Polymer Bulletin 25, 217–223 (1991)

Polymer Bulletin

Photosensitivity of modified natural polyisoprenes as function of the alipathic side chain

Leila L. Y. Visconte[1,*], Cristina T. Andrade[1], and Chiaki Azuma[2]

[1]Instituto de Macromoleculas, Universidade Federal do Rio de Janeiro, PO Box 68525,
20000 Rio de Janeiro, RJ, Brazil
[2]The University of Air, Wakaba, 2-11, Chiba 260, Japan

Summary

Modified natural rubber products were prepared by reaction with maleic anhydride followed by ring opening and condensation with different oxyalkylcinnamate esters. The values of T_g obtained for these photocrosslinkable polymers showed a complex relation to the number of C atoms of the aliphatic moiety. The kinetics of the dimerization reaction for thin films was followed by UV spectrometry. The film thickness plays an important role on conversion up to a threshold value, characteristic of each product. The expected relation between T_g and k_{obs} was observed for products when T_g values were markedly different.

Introduction

For the industrial application of photoresists, kinetic studies constitute an essential tool for the determination of their performance, concerning the final crosslinking reaction. Photoresist materials should present certain characteristics as stability to long-period storage, high resolving power, and should not be affected by oxygen and antioxidants. These properties have been observed for cinnamate-type photoresists (1).

Polydiene rubbers have demonstrated to be very useful materials for coatings, particularly because of their good adhesion to metallic substrates (1). The presence of multiple bonds in the polymeric chain has been used to introduce functional groups. Maleic anhydride has been successfully added to such groups by different procedures (2),(3) resulting in different products (2).

The chemical modification of synthetic cis-1,4-polyisoprene (IR-2200) by the introduction of oxyethylcinnamate groups has led to improved photoresist materials. It has been observed that the photosensitivity, which can be quantified by the efficiency of the photocrosslinking reaction, increases as the amount of photosensitive groups in the molecule also increases (4).

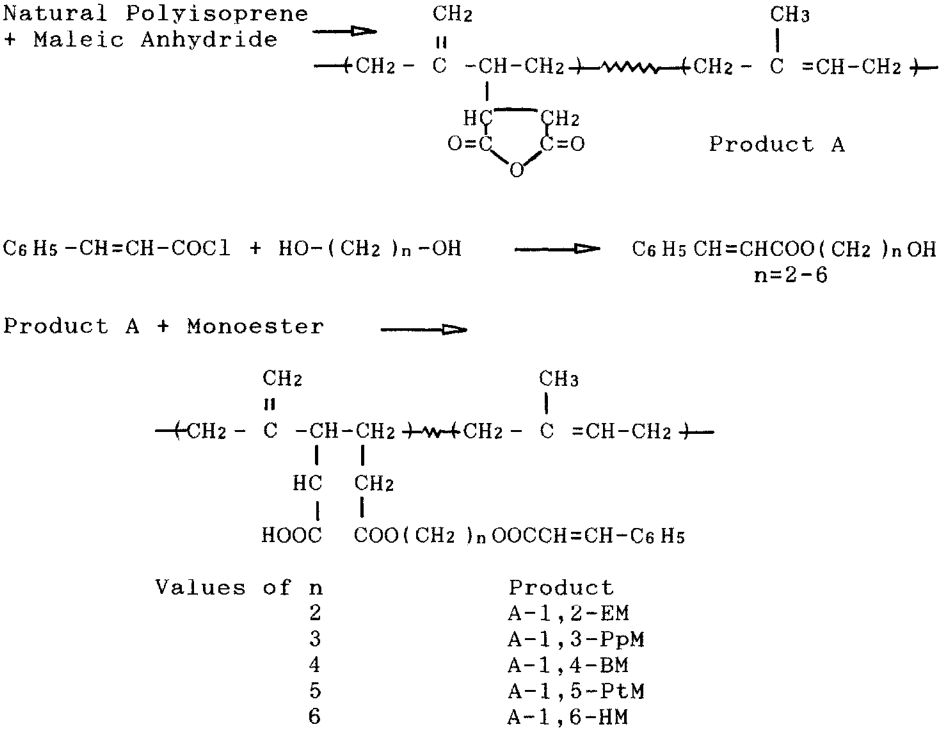
This work investigates the synthesis and the kinetic behaviour of modified natural polyisoprenes in which the pendant substituents consist of cinnamate groups differently separated from the main chain by homologous aliphatic moieties as spacers.

