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Kinetic treatment for the photodimerization reaction of modified natural polyisoprenes

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Summary

Natural polyisoprenes modified by the introduction of cinnamoyl groups have been obtained as films. In these polymers, aliphatic $-(CH_2)_n-$ spacers of different lengths separate the main chain from the photosensitive group. Density measurements have been carried out, and the kinetic treatment of the photodimerization reaction is described. The relation between T_g and k_{obs} to the size of the aliphatic spacer suggests that, at least for n=2 to 6, other factors may be affecting the reactivity of the cinnamoyl group.

Introduction

Several papers have been published on the reactivities of photosensitive groups (1-7). The photodimerization of the first synthetic photopolymer, poly(vinyl cinnamate), has been extensively studied, mainly as far as kinetic behaviour is concerned. As expected, it has been observed that in dilute solution, the reaction is preferentially intramolecular, whereas for solid films the main path takes place intermolecularly (8,9).

It has been observed that the reactivity of cinnamate groups depends on the nature of the polymeric chain to which it is linked. Also, much effort has been expended in order to correlate reactivity to molecular structure (10).

In the case of flexible chains in the solid state, the degree of interpenetration seems to have an important role on the dimerization efficiency (11,12). Natural rubber, which may be considered as constituted of flexible polymeric chains, was chosen as starting material for the production of photosensitive cinnamoylated polymers.

The kinetics of the dimerization reaction for thin films of these products was followed by UV spectrometry , and recently reported (13). The conversion seems to be affected by the film thickness up to a threshold value, which depends on each product.

In this work, the values of $C_0 . k_{obs}$ for the same samples are determined from Equation 1.

$$\frac{1}{C} - \frac{1}{C_0} = k_{obs} . t \qquad \text{Equation 1}$$

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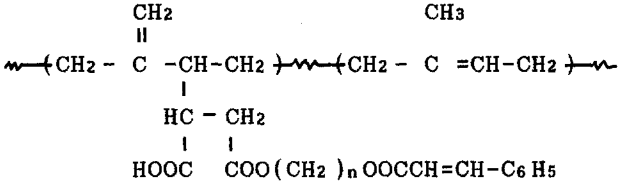
where C_0 is the initial concentration of cinnamoyl groups and may be obtained from each density value. The possible correlation between T_g and k_{obs} is also discussed.

Experimental

The photosensitive polymers represented in Figure 1 have been obtained by means of modification reactions on natural polyisoprenes, as described previously (13). In these copolymers, the elastomeric backbone is linked to the photosensitive cinnamoyl group by aliphatic spacers of different lengths. Figure 1 also presents density data obtained for uncrosslinked films from concentrated chloroformic solutions cast onto polyethylene.

A density gradient column for the interval 1.0 to 1.3 g/ml was prepared by mixing a solution of 632 ml carbon tetrachloride and 302 ml heptane to a solution of 408 ml carbon tetrachloride and 765 ml heptane, as recommended by ASTM D1505-68 method (14). Films heights in the density column were measured after a stabilization period of 12 hours.

Maleic anhydride content was estimated after titration of 1 ml chloroformic copolymeric solution with methanolic standard solution of sodium methoxide.



$$\sim(CH_2-\overset{\overset{CH_2}{\|}}{C}-\underset{\underset{\underset{HOOC\qquad COO(CH_2)_nOOCCH=CH-C_6H_5}{|\qquad\quad|}}{HC-CH_2}}{\overset{}{CH}}-CH_2)\sim\sim(CH_2-\overset{CH_3}{C}=CH-CH_2)\sim$$

n	Product	Density (g/ml)
2	A-1,2-EM	1.220
3	A-1,3-PpM	1.207
4	A-1,4-BM	1.198
5	A-1,5-PtM	1.196
6	A-1,6-HM	1.188

Figure 1- Molecular structure and density data determined for the photosensitive polymer films.

Results and Discussion

The initial concentration of cinnamoyl groups was obtained from density and composition data.

$$C_0 = \frac{d \cdot x}{M \cdot x + N} \qquad \text{Equation 2}$$

where d is the film density in g/ml, x is the molar fraction of cinnamoyl substituted units, M is the molecular weight of the cinnamoylated isoprene residue and N is the molecular weight of the unsubstituted isoprenic repeating unit.

