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Synthesis and Photochemical Crosslinking of Block Copolymers: Styrene-Isoprene Grafted with Photosensitive Groups

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Summary

This paper is relative to the synthesis and the photocrosslinking of a copolymer (styrene/isoprene) which is grafted with cinnamic structures, to give high added value to hydrocarbon polymers. The films of copolymers are irradiated in the presence of photosensibilizers and the decrease of double bonds are analysed by UV spectroscopy.

Introduction

The field of photocrosslinkable polymers is very large, and the change in solubility of many photocrosslinking systems is exploited in many applications of the photoresist layer.

Numerous film-forming polymers with cinnamic structures have been proposed (1-5). The photosensitive group belongs to a monomer which is polymerized (6-8). The photosensitive group is also introduced by grafting the cinnamic structures on the chain for example by condensations of cinnamoylchloride on the polyvinyl alcohol (9-10) or by condensations with modified polystyrene (11-12). In the last case the grafting on the backbone was about 3.5% which is not enough to obtain high crosslinking. In our case we have used block copolymers (isoprene-styrene , butadiene/styrene, styrene/isoprene/styrene) highly grafted to give them photocrosslinking and filmogenic properties. The hydrocarbon polymeric chain is metallated with sBuLi/TMEDA and grafted with oxirane under any of the conditions described in the previous paper (13). The cinnamoyl chloride is condensated with the hydroxyl functions and these grafted polymers are functionalized up to 40% of the units of the chain.

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Experimental

The block copolymer styrene/isoprene (25/75) grafted with oxirane was prepared according to the procedure of the previous paper (13). $\bar{M}_n$ = 15 000. The yield of grafting is 40%. The condensation of the cinnamic groups is carried out - by reaction between polyol and cinnamoyl chloride in HMPT solvent - or by the reaction of cinnamoyl chloride on the sodium polyalcoholate in THF solvent.

Qualitative test : the photosensitive grafted copolymers I/S, S/I/S, are coated on metallic plate (aluminium) and exposed to the light behind a glass filter to give a fast indication of the reticulation time.

Quantitative analysis : the polymers were dissolved in the methylethylketone with the sensitizer (Michler's ketone). Samples were coated under argon on a quartz plate and exposed to filtered light with a chemical band pass filter (a solution of diphenyl-2,3 indenone-1) (14) from a 250 Watt high pressure mercury arc.

The decrease of the cinnamate absorption at 272 nm is followed by changes in the UV absorption. In the measure of the absorption we have taken the changes at 272 nm in the spectrum of the cinnamate into account of the absorption of the sensitizer in a neutral polymer matrix (Fig.1 and 2) (same backbone without cinnamate units).

Different films, at various proportions of cinnamate units and sensitizer (Michler´s ketone) are irratiated

	A	B	C	D	E films
$\frac{[\text{cinnamate unit}]}{[\text{Michler's ketone}]}$ =	4,5	2,6	1,8	1,2	0,97

The quantum yields ϕ : number of double bonds which have disappeared divided by the number of absorbed photons is computed on the film C after 15 minutes of irradiation in using the formulae :

$$\phi_{c\ 15} = \frac{\Delta X}{(I_i - I_{tr})t}$$

and on all the films after 2 minutes of irradiation in using:

$$\phi_2 = \frac{\Delta X}{I_i(1-10^{-OD}).t}$$

ϕ ... : quantum yield
ΔX .... : cinnamate mole disappeared
I_i .... : incidental intensity (1,96.10^{-9} Einstein. s^{-1}.cm^{-2})
I_{tr}.... : transmittal intensity
OD.... : optical density (at 352 nm)
t .... : time

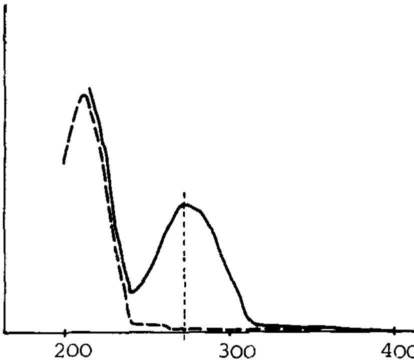

Fig.1 :neutral polymer (---)
grafted polymer (——)

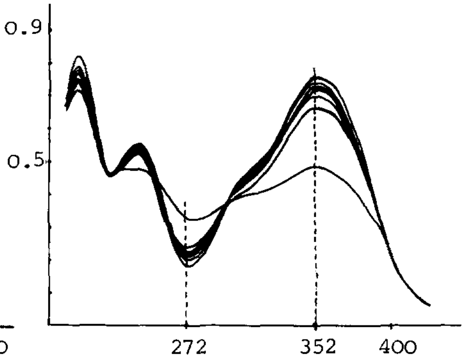

Fig.2 : sensitizer irradiated
in neutral polymer matri

The different values of ϕ are collected in the Table 1. The light intensity measurements are carried out by Hatchard-Parker actinometry with potassium ferrioxalate(15). These sensitized films (ABCDE) were exposed under argon to the radiation, at room temperature.3.

