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The analytical control of some photochromic materials

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In this paper we present the analytical results concerning synthesis, characterization of maleic anhydride copolymers with dicyclopentadiene (DCPD) and terpolymer with butyl-vinyl-ether (BVE)-DCPD, modified by condensative coupling reaction with azo photochrome dyes. Spectroscopic analysis (IR, UV-VIS) put into evidence on one hand the characteristic peaks to the initial materials (substrate and chromogen respectively), and on the other additional lines, showing the new polymer-chromogen links. The kinetic analyse supposes the determination of the sin-anti thermal isomerization rate and the determination of isomerization rate was make through the registration of specific absorptions in the UV-VIS area. The main feature of colored polymers is their capacity (as such, or as a mixture with other polymers) to exhibit colour; chemical bonding of chromophore groups would eliminate expensive dyeing techniques, but on the other hand would prevent dye losses (the undesired phenomenon called migration). However, another interesting feature of such structures is their potential to form liquid crystals; this fact allows applications in numerous fields of high technology. Not in the least, we have to mention another set of uses, known in general as non-linear optics (NLO). Polymers have a number of desirable properties which taken together should make them materials of choice for optical devices: may be tailored by conventional synthesis methods to meet specific device requirements (transparency at particular wavelengths and stability at particular temperatures); offer many processing options toward desired device formats which should reduce the cost of active device.

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1. Introduction

The incorporation of photochromic molecules by physical way (dissolution, dispersion) or chemical way (covalent bond) in organic chains (particular polymers) or organic-inorganic hybrids goes to development of a new class of materials, named photochromic materials. These photochromic materials have applications in the unconventional optic area, their properties can be moulding with help of light.

The modification of the properties doesn't referred merely to spectacular modifications of detected macroscopic colour, but also and to same of series microscopic properties which are variable in this transformation. Thus, amazingly consequence of physical order that cause the azo group photoisomerization which are included in polymers can be explicated by photoinduced anisotropy.

For example, the irradiation of photochromic molecules with polarized linear light causes a suite of photoisomerization cycles *E(anti)→Z(sin)→E(anti).* The immediately consequence at microscopic level is the perpendicular orientation of azo sequences on the polarized direction of the excitant radiations. So, from point of view macroscopic it shows a growth of the absorption and index of the refraction on the perpendicular direction of polarization. The subsequent irradiation of the material with unpolarized or circular light, practical remakes the isotropic behaviour previous irradiation. The phenomenon of relaxation is very quick in liquid mediums, in the same time at the rigid matrices level is as much else slow as structural, it is much contortioned.

Among all existing photochromic materials, azo polymers and azo-containing hybrid materials have been particularly studied for their optical properties: the photoinduced phenomena are in general efficient, due to the *E(anti)→Z(sin)* isomerization reaction, which proceeds reversibly with high quantum yields even in solid matrixes. In particular, it is remarkable that the reversibility of the anti-sin isomerization reaction of some azo compounds does not lead to a vanishing of the different photoinduced effects, such as photoinduced anisotropy and optical poling. There have been a limited number of studies dealing with other photochromic compounds; however, spiropyrans, diarylethenes, fulgides, and anils are also worthwhile to consider for some of these linear and nonlinear optical properties.

A great deal of synthetic work has been done to incorporate photochromes in polymers, as either main-chain or side-chain groups, with spacers of different lengths in the last case, and the studies of the influence of molecular interactions of photochromes with the matrix environment and of relaxation processes in all the orientation phenomena described above is an emerging field. The knowledge of these interactions is necessary if one wants to optimize both photoinduced ordering effects and stability of the optically inscribed information. The incorporation of photochromes in sol-gels or their organization in self-assembled monolayers also offers other optical materials with new optical properties.

The incorporation of photochromic molecules in photorefractive polymers could lead to new materials combining several properties (second-order NLO, photoconductivity, and photochromism), which has the potential to achieve reversible and efficient refractive index modulations.

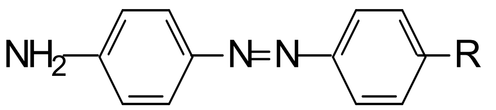
The interest for this class of compounds is justify on a side through the thermo and chemical stability, the easiness of the azo sequences generation, as well as through versatility of this sequences at action of energetic stimuli [1-6].

