# Cinnamates VI. Light-sensitive polymers with pendent *o*-, *m*- and *p*-hydroxycinnamate moieties

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*(Received 22 December 1992; revised 30 June 1993)*

In this paper, we outline the photochemical and spectroscopic properties of a new class of light-sensitive polymers obtained as a result of poly(styrene-*co*-2-bromoethyl methacrylate) and chloromethylated polystyrene modification by attaching a pendent hydroxycinnamate group. These specific cinnamates after addition of tertiary amine display characteristic dual fluorescence. Dual emission is attributed to the presence of two different forms of phenol group. Analysis of the kinetic data of the formation of the ionized form indicates a substantial difference between the polymeric and monomeric systems. Simultaneously, the addition of tertiary amine causes quenching of the singlet excited state. As a result, a sharp decrease in the sensitivity is observed. It is also shown that hydroxycinnamates are sensitive in both the neutral and ionized forms of the light-sensitive group. Based on experiments, a kinetic scheme for the processes taking place during irradiation is proposed.

**(Keywords: light-sensitive polymers; hydroxycinnamate pendants; photochemistry)**

## INTRODUCTION

Photopolymers are polymers that under direct ultraviolet or visible irradiation undergo a phototransformation leading to the formation of an insoluble product. The majority of photocrosslinkable polymers that have been studied have been prepared by the reaction of a functionally reactive photosensitive moiety with a polymer backbone[1-6]. The classical forerunner of this group, poly(vinyl cinnamate), is based on the reaction of cinnamoyl chloride with poly(vinyl alcohol) at the correct temperature[1]. Use of suitable chemical conditions allows the light-sensitive group to bond even to polysiloxane copolymers[7].

Most authors have studied polymers containing unsaturated aromatic acid moieties, e.g. cinnamic acid ester moiety, cinnamic acid derivatives[6,8-10] or cinnamylidene acetate derivatives[11,12]. A particularly interesting group of light-sensitive polymers are those containing more complex pendent cinnamates, e.g. the pendent *N*-(benzylidene)-4-acrylaniline ester group[13], the *N*-(4-acrylbenzylidene)aniline group[14] or the polymer with the 4-(dimethylamino)cinnamate moiety[15,16]. The former is an example of a photopolymer containing a chromophore with typical intramolecular charge-transfer properties. The other kind of light-sensitive polymer contains the *p*-phenylenebis(acrylic acid) moiety[17,18] built in a linear polyester chain.

The sensitivity of the negative-type photopolymers depends on the structure of the light-sensitive group. The improvement of the efficiency of photocrosslinking can be attained by the following methods: (1) employing suitable sensitizer[1,19,20]; (2) introducing as many light-sensitive groups as possible into the polymer chain; (3) preparing the proper mixture of two polymeric systems[21]; or (4) modifying the photofunctional group[13,16].

Therefore, it is important to describe the nature of various photochemical and photophysical processes leading to an increase or decrease in sensitivity of photopolymers containing more complex light-sensitive groups. It is our intention in this work to outline the photochemical properties of a new class of light-sensitive polymers containing the cinnamate pendent group. The tested polymers contain pendent hydroxycinnamate moieties covalently bonded to the polymer backbone.

## RESULTS AND DISCUSSION

### *Synthesis*

The light-sensitive polymers with pendent hydroxycinnamate groups (see *Scheme 1*) were successfully prepared by esterification of the bromoethyl group of poly(styrene-*co*-2-bromoethyl methacrylate) or of chloromethylated polystyrene (poly(styrene–vinylbenzyl chloride)) using potassium salts of *o*-, *m*- and *p*-hydroxycinnamic acids. The syntheses of light-sensitive polymers with pendent *o*-hydroxycinnamate (poly-*o*HC), *m*-hydroxycinnamate (poly-*m*HC) and *p*-hydroxycinnamate (poly-*p*HC) moieties were carried out in dry dimethylformamide (DMF) below 40°C, using tetrabutylammonium bromide (TBAB) as phase-transfer catalyst. The potassium

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0032-3861/94/04/0692-07

salt of the appropriate hydroxycinnamic acid was prepared after comparison of p$K_a$ values of carboxylic groups and phenolic groups of hydroxycinnamic acids[22]. The starting poly(styrene-*co*-2-bromoethyl methacrylate) was prepared by free-radical polymerization (see 'Experimental' section) of 2 mol of styrene and 1 mol of 2-bromoethyl methacrylate in bulk using benzoyl peroxide as free-radical initiator. Chloromethylated polystyrene (poly(styrene–vinylbenzyl chloride)) was prepared by copolymerization of 3 mol of styrene and 1 mol of vinylbenzyl chloride (mixture of 60% *meta* isomer and 40% *para* isomer). The resulting polymers contain 2.22 mmol g$^{-1}$ of $-CH_2Br$ groups (theoretically 2.50 mmol g$^{-1}$) and 2.15 mmol g$^{-1}$ of $CH_2Cl$ groups respectively.