RESULTS AND DISCUSSION

The changes in UV spectra of the ABCDE films due to the photoreaction are illustrated on the Fig.3. The Fig.4 shows the yield (%) of disappearance of the cinnamate group versus tim from every film.

The initial rate is strongly dependant on the ratio [cinnamate]/[sensitizer]; the rate is highest when the compound

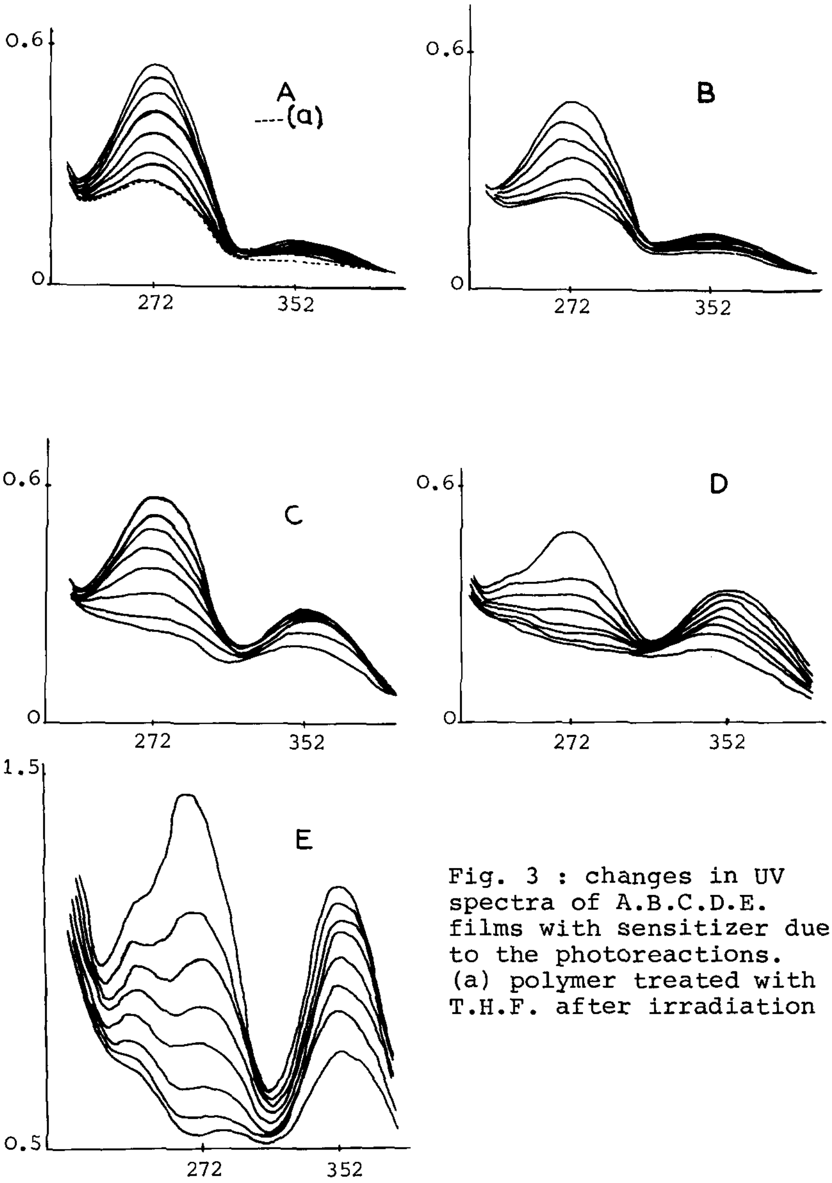

Fig. 3 : changes in UV spectra of A.B.C.D.E. films with sensitizer due to the photoreactions. (a) polymer treated with T.H.F. after irradiation