The goal of this paper regards the synthesis and characterization of the new photochromic materials obtained starting to the two new polymer substrates: maleic anhydride-dicyclopentadiene (MA-DCPD) and maleic anhydride-dicyclopentadiene- butyl vinyl ether. The selection of the maleic anhydride copolymers is justify by MA tendency for forming alternant copolymers, what permits to obtain architectures with big degree of structural regularity as well as of the anhydridic group reactivity in reaction with primary amines [7-10].

2. Experimental

2.1. Synthesis

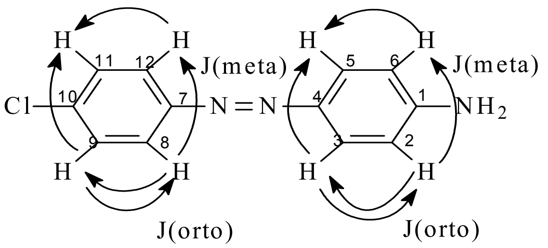
The synthesis and characterization of the azobenzene derivates and the synthesis of the basic copolymers, MA-DCPD and BVE-MA-DCPD respectively, are describes elsewhere [11-15]. For prepare modified polymers with azoderivate sequences, we applied the Patels and co-workers procedure [2], as for amic such as imidic structures. We used for this syhthesis: Maleic Anhydride 99% from Fluka, purified by CH_3Cl recristalyzation; dicyclopentadiene 99%, from Fluka, butyl-vinyl ether from Merck; 2,2'bis azoizobutironitrile (AIBN) as initiator, purified by CH_3Cl/CH_3OH (1:1 vol) recristalyzation. Have used the solvents are 1,4 dioxane and N,N'dimethyleformamide, purified by anhidryzation procedure. The initial characteristics of the polymer substrate are: MA-DCPD: $M_n \approx$ 2300, $X_{MA} \approx 64.65\%$; $GP_n \approx 12$; BVE-MA-DCPD: $M_n \approx 30\ 000$, $X_{MA} = 50\%$ $GP_n \approx 20$.The dyes structure is presented in Fig. 1.

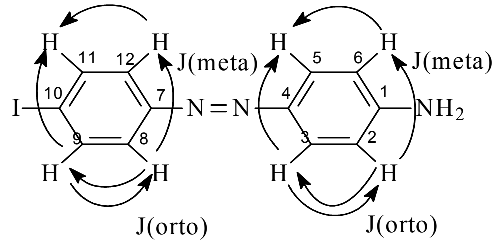


where: R = -Cl (compound I), -I (compound II).

Fig. 1. The azoic dyes structure.

The synthetized compounds were characterized by NMR spectroscopy using an Varian Gemini 300BB apparatus, the frequency of registration be in the case ^{13}C-NMR of 75 MHz, and in the case ^1H-NMR of 300 MHz, using deuterated dimethyl-sulfoxide as a solvent.





The ^1H- NMR spectra for compound I: $(H^6)H^2$ split doublet δ_H: 7.56 ppm with the coupling constants orto J(2,3) = 8.64 Hz; $(H^5)H^3$ split doublet δ_H: 7.80 ppm with the coupling constants orto J(3,2) = 8.64 Hz; $(H^{12})H^8$ split doublet δ_H: 7.67 ppm with the coupling constants orto J(8,9) = 8.64 Hz; $(H^9)H^{11}$ split doublet δ_H: 6.83 ppm with the coupling constants orto J(9,8) = 8.64 Hz.

The ^1H- NMR spectra for compound II: $(H^6)H^2$ split doublet δ_H: 7.87 ppm with the coupling constants orto J(2,3) = 8.00 Hz; $(H^5)H^3$ split doublet δ_H: 7.68 ppm with the coupling constants orto J(3,2) = 8.70 Hz; $(H^{12})H^8$ split doublet δ_H: 7.70 ppm with the coupling constants orto J(8,9) = 8.64 Hz; $(H^9)H^{11}$ split doublet δ_H: 6.72 ppm with the coupling constants orto J(9,8) = 8.64 Hz.