The microstructure of the tested polymers can be confirmed after analysis of the following properties and data: (i) The resulting polymers are quite soluble in a series of solvents. This shows that there is no reaction involving phenolate residue, because otherwise the products would be crosslinked and completely insoluble. Additionally, the i.r. spectra of poly-HCs indicate the presence of –OH groups. (ii) The n.m.r. spectra of the monomeric equivalents obtained below 40°C and using a large excess of hydroxycinnamic acid potassium salts (the condition applied for the synthesis of poly-HCs) do not indicate the presence of the phenyl ether residue. $^1$H n.m.r. spectra of polymers show a close relation between the n.m.r. spectra of polymers and their monomeric equivalents. (iii) The absorption and emission spectra indicate the presence of phenolate residue (dual fluorescence spectra).

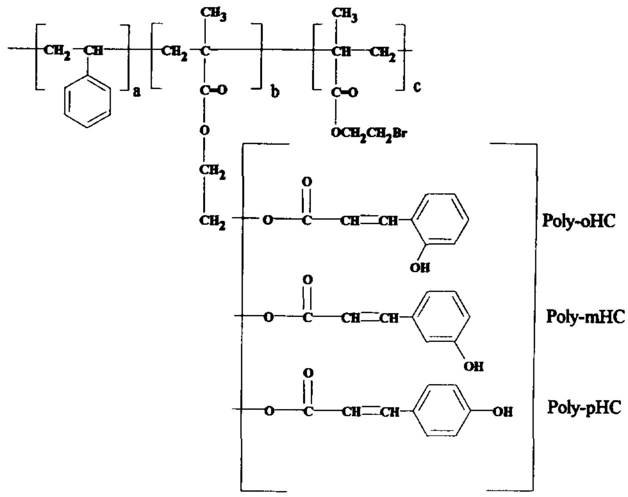
All the above-mentioned properties of the polymers and their monomeric equivalents allow one to establish the structures of the polymers studied (*Scheme 1*).

Using similar methods as for poly-HCs, polymers containing the methoxy group at *ortho*, *meta* and *para* positions were prepared (poly-*o,m,p*-MC). Additional syntheses were performed using chloromethylated polystyrene, giving PS-*o,m,p*HC. The basic properties of the resulting polymers are summarized in *Table 1*.

### *Photochemical and spectroscopic properties*

Spectroscopic properties were characterized by both absorption and emission spectra. The electronic absorption spectra of both the light-sensitive polymers and their monomeric equivalents are strongly affected by the pH of the solution. *Figure 1a* shows the electronic absorption spectra for propyl-2-hydroxycinnamate (P2HC) in hexane and in MeOH solutions. The electronic absorption spectra for P2HC in hexane, in hexane plus 1,4-diazabicyclo[2.2.2]octane (DABCO) and in hexane with a trace of NaOH are shown in *Figure 1b*. The absorption spectra for poly-*o*HC film in neutral form and for the ionized form of hydroxycinnamate residue are presented in *Figure 1c*. From the figures one can see that hydroxycinnamic acid can form in its ground state two differently charged species, e.g. protonated (neutral) and ionized forms of the phenolate function. *Figures 2–4* show the absorption and fluorescence spectra of all tested polymers. The electronic absorption data are also summarized in *Table 1*.