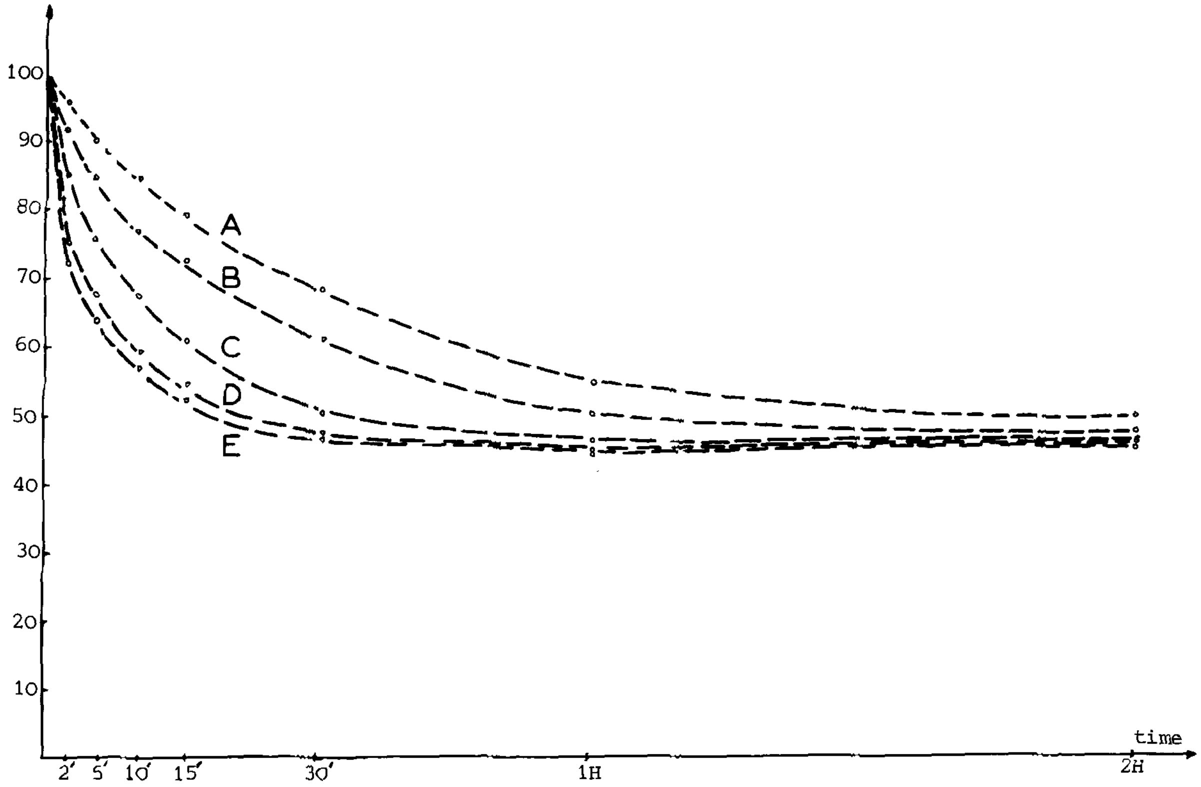

Fig. 4 : yields of disappearance of the double bonds of the cinnamate groups in relation to the time for five films A.B.C.D.E.

contains a sensitizer concentration equal to the cinnamate concentration. This ratio is very small account on the yield of the disappearance of the double bond at the end of the irradiation. The crosslinking gives networks. The percentage of the disappearance of the double bonds in the networks leads to a limit.

The decrease of the double bonds during exposure corresponds to the formation of bridges between two cinnamate groups carried by different backbone (16). The crosslinking is proved by extraction with THF. The UV spectrum after drying of the films is the same that the initial spectrum, except for the UV part corresponding to the sensitizer (352 nm) which is eliminated during the extraction (Fig. 3 , curve"A - (a)").

The initial velocity concerning the disappearance of the double bonds from each film was obtained from the tangential slope at the origin of the curves. The different values of v_i are collected in the Table 1, with the quantum yield in each case.

films	A	B	C	D	E
$\frac{[\text{cinnamate unit}]}{[\text{KM}]^*}$ ..	4,5	3	1,8	1,2	1
v_i (% s^{-1})	0,030	0,072	0,125	0,202	0,233
limiting cross-linking time	105'	90'	45'	30'	30'
Φ_2^{**}	0,017	0,023 Φ_{c15} =0,01	0,034	0,040	0,070

Table 1

*) KM : Michler's ketone **) Φ_2 : quantum yield after 2 mn.

The dimerization reaction occuring, is considered a topochemical reaction in the films, and many pairs of cinnamoyl groups adjacent may exist to be ready to dimerize in the film. If the incident light is absorbed by such a pair of groups, dimerization will occur.

These experiments show that the networks are completely carried out for all the films, when the disappearance of the double bonds achieves around 50-55%. The remaining double bonds are out of reach; it is possible to observe that in these copolymers films, 50-55% cinnamate unit are in the best positions on the backbone to produce the dimerization reaction. The concentration of the sensitizer in our experiments is higher than the usual concentrations (10 wt.%) . The increase of the photosensitizer concentration increases the initial rate and v_i is the best when [cinnamate unit] = [KM]. If the transfer of energy is the rate determining stage, the higher concentration of sensitizer is more effective, because the transfer of energy may most effectively occur through the contact area occupied by each of these molecules. The grafted copolymers thus obtained have good properties for use as a photo-resist layer.

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