicated by the high excimer-ionomer intensity ratio. The solvent dependence of the fluorescence suggested a hydrophilic environment for pyrene in the polyurethane cationomer, where an increased excimer emission was observed.
2. The fluorescence study of the stilbene polyurethanes showed different properties in solution and film state. Especially, aggregation produces strong effects on the photophysics of stilbene chromophores. Thus, a red shift of emission band in film state occurs and formation of excimers in both state was observed
3. It was shown that a well-defined pattern can be printed in an azo-polymer film illuminated by a low-power coherent beam. Information about the structure is brought by a weak confined laser beam. The experiments suggest applications in optoelectronics in which a low-power compact laser source can be used to encode information that will be transferred to a polymer film assisted by a strong incoherent light source. Interestingly, we see that a complex structure is built from moving objects although the structure is ignored at the individual level. Further study will be devoted to the investigation of the nonlinear behavior of the coherent-incoherent beam interaction leading to pattern formation: nonlocal, threshold, coherence, and temporal effects.

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\*Corresponding author. mstrat@uaic.ro