---

[*] To whom offprint requests should be sent

Experimental

The synthetic route from natural rubber to photocrosslinkable products may be visualized in Figure 1.



Values of n	Product
2	A-1,2-EM
3	A-1,3-PpM
4	A-1,4-BM
5	A-1,5-PtM
6	A-1,6-HM

Figure 1- Synthetic route to photosensitive polyisoprenes.

Natural polyisoprene, supplied as type I latex, was coagulated by addition of diluted acetic acid, and purified by dissolution in benzene followed by precipitation in methanol. Maleic anhydride (2 moles) was added to 1M solution of polyisoprene in o-dichlorobenzene, the misture was flushed with N_2 under vacuum during 30 minutes, then heated and maintained at 180-190°C under stirring for 16 hours. At the last stage of the reaction, part of the solvent was distilled off. The adduct NR-MA (Product A) was isolated by precipitation in heptane-ethyl ether and was kept in a refrigerator as chloroformic solution.

The monoesters were obtained by adding cinnamoyl chloride (0,2 moles) to a pyridine solution of the diol (0.4 moles) and stirring for 1 hour at temperatures below 30°C. The reaction mixture was poured onto distilled water and the product extracted by chloroform. After being washed with distilled water, diluted H_2SO_4, saturated Na_2CO_3 and again water, the extract was dried with $MgSO_4$, chloroform was evaporated under vacuum and the monoester products were distilled . Yields and boiling points of the 5 monoesters are shown in Table 1.

Table 1:Yields and boiling points of the monoester reagents

Monoester		Yield (%)	Tb (°C/mmHg)
1,2-ethanediolmonocinnamate	(1,2-EM)	61	159/3.2
1,3-propanediolmonocinnamate	(1,3-PpM)	55	179/4.1
1,4-butanediolmonocinnamate	(1,4-BM)	79	195/5.4
1,5-pentanediolmonocinnamate	(1,5-PtM)	53	158/0.05
1,6-hexanediolmonocinnamate	(1,6-HM)	42	210/4.0

To 20 ml chloroformic solution of Product A, the selected monoester was added in excess. The mixture was heated to 75-80°C under stirring for 21 hours. Each product was recovered by decantation after pouring the reaction mixture onto methanol, then was dried and kept in the refrigerator as a chloroformic solution.

All products were characterized by infrared spectrometry (FTIR Perkin-Elmer Spectrometer model 1720X) and differential scanning calorimetry (Perkin-Elmer model DSC-2).

Concerning the kinetics of the photodimerization reaction, the films prepared on quartz plates from chloroformic solution were irradiated under nitrogen at 30°C by means of high pressure mercury lamp of 200 W (Ushio Electric, model UI-501), distant 10 cm from the source. The course of the photochemical reaction was followed by measuring UV absorption changes (UV Varian Spectrometer Model Cary 17).

Results and Discussion

The reaction series presented in Figure 1 allowed the preparation of five samples of modified natural polyisoprene.

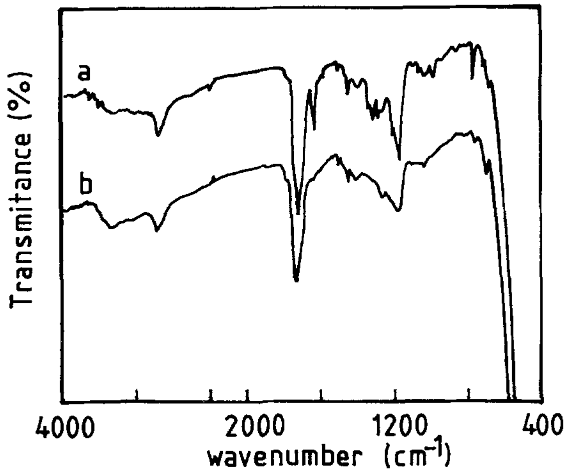


Figure 2: Infrared spectra for A-1,4-BM film before (a) and after (b) irradiation.