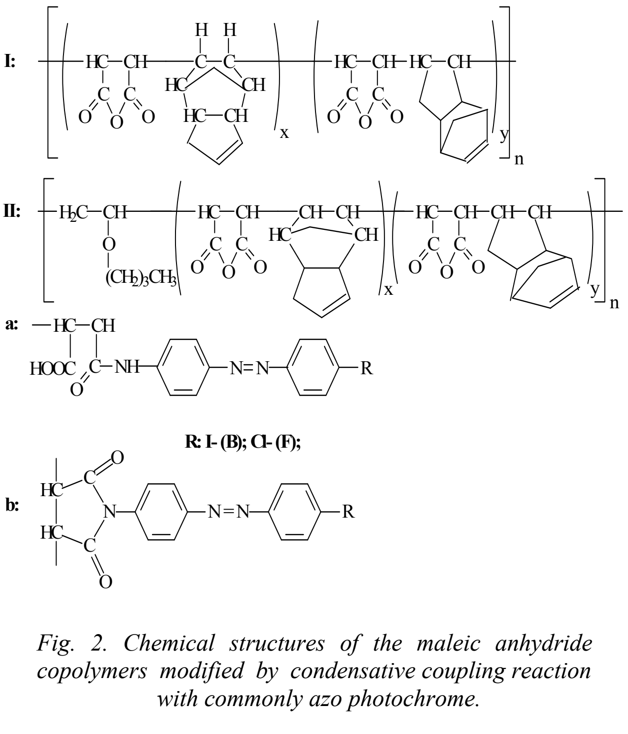


Fig. 2. Chemical structures of the maleic anhydride copolymers modified by condensative coupling reaction with commonly azo photochrome.

2.1. Measurements

The UV–VIS spectroscopy used SECOMAM S750 UV–VIS spectrophotometer utilizing the vat from quartz for record the UV–VIS spectra of the dyes and polymeric materials before and after irradiation with an experimental installation with Hg lamp.

The IR spectroscopy offers the semiquantitative information's concerning material structure. Thus, in accordance with procedures of literature [1, 2] it can appreciated the report between anhydridic and amidic groups, and as well as amidic-imidic. The determinations of IR spectroscopy were made utilized a Testscan - Shimadzu FTIR 8000 apparatus.

The first stage in this study consists in the strict qualitative analysis of synthesised compounds obtained by IR spectra. The imidization is demonstrated through the diminution and the diminution of specific peak for amic acid.

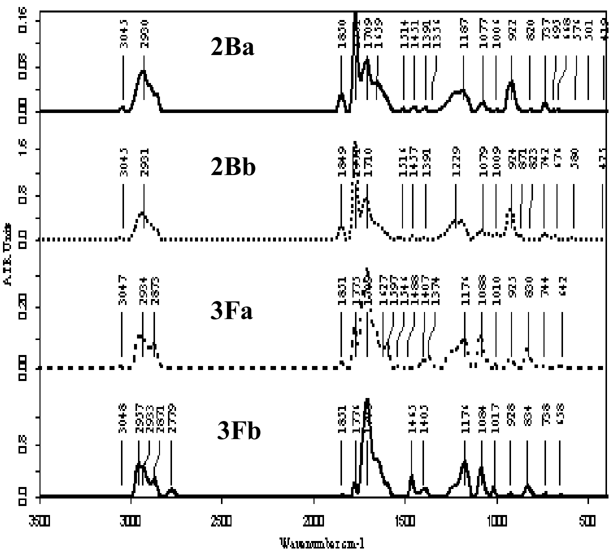


Fig. 3. The exemplifying FT-IR spectra of amic (a) and imidic (b) derivative from MA-DCPD modified with I azoderivat and MA-DCPD-BVE copolymer modified with Cl azoderivate.

In the FT-IR spectra can be distinguished the structural differences between the amic and imide forms of the transformed copolymers and in the same time as the specific vibration band of the copolymer support. Thus, all polymer supports presented the characteristic peaks of the MA (1851-1852 and 1776-1777 cm^{-1}, respectively). For the amic compounds (see Fig. 3) we remark the peaks at 3600 cm^{-1} (OH from the carboxyl group) and the carbonyl peak at ≈1710 cm^{-1}. The amide I and amide II group are situated around 1660-1600 cm^{-1}, 1598-1544 cm^{-1}, respectively.