Hydroxycinnamic acid can form two differently charged species in solution owing to the presence of two



Scheme 1

Table 1 Characteristics and the electronic absorption data of tested polymers

| Polymer | Solvent | $A_{\lambda_{max}}$ (nm) | $A/g^a$ | $\varepsilon_{\lambda_{max}}$ monomer | $X_{Hal}{}^b$ (mmol g$^{-1}$) | $X_{CA}{}^c$ (mmol g$^{-1}$) |
|---|---|---|---|---|---|---|
| Poly-*o*HC | $CHCl_3$ | 280–282 | 4.24 | 20300 | 1.62 | 0.60 |
| | | 323–325 | 1.92 | 6700 | | |
| | Film | 280–282 | – | – | | |
| | | 328–330 | – | – | | |
| Poly-*m*HC | $CHCl_3$ | 283–285 | 3.59 | 19700 | 1.46 | 0.72 |
| | | 320 | 1.20 | 6570 | | |
| | Film | 280–282 | – | – | | |
| | | 320–322 | – | – | | |
| Poly-*p*HC | $CHCl_3$ | 313–315 | 3.81 | 13500 | 1.62 | 0.60 |
| | Film | 313–315 | | | | |
| PS-*o*HC | $CHCl_3$ | 278–280 | 18.63<br>9.54 | – | 0.99 | 1.16 |
| PS-*m*HC | $CHCl_3$ | 283–285 | 9.72<br>2.69 | – | – | 2.15 |
| PS-*p*HC | $CHCl_3$ | 313–315 | 11.61 | – | 0.459 | 1.691 |

[a] Measured absorption of a 1 g l$^{-1}$ polymer solution at the maximum of absorption spectra
[b] Contamination of bromomethyl or chloromethyl groups in polymers after esterification
[c] Contamination of cinnamate residue in tested polymer

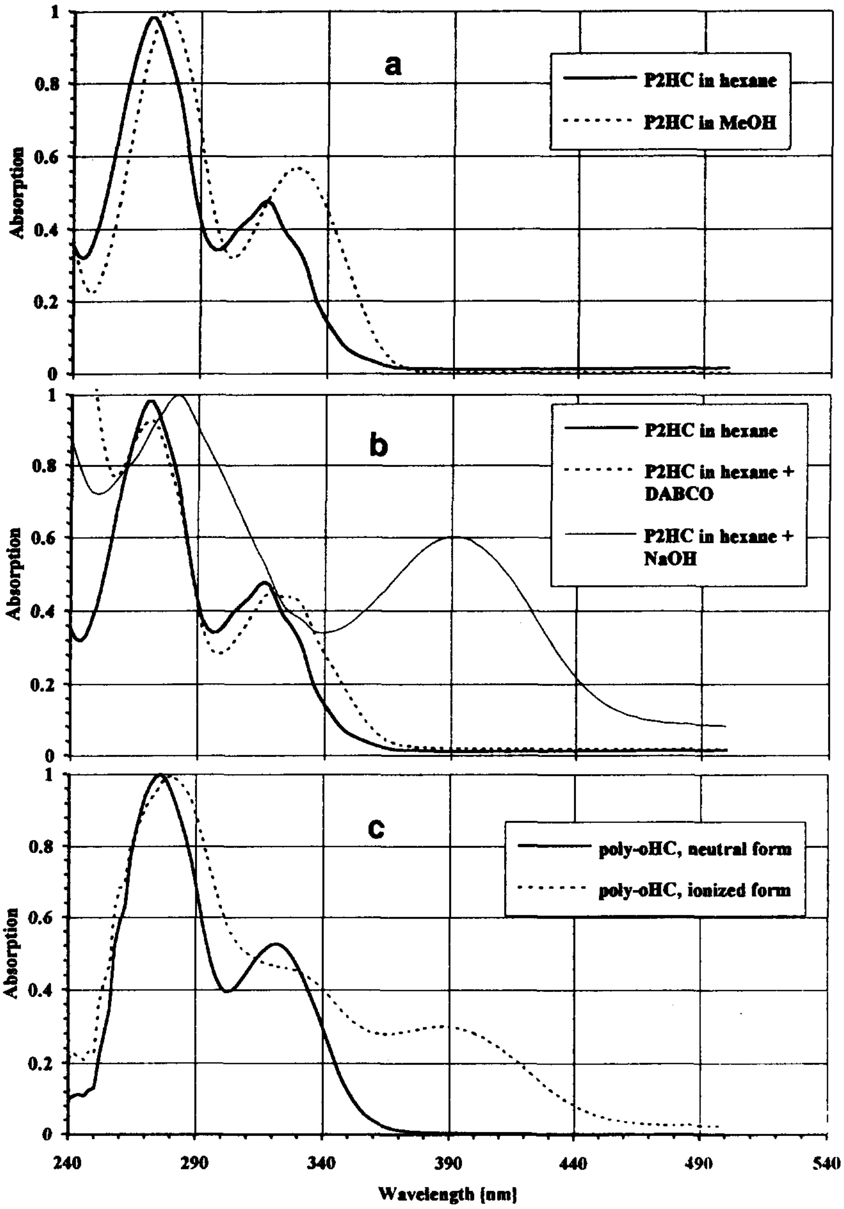


**Figure 1** The electronic absorption spectra of P2HC and poly-*o*HC in various solvents, in the presence of organic base (tertiary amine DABCO) and inorganic base (NaOH) — see text for further details

