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A. Natansohn and P. Rochon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
Queen's University
Kingston, Ontario
K7L 3N6
Canada

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Orientation of azobenzenes in polymers depends on the neighbouring unit in the same polymer and on the thermodynamic tendency of the polymer to form oriented domains. These two factors are briefly discussed in the context of current work.

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A. Natansohn and P. Rochon

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Kingston, On., Canada

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AZOBENZENE-CONTAINING POLYMERS: SOME OPTOELECTRONIC PROPERTIES

Almeria Natansohn[1] and Paul Rochon[2]

[1]Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6 Canada
[2]Department of Physics, Royal Military College, Kingston, Ontario K7K 5L0 Canada

Azobenzene-contaning polymers are receiving a lot of scientific interest due to specific properties which make them potentially useful in optoelectronics. The most interesting potential application is in nonlinear optical materials. Typically, azobenzene groups are substituted with electron-donor and electron-acceptor substituents in the para position. This creates a charge delocalization which allows the alignment of the azobenzene dipoles parallel to an applied electric field. This orientation creates second harmonic generation properties. Based on this properties, interferometers can be build or photorefractive optical storage can be achieved. The main role of the polymer to which the azobenzene groups are usually bound or dissolved in, is to "freeze" the orientation created by the electric field below its glass transition temperature (Tg). Two very recent reviews on these phenomena include the use of azobenzene-containing polymers [1,2].

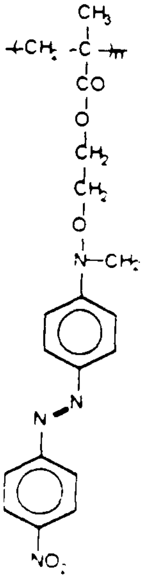
Research in our laboratory concentrates around the reversibility of laser-induced reorientation of azobenzene groups bound in various - mainly amorphous - polymers. Using polarized light, a preferred orientation perpendicular to the polarization direction is achieved in otherwise randomly distributed azobenzene groups. Unlike the poling procedure described in the previous paragraph, there is *no dipolar preference* of orientation, only directional preference. To achieve dipolar orientation, irradiation can be performed in the presence of an electric field, or the laser electric field can itself be used. The restoration of random orientations of the azobenzene groups can be obtained by heating above the Tg of the polymer or by irradiating with circularly polarized light. Apart from the photoinduced dichroism, a net phase retardation can be measured as birefringence and typical values for amorphous polymers are in the range 0.06 - 0.1, which is a very high stable birefringence.

The simplest polymer investigated consisted of a polyacrylate with disperse red 1 groups bound at each structural unit [3]. A similar homopolymer containing disperse red 13 showed increased birefringence, but a slightly longer time required to achieve the saturation level [4]. These differences were explained in terms of maximum absorbances of the two dyes (disperse red 13 had a higher absorbance at the laser wavelength) and in terms of steric hindrance (disperse red 13 has a chlorine atom in ortho to the azo bond). The effect of the film thickness on net phase retardation and writing speed has also been demonstrated [5]. For homopolymers or polymers containing high concentrations of absorbing dye groups, there is a limit of the thickness of the film which can be used for optical storage. This limit is directly related to the absorption coefficient of the film.

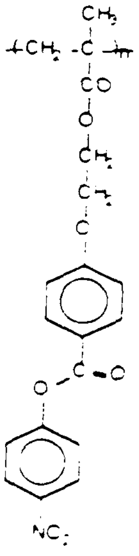
Recently we started two series of studies which will be partly covered in this presentation. The first series is a systematic investigation of photoinduced orientation of azobenzene groups in the presence of other mesogenic groups, either in the side chain together with the azobenzene groups, or in the main chain. Polymers containing such groups may show a thermodynamic tendency to form organized domains, i.e. have a semicrystalline or liquid crystalline temperature range. If this is the case, the photoinduced birefringence is much greater in such materials than in purely amorphous polymers [6]. Hence, if one plans to use these materials as WORMs (Write Once Read Many times), there is a clear advantage in the higher contrast. There are two disadvantages: first is the much slower rate of inducing the dichroism and birefringence. In order to move whole organized domains (crystalline or liquid crystalline), much more time is needed, at least one order of magnitude longer. The second disadvantage is also related to the thermodynamic tendency of these materials to stay oriented, hence erasing the writing is much harder and also requires much longer time.

The second series of studies is an investigation of the effect of azobenzene group concentration on the photoinduced dichroism and birefringence. We have already demonstrated that there is a clear difference in the behavior of copolymers and blends containing the same concentration of azo groups [7,8]. This means that the neighboring group, directly bound to a certain azobenzene group, has probably a much decisive influence than a spatially close group bound on another polymer chain. The first series of copolymers and blends analyzed contained the "disperse red 1 acrylate (DR1A) or methacrylate (DR1M)" structural units and methyl methacrylate (MMA) units, which are not only inactive under illumination, but also have a completely different shape than the azobenzene groups.

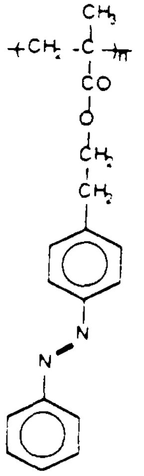
The structural units of the pairs of copolymers and blends which will be presented here are shown below. They are: a pair of similarly shaped groups, one photoactive (azobenzene, DR1M) and the other inactive (ester, BEM). These copolymers and blends are amorphous because the spacer separating the main chain from the "mesogenic" group is too short to allow spontaneous organization. Photoinduced orientation of the azobenzene groups produces an orientation by sympathy of the ester groups bound on the same chain. Another pair has a combination of two types of azobenzene groups: one is DR1M and the other one has no electron-donor or electron-acceptor on it (MEA), making it "transparent" in the visible domain. This pair can be activated either in the UV region of the spectrum (when only MEA is responsive) or in the visible region of the spectrum (when mainly DR1M is responsive). An amplification effect is again observed in either case. Finally, the last pair contains MEA and MMA and is being used to elucidate two important factors in cooperative orientation of neighboring groups. Is this orientation by "sympathy" mainly a steric effect (groups of the same shape moving in concert) or mainly a dipolar effect (the donor-acceptor substituted azobenzenes have a significant dipole moment) or both? If reorientation follows the same rules in MEA copolymers with MMA as in DR1M copolymers with MMA, then the dipole is less important than the shape of the mesogen.



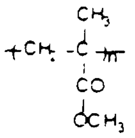
DR1M



BEM



MEA



MMA

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