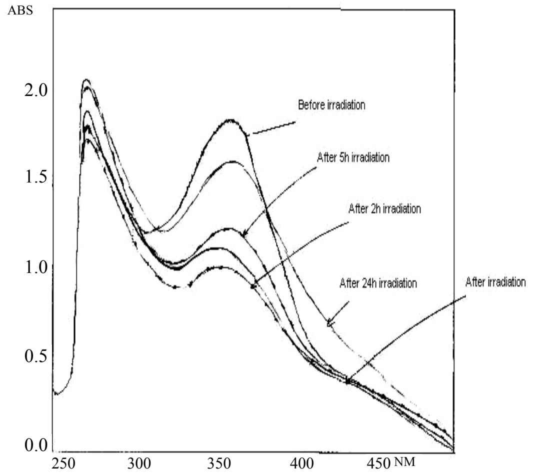
The imide forms are characterized by diminution of the 3600 cm^{-1} peak in the same time with the shift of the carbonyl peak (1710→1700 cm^{-1}).

As the same time is remarked diminution of the peak to the 1851 cm^{-1} and increasing for them to the 1776 and apparition of the amide III band situated around 1333 cm^{-1}. Unluckily, the absorption band characteristic to the substituent is not identifiable. They are overlapped by the vibration of the skeleton (500 cm^{-1}, ν_{Cl} 600 cm^{-1} ν_{CCl}, 1020-1275 cm^{-1} $\nu_{C\text{-}O\text{-}C}$).

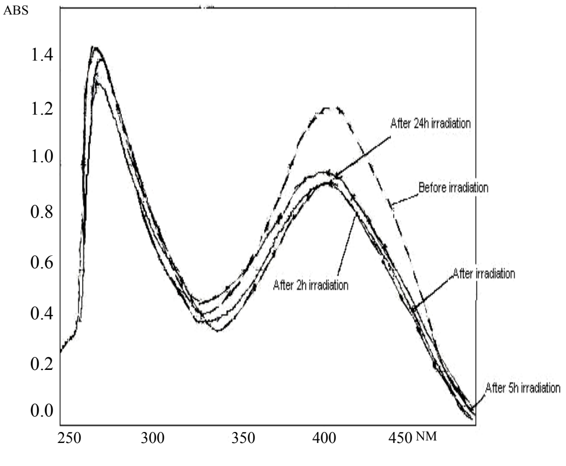
The evidence of major optic properties is banked on the UV-VIS spectroscopy, most accessible method of characterization who hints the formulation of induced structural particularities at the level of polymeric chain by chemical transformation process. The results are synthetically presented in the Table 1 and 2.

Table 1. UV-VIS absorption for chromogen and modified copolymers.

R	λ_1 (nm)		λ_2 (nm)		ε_1 (L/(mol/cm)		ε_2 (L/(mol/cm)		Cop code
	dye	cop	dye	cop	dye	cop	dye	cop	
Cl		270		397					2Fb
	262	272	407	411	2173	4693	1568	4337	3Fa
		272		355					3Fb
I	294	269		397					3Ba
		269	405	380	1075	6307	5360	1141	3Bb
		269		380					2Bb



MA-DCPD b



MA-DCPD-BVE a

Fig. 3. The UV-VIS spectrum for MA- DCPD imidic form and MA-DCPD-BE amic form, before and after irradiation with Hg lamp (250 W) for R = -Cl.

Analysing the results presented in the Table 1 and 2, it is remarked the fact that don't appear the significant modifications of the λ_{max} UV for amic forms for chlorine, just for iodine.

The intensity of absorption before and after irradiation with Hg lamp was measured with the same UV–VIS spectrophotometer. The solutions were exposed to UV light to increase the rate of *Z(sin)-E(anti)* isomerization.

In Fig. 3. were presented the UV-VIS spectrum for MA- DCPD imidic form and MA-DCPD-BVE amic form, before and after irradiation with Hg lamp (250 W) for compound with chlorine.

The modifications that appear at wavelength level are the consequence of photochrom structural modification by coupling reaction with polymeric material (who it has just support role for chromophore sequences). Accordingly, the inclusion of chromophore molecules in polymeric structures doesn't affect basic properties of the chromophore (in main of optic nature).

