

## THE INTERSECTION SYNTHESSES FOR THE PHOTOCHROMIC MATERIALS BY POLYMERIC TYPE

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**Abstract:** *The present paper aims to demonstrate the feasibility of synthesis processes of polymeric materials with chromophore sequence, highlighting features of procedure and that the property where appropriate.*

**Keywords:** *photochrome, copolymer, intersection syntheses*

### 1. INTRODUCTION

The organic macromolecules with extended conjugated sequence remain one of the most attractive routes for the synthesis of materials with specialized applications.

Why polymer material systems?

These materials offer the possibility of design and realization of optical devices, thanks to their high structural flexibility of composition, as compared with inorganic systems, whose uses are already established in the optics field, but limited by the fragility. The implementation of polymeric materials is due, on the other hand, and their processing facility. A major advantage is that the polymer architecture can be built based on beneficial electronic effects, which are composed with relative lower values of dielectric constant, high speed of operation, serving communication systems. Moreover, polymer materials are much better than inorganic systems for optical switching applications, allowing a compositional structural optimization with respect to the desired application.

Starting from these general considerations, this work aims to demonstrate the feasibility of the synthesis process of polymer materials with chromophore sequence, underlining, where appropriate, procedure and/or property peculiarities.

Radical copolymerization studies with a wide range of monomers present both theoretical interests mainly applicative. In the last 40 years of researches, has been demonstrated, for copolymerization of maleic anhydride (MA) with olefins, diolefine, styrene, acrylic, methacrylic, monomers, preferential formation of alternating polymer structures with broad applicability

The simultaneous presence of the vinyl group and the anhydride group, recommend MA both obtaining materials by step-by-step polymerization (paint, polyester paint) as well as by and additive polymerization [1-4]. In this idea, have been betake to investigate the additive polymerization, followed by chemical transformations, for obtaining the potential photochromic and/or photorefractive materials.

The choice of MA copolymers is justified both by the tendency of MA to form alternating copolymers which allows obtaining highly regular architecture structural as well as to the reactivity of anhydrides group versus primary amines.

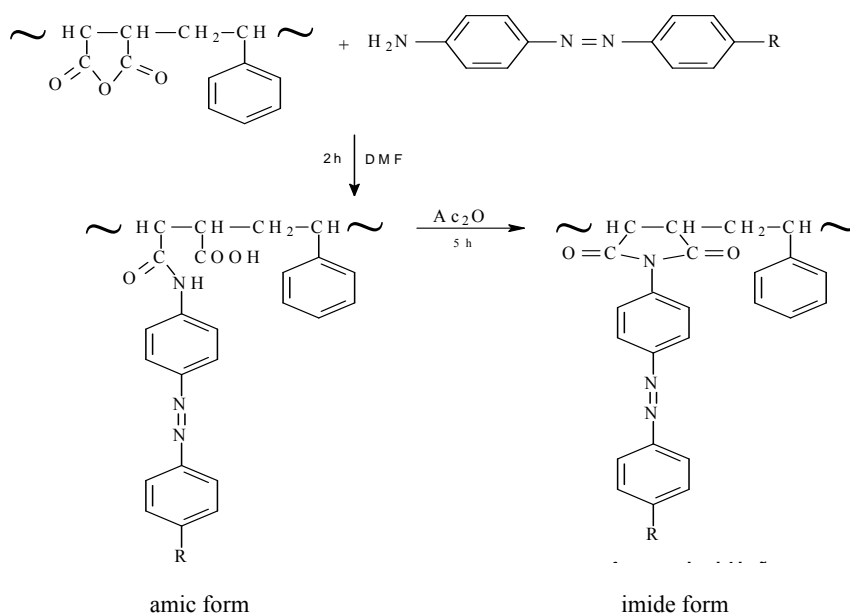
Theoretically, the copolymerization of MA-styrene (St) has exhibited a particular interest. The products of this polymerization process are characterized by alternating structure and equimolecular composition, regardless starting substrate composition, the rate of polymerization have a maximum for an equimolecular starting substrate.

The MA copolymers, intensively studied as models of alternating copolymerization, can be obtained in the heterogeneous system [5, 6]. Because the homogeneous polymerization techniques are kinetically and dimensional limited by a series of secondary processes, in the past, the MA copolymers were prepared by suspension polymerization [7-9]. More recently Ströver's group, develop precipitating polymerization method for obtaining monodispersed particles, MA-divinyl benzene used as ion exchange [16-17].

## 2. EXPERIMENTAL

Materials with potential photochromic properties was obtained by the chemical modification of a MA-St copolymer, in toluene (T), by precipitating process (MA-St;  $M_n \approx 95\ 000$ ,  $GP_n \approx 470$ ;  $X_{MA} = 50\%$ ).