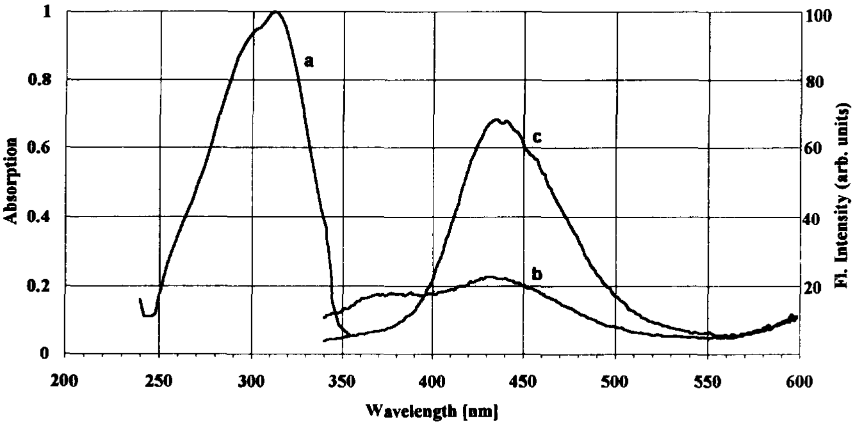


**Figure 2** The electronic absorption and fluorescence emission spectra of poly-*p*HC: (a) absorption spectrum in $CHCl_3$ solution, (b) fluorescence spectrum, and (c) fluorescence spectrum after DABCO ($1 \times 10^{-2}$ M) addition

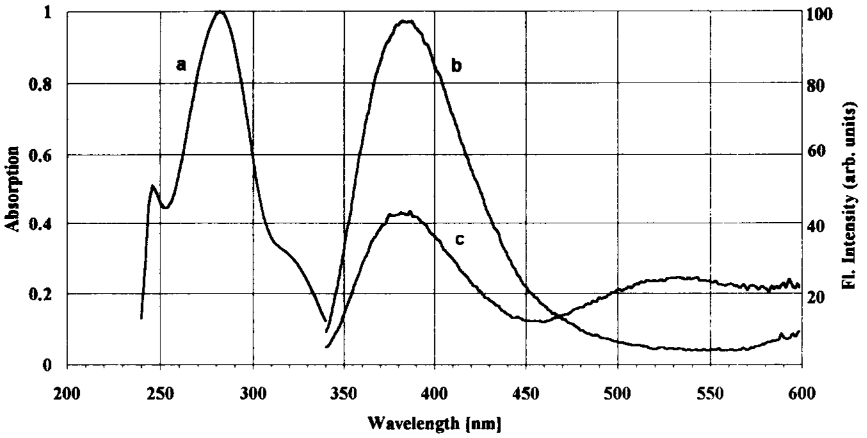


**Figure 3** The electronic absorption and fluorescence emission spectra of poly-*m*HC: (a) absorption spectrum in $CHCl_3$ solution, (b) fluorescence spectrum, and (c) fluorescence spectrum after DABCO addition ($1 \times 10^{-2}$ M)