The existences of two maximums of absorption for all the dyes on covering curve in visible zone indicate the possibility of a micromolecular disturbance of conformational order in the polymer structures that was transformed. All this proved the existence of two isomeric forms *Z(sin)-E(anti)* [11].

The anisotropy was putted in evidence after solutions irradiation with lamp UV. Thus, in conformity with Lambert–Beer law, the percent proportion of *Z(sin)* isomer [10,16], in solution (Table 3) was evaluated on base equation:

$$\% C_s = \frac{1}{E/A + 1}$$

where: C_s = the concentration of Z*(sin)* isomer;

$E = \varepsilon_a/\varepsilon_s$; $A = A_o/A_t$;

ε_a, ε_s = the values of extinction molar coefficients before (a) and after irradiation (s);

A_o = the absorption before irradiation;

A_t = the absorption on proper times subsequent irradiation.

Table 2. The absorption data in UV-VIS area for modified polymers.

Polymer	UV Irradiation	λ_1	A_1	λ_2	A_2
MA-DCPD b (R: - Cl)	Before irradiation	269.7	1.858	397.3	1.892
	After irradiation	269.7	1.970	360.0	1.150
	After 2h from irradiation	269.7	2.052	361.3	1.125
	After 5h from irradiation	269.0	2.088	358.2	1.255
	After 24h from irradiation	269.2	2.111	360.9	1.553
MA-DCPD-BVE a (R: - Cl)	Before irradiation	271.7	1.388	411.0	1.263
	After irradiation	271.7	1.334	408.6	0.933
	After 2h from irradiation	271.9	1.410	409.5	0.916
	After 5h from irradiation	271.8	1.410	409.3	0.939
	After 24h from irradiation	271.7	1.472	408.6	0.975
MA-DCPD-BVE b (R: - Cl)	Before irradiation	271.7	2.478	355.1	1.851
	After irradiation	271.7	2.503	341.4	1.404
	After 2h from irradiation	271.7	2.506	332.6	1.406
	After 5h from irradiation	271.7	2.498	375.5	1.417
	After 24h from irradiation	269.4	2.452	390.1	1.314
MA-DCPD-BVE a (R: - I)	Before irradiation	268.6	2.433	397.3	0.414
	After irradiation	268.7	2.450	370.5	0.400
	After 2h from irradiation	268.6	2.431	379.0	0.315
	After 5h from irradiation	268.6	2.437	397.0	0.492
	After 24h from irradiation	271.3	2.501	379.3	0.543
MA-DCPD-BVE b (R: - I)	Before irradiation	269.0	1.634	379.8	0.301
	After irradiation	269.1	1.608	380.1	0.120
	After 2h from irradiation	269.2	1.615	379.7	0.123
	After 5h from irradiation	269.1	1.621	378.3	0.230
	After 24h from irradiation	269.2	1.629	379.9	0.298
MA-DCPD b (R: - I)	Before irradiation	269.3	2.407	379.7	0.598
	After irradiation	269.7	2.405	379.5	0.304
	After 2h from irradiation	269.1	2.401	379.2	0.433
	After 5h from irradiation	269.3	2.400	379.1	0.511
	After 24h from irradiation	269.3	2.400	379.7	0.539

a = amic form; b = imidic form

Table 3. The Z(sin) percent at different irradiation times.

R	Code *	λ_2 (nm)	±Dλ ** (nm)	% *Z(sin)*			
				inst.	at 2h	at 5h	at 24h
-Cl (support MA-DCPD)	b	397	-	39	40.5	34	27.9
-Cl (support MA-DCPD-BVE)	a	411	-	36	37.5	35.7	32.8
	b	355	(+)21÷35	24	24	23.4	29

* a = amic form; b = imidic form; **: (-) bathochromic movement; (+) hypsochromic movement.

The analysis of synthesized results shows:

- the maximum of absorption modification after irradiation;
- the monotonous decreasing of percent *Z(sin)* isomer after irradiation;
- the *Z(sin)* isomer percent is bigger in the case of imidic forms, which shows a steric hindrance at reversion *Z(sin)–E(anti)*, caused of reinforcing by closing of imidic cycle.

Except of derivatives form MA-DCPD-BVE support with a catena flexibility degree bigger, because of the presence of BVE sequence.