Procedures for chemical modifications of MA-St with aromatic amines were described in the literature [12, 13]. In this study, the amic and imide forms of MA-St, was prepared by using photochrome derivate.

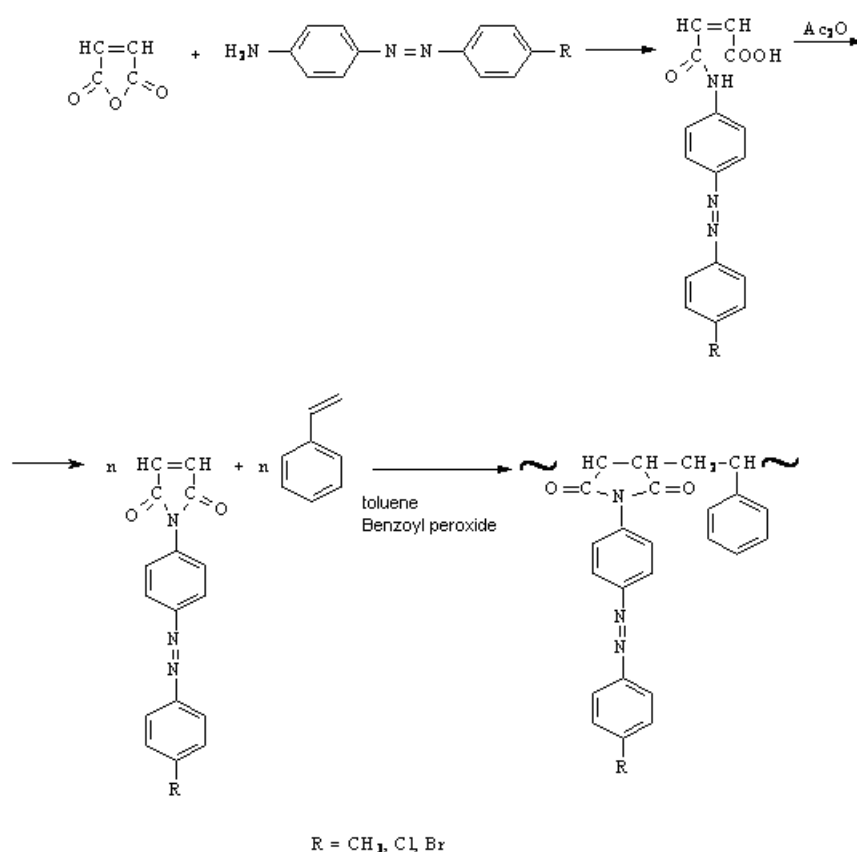


**Fig. 1. The chemical transformation of the copolymer MA-St copolymer**

The amic derivate (Fig. 1.) was obtained by reaction between co-polymer and primary amine (copolymer: amine = 1:1 molar) in N, N-dimethylformamide (DMF) solution at room temperature for 2 hours. Consecutive to the amic acid, imide form was obtained by dehydrating with acetic anhydride/sodium acetate at 60<sup>0</sup>C for 5 hours.

The obtaining of imide form was placed in the presence of acetic anhydride and sodium acetate. Thus, we added to a solution of 4% copolymer (w) the acetic anhydride so that the volume ratio and acetic anhydride /DMF 1: 1 (vol.) and one mole of sodium acetate. The temperature reaction was 60<sup>0</sup>C, the reaction is taking place for 5 hours while stirring. The synthesis yields were about 40%.

For confirming, the structure assigned for photochromic compounds mentioned was carried out in the second stage, the following intersection synthesis:



**Fig. 2. Intersection Synthesis**

The condensation of the amine-chromophore with MA was performed in ethyl ether at an equimolecular ratio of reactants at room temperature, stirring for one hour.

By cooling to  $0^\circ\text{C}$  the colored powder precipitate, which is isolated by filtration and drying. By dissolving it in acetic anhydride and heating on the water-bath in the presence of sodium acetate for 30 minutes takes place the formation of amide monomer, which was precipitated. The product was isolated by filtration, washed with petroleum ether, and dried at room temperature. Table 1 shows data of azoimides maleic acid synthesis.

**Table 1. Synthesis of azoimides maleic acid**

No.	Maleic anhydride		Azoderivate			Diethyl ether (ml)	Acetic anhydride		Imide	
	mol	g	R	mol	g		mol	g	g	$\eta\%$
1	0.02	1.96	$\text{CH}_3$	0.02	4.22	100	0.04	4.08	4.947	85
2	0.02	1.96	Cl	0.02	4.63	100	0.04	4.08	5.544	89
3	0.02	1.96	Br	0.02	5.52	100	0.04	4.08	6.123	86

The styrene copolymerization with azo-imide compounds was achieved by styrene copolymerization with azoimide in equimolecular ratio in the presence of benzoyl peroxide using as solvent T. The process occurs at the solvent reflux temperature within approximately 60 minutes. The copolymer separation takes place by filtration followed by drying at  $60^\circ\text{C}$  till constant mass.