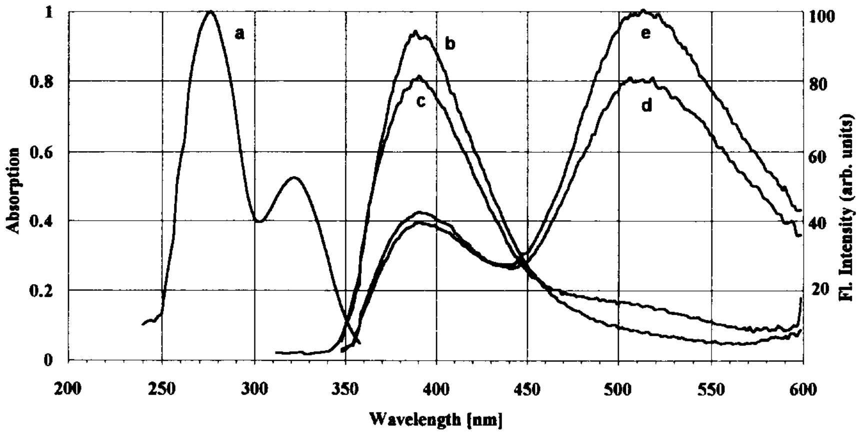


**Figure 4** The electronic absorption and fluorescence emission spectra of poly-*o*HC in $CHCl_3$ solution: (a) absorption spectrum, (b) fluorescence spectrum, (c) fluorescence spectrum after DABCO addition ($1 \times 10^{-2}$ M), (d) fluorescence spectrum after addition of DABCO ($2 \times 10^{-2}$ M), and (e) fluorescence spectrum for DABCO concentration of $5 \times 10^{-2}$ M

hydroxy groups capable of dissociation[22]. Polymeric and monomeric derivatives of hydroxycinnamic acid exist in the ester form; so the electronic absorption spectra of analysed photopolymers can be treated as the absorption spectra of phenols. The long-wavelength and weaker bands at 320–330 nm are bands of the displaced and intensified long-wavelength transition of the aromatic $\pi$-electron system. The intense absorption at 280 nm ($\varepsilon$ over 10 000) marks an electron transfer (ET) transition in which a p electron of oxygen is transferred to the $\pi$ orbital of the system. The latter process requires less energy in the anion than in the protonated form. As a result, the $\lambda_{max}$ of the anionic form of phenol is red-shifted. The formation of the anionic form requires relatively low pH value and, as *Figure 1* illustrates, needs the presence of a strong inorganic base. The slight red-shift caused by the addition of DABCO can be explained as a solvent polarity effect on the ET transition, rather than ionization of the phenolate group.

The fluorescence emission spectra of tested polymers are more interesting. Only one single fluorescence band is observed at room temperature for poly-HCs, PS-HCs and their monomeric equivalents in various solvents as well as in polymeric films (see *Figures 2–4*). It is well known that there are large differences in the p$K_a$ values of the ground and first excited singlet states of phenols[23,24]. The single fluorescence band indicates that, even in the first excited state, the acidity of the phenol group remains weak. In order to observe whether the emission from the excited anionic form exists, a tertiary amine (DABCO) was added to the solution of the polymer or its monomeric equivalent. It is apparent (*Figures 2–4*) that a new broadened, red-shifted emission band appears in the fluorescence emission. The efficiency of the long-wavelength emission is DABCO-concentration-dependent. It is necessary to emphasize that the addition of DABCO to the solution and solid film of poly-MCs does not change the character of the emission spectra. Based on Förster's theory[23,24], we attribute the blue emission bands to the fluorescence of neutral hydroxycinnamates, while the green emission is assigned to the excited phenolate anion. The fluorescence emission data are summarized in *Table 2*.

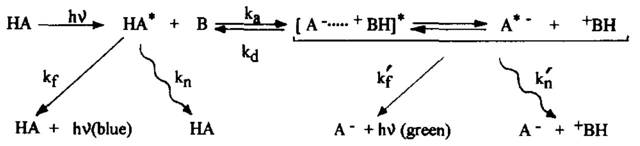
The mechanism of formation of the ionized form can be described by adapting the model used for the description of excited-complex (exciplex) formation. For illustration, we present the analysis of the properties for poly-*o*HC an P2OH.

The process of excited-state ion-pair formation can be described as in *Scheme 2*. In that scheme: HA is

**Table 2** Summary of the fluorescence data of light-sensitive polymers studied

| Polymer | Solvent | $F_{\lambda_{\max}}$ (nm) | Anionic form $F_{\lambda_{\max}}$ (nm) | Notes |
|---|---|---|---|---|
| Poly-*o*HC | Benzene | 380–381 | 491–492 | |
| | $CHCl_3$ | 392–392 | 504–505 | |
| | DMF | 413–414 | 520–521 | |
| | Film | 392–393 | 485–486 | |
| Poly-*o*MC | $CHCl_3$ | 384–385 | – | Addition of DABCO quenches $I_F$ |
| | Film | 387–388 | – | |
| Poly-*m*HC | Benzene | 379–380 | 493–494 | Quenches |
| | $CHCl_3$ | 392–393 | – | |
| | DMF | 414–415 | – | |
| | Film | 384–385 | ~495[a] | |
| Poly-*m*MC | $CHCl_3$ | 381-382 | – | Addition of DABCO quenches $I_F$ |
| | Film | 381-382 | – | |
| Poly-*p*HC | Benzene | 365–367[a] | 420–421 | |
| | $CHCl_3$ | 370–372[a] | 431–432 | |
| | DMF | 379–380[a] | 441–442 | |
| | Film | 367–369[a] | +[a] | |
| Poly-*p*MC | $CHCl_3$ | 378–380[a] | – | Addition of DABCO quenches $I_F$ |
| | Film | 355–360[a] | – | |