For the same polymeric chain, the *Z(sin)* isomer percent increases in the case of amic forms with the substituent volume and the electron repellent inductive character, meantime at the imidic forms, a inverse evolution is presented.

3. Conclusions

In this work, the preliminary results concerning synthesis and characterisation of photochromic structures obtained by polymer analogue reaction are presented. As polymeric support were used two maleic anhydride copolymers (MA-DCPD, MA-DCPD-BVE), co-reactants of this were been five azo dyes which synthesis wasn't include in specialty literature.

The introduction of chromophore molecules in polymeric chains doesn't affect the basic properties of the chromophore (in main of optic nature), but can improves them.

The chemical bonding of azoic chromophores at carbocatenary polymers presents multiple advantages, inclusively the easiness of photochromic properties investigation and the *Z(sin)-E(anti)* transformations [11-12].

References

[1] S-S Lee, T.O. Ahn, Journal of Applied Polymer Science, Direct polymer reaction of poly(styrene-*co*-maleic anhydride): Polymeric imidization, **7**, 1187 (1999).

[2] J. S. Parmar, C. G. Patel, D. K. Patel, High Performance Polymers., Functional poly(N-phenylmaleimide) as a cation exchanger – II, **3**(2), 89 (1991).

[3] J. A. Delaire, K. Nakatani, Chem. Rev.; (Review), Linear and Nonlinear Optical Properties of Photochromic Molecules and Materials, **100**(5), 1817 (2000).

[4] A. Natansohn, P. Rochon,Chem. Rev., (Review); Photoinduced Motions in Azo-Containing Polymers, **102**(11), 4139 (2002).

[5] A. Natansohn, P. Rochon, M.Pezolet, P.Audet, D. Brown, S. TO, Macromolecules, Azo Polymers for Reversible Optical Storage. 4. Cooperative Motion of Rigid Groups in Semicrystalline Polymers, **27**(9), 2580 (1994).

[6] P. Rochon, J. Gosselin, Applied Physics Letters, Optically induced and erased birefringence and dichroism in azoaromatic polymers, **60**(1), 4 (1992).

[7] B. C. Trivedi, B. M. Culbertson, cap.10-Alternanting addition copolymerizations. Maleic Anhydride, Plenum Press, New York,1982, p.337.

[8] A. Natanshon, P. Rochon, Canadian Journal of Chemistry./Rev. can. chim., The versatility of azobenzene polymers **79**(7), 1093 (2001).

[9] D. Hore, A. Natanshon, P. Rochon, Canadian Journal of Chemistry./Rev. can. chim., Irradiance and temperature dependence of photoinduced orientation in two azobenzene-based polymers, **76**(11), 1648 (1998).

[10] H. J. Haitjema, G. L. Von Morgen, Y. Tan, G. Challa, Macromolecules, Photoresponsive Behavior of Azobenzene-Based (Meth)acrylic (Co)polymers in Thin Films, **27**(21), 6201 (1994).

[11] I. Ioniță, A.-M. Albu, C. Tărăbașanu–Mihailă, R. Bădulescu, C. Rădulescu, Photochromic polymeric materials. Synthesis and characterization, International Conference Polymeric Materials 2004, 29 september-1 october 2004, Halle/Saale, Germany, PI40.

[12] I. Ioniță, C. Tărăbășanu–Mihailă, C. Rădulescu, The Annals of University Ovidius Constanta, Azo dyes with photochromic proprieties, vol. XIV, 2003, p.118-121.

[13] E. Rusen, B. Marculescu, A.-M. Albu, D. M. Vuluga, A. Boborodea, D.S. Vasilescu, , Polym. Int. **54**, 215 (2005).

[14] B. Marculescu, E. Rusen, A.-M. Albu, D. Stanciu, D. S. Vasilescu, J. Macromol. Sci., Part A **43**(2), 383 (2006).

[15] E. Rusen, B. Marculescu, A.-M. Albu, D. S. Vasilescu, , Polym. Bull. **56**, 369 (2006).

[16] J. Krzysztof, M. Katarzyna, S. Juliusz, Materials Science, Kinetics of photochemical processes in photochromic azobenzene derivatives.Effect of matrix and of the phase stability **20**(3), 45 (2002).

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