### 3. RESULTS AND DISCUSSIONS

The characterization of materials obtained, for comparison, was made by FT-IR and UV-Vis spectroscopy.

The UV-Vis spectra were recorded in  $\text{CHCl}_3$  solution using a spectrophotometer SECOMAN S750 UV – Vis and FT-IR spectra were recorded on a Bruker EQUINOX 55 with crystal diamond.

The first evaluation was done by FT-IR spectroscopy (Fig. 3.) for both types of materials. The spectra analysis exemplified in Figure 1 reveals the main difference between amic and imide form. Thus, all materials show the characteristic peak sites (1851-1852 and 1776-1777  $\text{cm}^{-1}$  respectively). For amic forms, distinguish the presence of peak from 3600  $\text{cm}^{-1}$  (OH for carboxyl group) and carbonyl peak at  $\approx 1710 \text{ cm}^{-1}$ . The amide I and respectively II bands are located around 1660-1600  $\text{cm}^{-1}$ , 1598-1544  $\text{cm}^{-1}$ . The imide forms are characterized by diminution of peak from 3600  $\text{cm}^{-1}$  simultaneously with the movement carbonyl's peak from (1710 $\rightarrow$ 1700  $\text{cm}^{-1}$ ).

It also noted the reduction of carbonyl's peak from 1851  $\text{cm}^{-1}$  and the appearance of amide III band around 1333  $\text{cm}^{-1}$ . Unfortunately, the absorption bands characteristic to the substituent is not identifiable because are overlapped by the vibration of the skeleton (500  $\text{cm}^{-1}$ ,  $\nu_{\text{Cl}}$  600  $\text{cm}^{-1}$ ,  $\nu_{\text{C-Cl}}$ , 1020-1275  $\text{cm}^{-1}$   $\nu_{\text{C-O-C}}$ ).