[a] Extremely weak emission
Luminescence properties for PS-HCs are similar to that observed for poly-HCs
Addition of NaOH to the polymer solution or film leads to the exclusive emission from anionic form excited state



**Scheme 2**

hydroxycinnamic acid in its ground state and HA* the excited singlet state; B is the organic base, $[A^{-}\cdots\cdots{}^{+}BH]^{*}$ the excited-state tight ion pair, $A^{*-}$ the anionic form of the excited singlet state and $^{+}BH$ the protonated organic base; $k_f$ and $k_f'$ are the rate constants related to the fluorescence emission of protonated and dissociated excited singlet states; and $k_n$ and $k_n'$ are the rate constants of the non-radiative deactivation of the protonated and ionized excited singlet states of hydroxycinnamate.

The relative quantum-yield measurements for both fluorescence components $\Phi/\Phi_m$ (where $\Phi_m$ is the maximum fluorescence quantum yield for protonated form) and $\Phi'/\Phi_m'$ (where $\Phi_m'$ is the maximum fluorescence quantum yield for ionized form) as a function of triethylamine (TEA) concentration for P2HC and poly-*o*HC are presented in *Figure 5*.

From the results shown in *Figure 5* one can see a slight difference between the monomeric and polymeric systems. It is possible to conclude that the polymeric chain forms a specific microenvironment, changing the properties of both fluorescence emissions. Assuming the fluorescence lifetime to be the same for a cinnamate residue for polymeric and monomeric systems, one can conclude that the $K_a$ value differs for both systems. This might be controlled by the polymeric chain close to the fluorescing molecule[25].

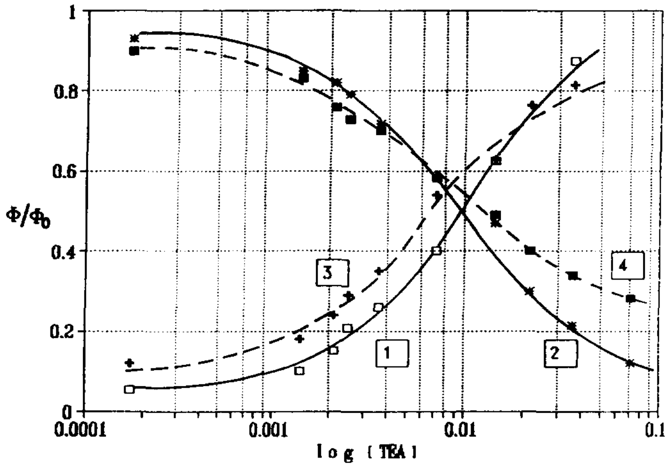


**Figure 5** The relative fluorescence quantum yield for emission from neutral form (negative slopes) and ionized form (positive slopes) for: monomeric system, curves 1 and 2; and polymeric system, curves 3 and 4

Additional information describing the influence of the polymeric chain on the fluorescing molecule can be obtained from measurements of fluorescence quenching for the monomeric and polymeric derivatives of methoxycinnamate. *Figure 6* presents the classical Stern–Volmer relationships for P2MC and poly-*o*MC. The phenomenon observed is as one expects. There are substantial differences between properties observed for a free molecule and for the molecule covalently attached to the polymeric chain.

From the data presented in *Figures 5* and *6*, one can conclude that the polymeric chain, owing to the formation of a specific microenvironment, distinctly affects the photophysical process of luminescing hydroxy- or methoxycinnamate molecules.