This C_o value, obtained by means of Equation 2 represents the total concentration of cis and trans-cinnamoyl groups. As the photodimerization reaction takes place with the trans isomer only, the actual concentration C_{to}, related to the trans isomer, may be determined as a fraction of C_o. Taking into account that A_o and A_{to} are expressed in terms of the Lambert-Beer's law, where ℓ is the optical path (film thickness in this case) and ε_t and ε_c are the trans and cis isomer molar absortivities, respectively, Equations 3 and 4 give the total initial absorption (A_o) and the initial absorption corresponding to the trans form (A_{to}).

$$A_o = \ell \left(\varepsilon_t C_{to} + \varepsilon_c C_{co} \right) \qquad \text{Equation 3}$$

$$A_{to} = \ell \left(\varepsilon_t C_o \right) \qquad \text{Equation 4}$$

As $C_o = C_{to} + C_{co}$, C_{to} may be calculated (15) by

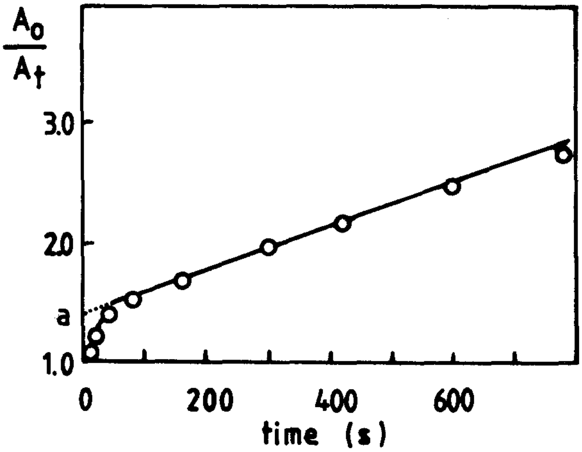
$$C_{to} = C_o \frac{\dfrac{\varepsilon_t}{\varepsilon_c \cdot a} - 1}{\dfrac{\varepsilon_t}{\varepsilon_c} - 1} \qquad \text{Equation 5}$$

and the photodimerization rate constant is given by

$$k_{obs} = \frac{\tan \theta}{a\, C_{to}} \qquad \text{Equation 6}$$

where the parameter *a* is the linear coefficient for the straight line due to the dimerization reaction (15). Figure 2 shows the graphical determination of the parameter *a* for the A-1,2-EM product.

Figure 2- Graphical determination of parameter *a*.



Values of C_o, C_{to} and k_{obs}, determined as explained above, are collected in Table 1.

Table 1- Values of C_o, C_{to} and k_{obs}.

Polymer	$C_o \cdot 10^3$ (mol . cm^{-3})	$C_{to} \cdot 10^3$ (mol . cm^{-3})	k_{obs} ($s^{-1}.mol^{-1}.cm^3$)
A-1,2-EM	1.97	1.08	1.23
A-1,3-PpM	1.91	1.60	0.56
A-1,4-BM	1·85	1.27	4.16
A-1,5-PtM	1.81	0·93	3.24
A-1,6-HM	1.76	0.84	2.62

The determination of C_o and A_o allowed the calculation of the molar absortivity, ε, for each product, from the Lambert-Beer equation. Table 2 shows the experimental values for film thicknesses, ℓ, as well as ε values.

Table 2- Film thicknesses and molar absortivities.

Polymer	$\ell \cdot 10^3$ (cm)	$\varepsilon \cdot 10^{-2}$ ($mol^{-1} . \ell . cm^{-1}$)
A-1,2-EM	0.91	1.95
A-1,3-PpM	0.91	2.92
A-1,4-BM	0.10	20.66
A-1,5-PtM	0.84	2.98
A-1,6-HM	0.75	3.70

One of the outstanding intentions of this research was to arrive at some correlation of T_g and k_{obs} to the size of the aliphatic spacer. However, the observed glass temperatures vary in a peculiar way (13). Figure 3 shows T_g and k_{obs} results in function of the number of carbon atoms of the side chain. The relation between T_g and k_{obs} is not so simple as expected, and seems to depend also upon other factors. Nevertheless, the possibility of having these effects levelled off, by further increase in the spacer length, may be envisaged.

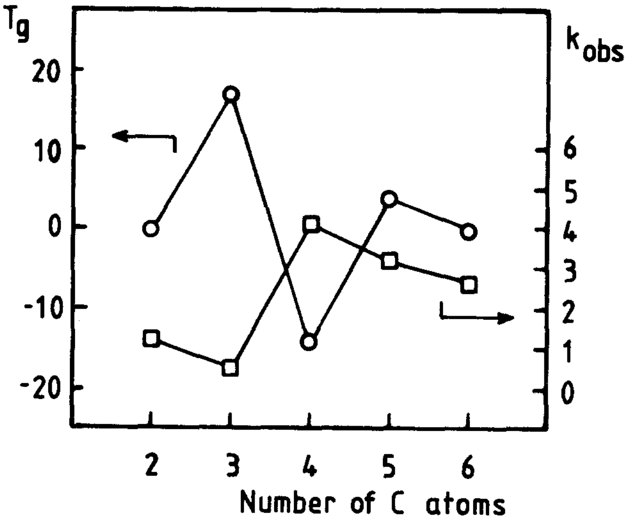


Figure 3- T_g and k_{obs} results in function of the number of carbon atoms of the side chain.

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