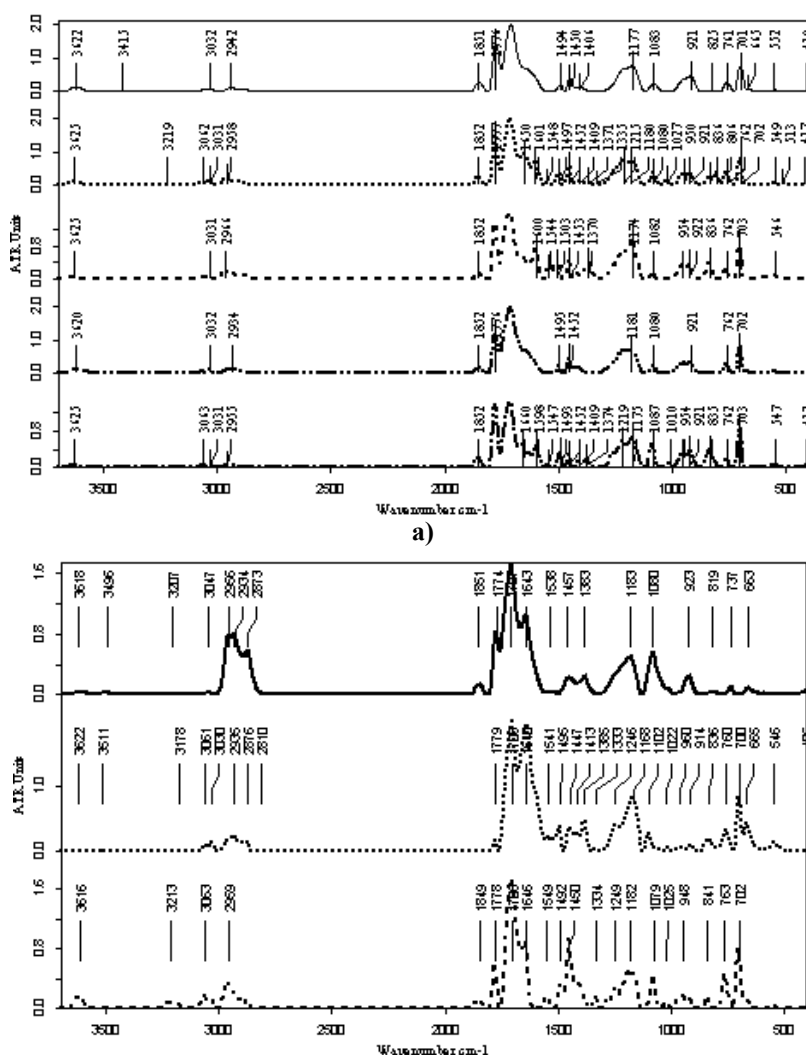


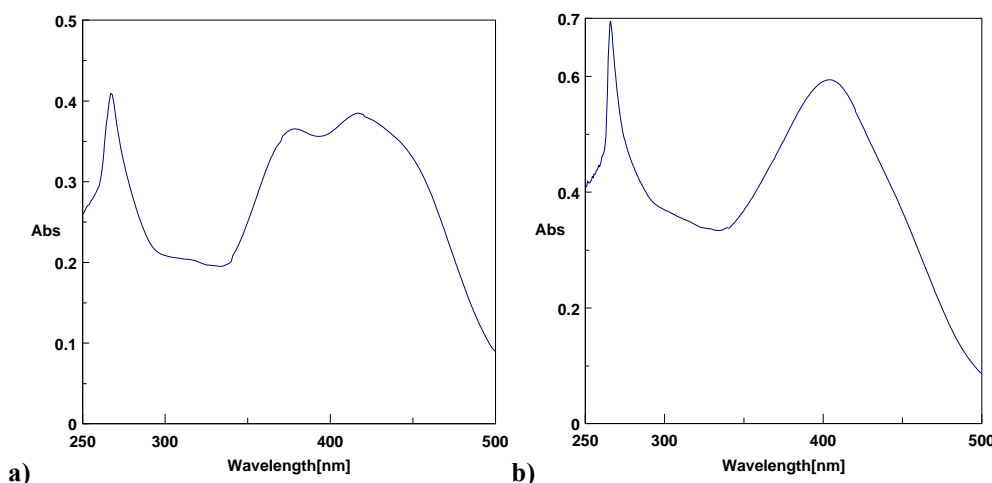
Fig. 3. The examples of FT-IR spectra for MA-St copolymers  
a) amic forms b) imidic forms

**Table 2. The UV-Vis absorption data for dyes and modified polymer**

R	$\lambda_1$ col (nm)	$\lambda_2$ col (nm)	$\epsilon_1$ (L/mol·cm)	$\epsilon_2$ (L/mol·cm)	$\epsilon_1$ cop (nm)	$\epsilon_2$ cop (nm)	X*	Form
-CH <sub>3</sub>	261	403	3790	4327	269	411	0.5873	amic
-Cl	261	406	4693	4337	269	419	0.6056	amic
					272	419	0.6056	imide

\* Fraction of photochromic sequences were evaluate strength on the specific absorption of pure dye and modified polymer  $\left[ x = \frac{A_{dye}}{A_{polymer} + A_{dye}} \right]$ .

The UV-Vis spectroscopy (Fig. 4.) revealed the existences of two maximums of absorption on envelope curve in visible region. This means the existence of two isomeric forms *Z(sin)-E(anti)*. The bathochrome or hypsochrome displacements are a direct consequence of the azo chromophore, responsible on the one hand for the movement of the maximum absorption in visible region. On the other hand, the nature and volume of substituent enhances these phenomena. The selection of solvent (DMF) was required for further use in polymer analogous reactions. The preference for DMF is justified by the fact that it is solvent for both dye and polymer substrate.

**Fig. 4. The UV-Vis spectra for: a) dye and b) amic form**

The imide forms are generally characterized by a bathochrome shift of the second absorption maximum, probably due to stiffness caused by closing of imide ring. In fact, changes occurring in the wavelength of the photochromic structural changes are the result from the coupling reaction with polymer material. The latter have been only support role of chromophore sequences.

Therefore, the inclusion of the chromophore molecules in polymer structure does not spoil the basic optical properties of the chromophore, but they can improve by increasing the chromophore density in unit volume.

#### 4. CONCLUSIONS

The intersection synthesis for photochrome materials by polymer type which including maleinimide–styrene sequences demonstrates the validity of the structure attributed to photochromic materials obtained by polymer analogous reactions starting from MA-St copolymerization.

Based on photocrome study, the polymer films chromophore, with azo groups may be varied photorefractive properties with potential applications in areas such as holographic data storage, photo-switching sensors (On-Off) and others [14-16]. The linearly polarized light interaction with azo chromophore groups in a polymer film can lead to polarization orientation perpendicular to the light of these groups, thus generating the **birefringence and dichroism** [17, 18]. The modelling of the surfaces induced by light is another effect caused by photo-isomerization, which has attracted the attention of many researchers [19, 20].

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