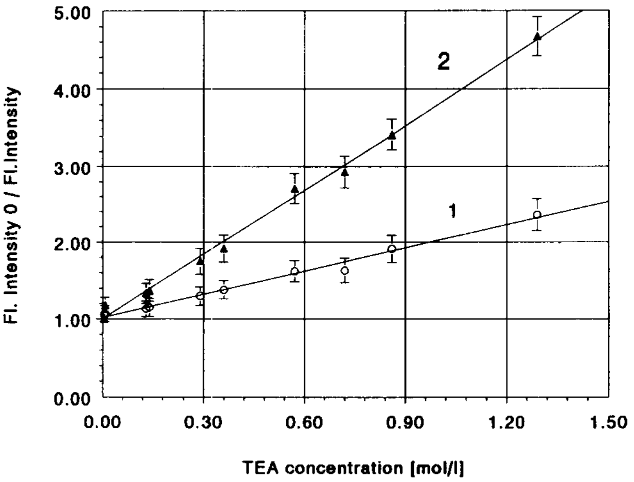


**Figure 6** Stern–Volmer plots for P2MC (curve 2) and poly-*o*MC (curve 1)

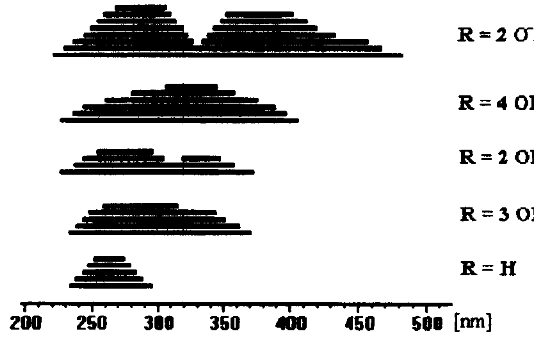


**Figure 7** Spectrosensitograms of the tested photopolymers

### *Photochemistry of solid poly-HCs*

From the light-sensitivity point of view, the main question is whether the addition of the proper amount of compounds forming the phenolate anion (tertiary amine) to the polymeric system increases or decreases the sensitivity of the polymer. In order to confirm this experimentally, the spectrosensitograms for the tested polymers have been made (*Figure 7*). The addition of DABCO to poly-HCs causes a sharp decrease in sensitivity.

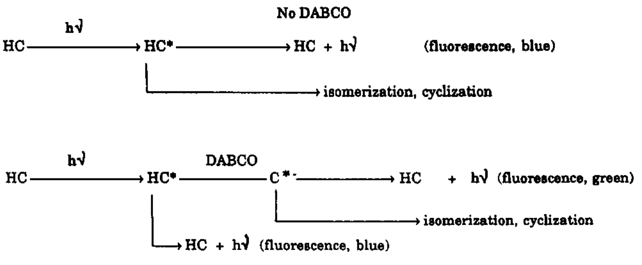
There are several possible explanations for the observed phenomenon. First, it is possible that the anionic form is not light-sensitive; a second explanation is that DABCO quenches the excited states of the tested polymers. Both possibilities were confirmed experimentally.

The different p$K_a$ values for phenols in their ground and excited states (reaches 8.3 p$K_a$ units between $S_1$ and $S_0$ states[22]) suggest that the $S_1$ excited state of the phenolate anion is formed after excitation of the undissociated form of hydroxycinnamate. Consequently the formation of the phenolate anionic form in the singlet excited state requires much lower concentration of base (DABCO) than the formation of the anionic form in the ground state. *Figure 1* shows that the addition of DABCO does not cause the formation of the phenolate anion in the ground state.

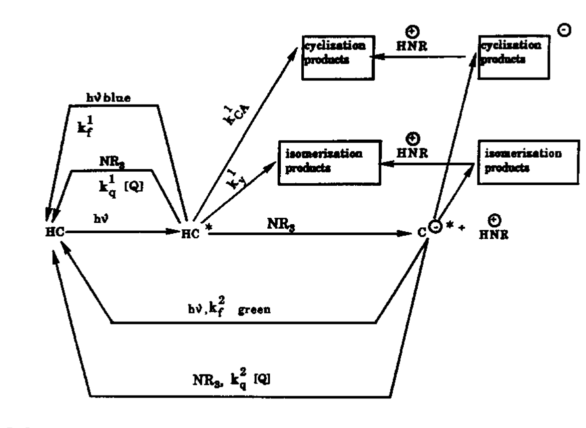
The red-shift for spectral sensitivity of tested polymers requires the red-shift in the absorption spectra. The addition of DABCO, even at high concentration (*Figure 1*), only slightly changes the character of the absorption curves (solvent polarity effect). From a study of the photophysical properties of the tested light-sensitive group in solution, it is known that the addition of a tertiary amine quenches the excited singlet state. The green emission of poly-HCs occurs at a concentration lower (by two orders of magnitude) than the necessary DABCO concentration required for visible change in the absorption spectra. Consequently, we can conclude that the main reason for the sensitivity decreasing is the excited-state quenching process. On the other hand, the transformation of protonated phenolate forms of poly-HCs into sodium salts changes the spectral sensitivity of the polymers. This indicates that the anionic form of hydroxycinnamate remains light-sensitive and shifts sensitivity to the red.

The experiments show that the kinetic scheme shown (*Scheme 3*) can explain the observed properties for the poly-HCs, if $k_q[Q][HC^*]+k_q[Q][C^{-*}]>k_{CA}[HC^*]+k_{CA}[C^{-*}]$.

Continued irradiation at $\lambda_{max}$ causes complex changes in the electronic absorption spectra both in polymeric film and in solution. *Figure 8* illustrates the type of changes observed upon irradiation at 280 nm. Analysis of the properties of the monomeric equivalents of the tested polymeric systems, the properties of 1,3-trimethylene dihydroxycinnamates[26] and behaviour of the light-sensitive polymers do not allow one to separate the various kinds of photochemical processes caused by irradiation. Analysis of the data from *Figure 8* does not allow one to separate the cyclization, *trans–cis* isomerization and coumarine formation (only for 2-hydroxycinnamate) processes. Based on Schnabel and Frings' work[27], one can conclude that all processes take place in the polymeric systems. *Scheme 4* summarizes all the possible processes taking place in the irradiated poly-HCs, both in the solid film and in solution.



Scheme 3



Scheme 4

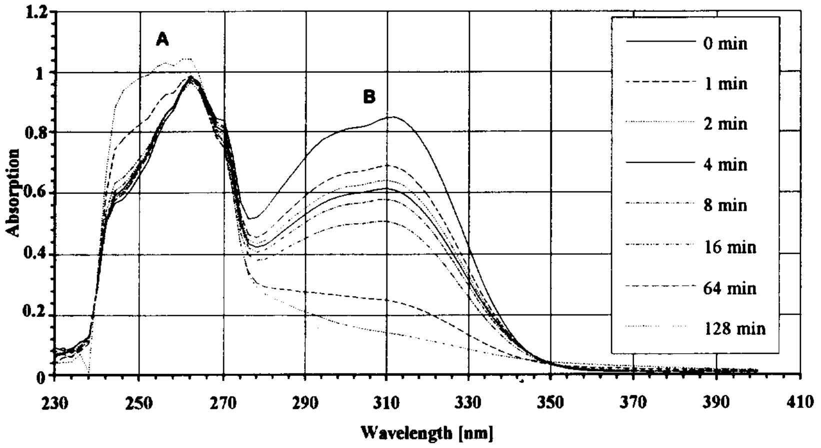


**Figure 8** The changes of the electronic absorption spectra of poly-*p*HC in $CHCl_3$ solution during continuous irradiation; times of irradiation as indicated in the legend. Part A of the spectra displays the absorption of the polymeric carrier, part B is the absorption of the light-sensitive group

## EXPERIMENTAL

Hydroxycinnamic acids were purchased from Merck. All solvents were spectroscopic grade (POCH, Poland; Merck) and were used without further purification. The electronic absorption spectra were recorded with an HP 8452A Diode Array Spectrophotometer. The steady-state luminescence measurements were carried out using multifunctional modular Cobrabid MEF 102 and Hitachi F 4500 spectrofluorimeters. The continuous monochromatic irradiation was from a Cobrabid high-intensity monochromator fitted with a Philips CXS 150 W lamp.

The spectrosensitograms were obtained using the ISP-30 (Russia) spectrograph fitted with an XHP 900 W xenon high-pressure lamp (Tungsram). The intensity of the light was modulated by a grey scale placed in the optical path of the apparatus. The spectrosensitivity measurement method was described earlier[15]. The $^1$H n.m.r. spectra were performed using a Varian XL-200 (200 MHz) spectrometer. The high-pressure gel permeation chromatograms were run on a Waters Associates instrument with u.v. detection and $\mu$-Styragel columns.

Synthesis procedures are described in our earlier paper[28].

## ACKNOWLEDGEMENTS

This work is supported by the Polish Academy of Sciences, grant CPBP 01.14, subject 3.11, and in part by KBN grant No. 7 7709 92 03

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