Figure 2 shows the FTIR spectrum of Product A-1,4-BM, before and after irradiation. Similar pairs of spectra can be obtained from the other products of the series. Upon irradiation, the crosslinking reaction takes place and the absorption at 1637 cm^{-1}, due to carbon-carbon double bonds of cinnamate groups, disappears.

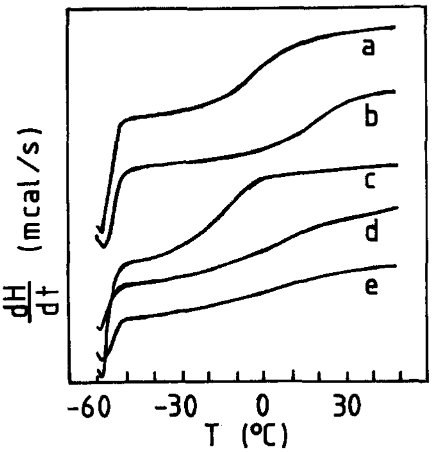


Figure 3: DSC curves for photosensitive polymers (a) A-1,2-EM, (b)A-1,3-PpM, (c)A-1,4-BM, (d)A-1,5-PtM, (e)A-1,6-HM.

The heating DSC curves at 10°C/min of the different photosensitive polymers are shown in Figure 3. The observed T_g values vary with the length of the homologous aliphatic chain in a very complex way. This peculiar behaviour seems to be altered whether an odd or an even number of carbon atoms is present (Figure 4). Such a trend has been detected for the crystaline melting point of homologous series of condensation polymers.

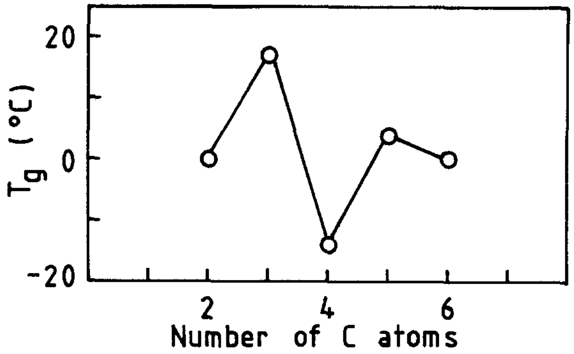


Figure 4: Dependence of T_g on the number of aliphatic C atoms.

Figure 5 shows the UV absorption changes observed as the photodimerization reaction of the A-1,4-BM product takes place. The intensity of the absorption at 278 nm, attributed to the π - π^* transition of the cinnamate group decreases with time. The same pattern was observed for the other products.

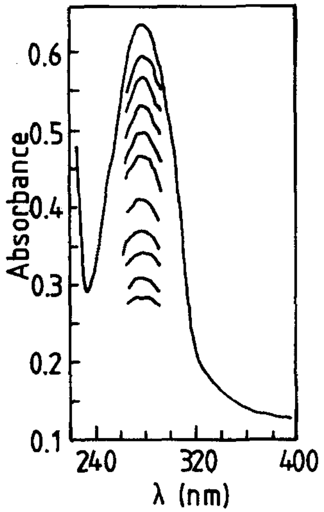


Figure 5: UV absorption spectra of A-1,4-BM as function of irradiation time.

One of the essential points to be cleared up in this study is the effect of the length of the spacing group between the main chain and the photosensitive moiety on the dimerization reaction efficiency. It has been recognized that the observed photodimerization rate constant increased linearly with the increase of the reciprocal of the film thickness up to a critical value after which it remains constant (4). The same reasoning may be achieved by plotting reaction conversion versus time for the products of the homologous series. The film thickness plays an important role on conversion up to a threshold value, characteristic of each product. Films in this thickness range were considered in the kinetic study. This behaviour can be observed in Figure 6 for A-1,6-HM product. Figure 7 shows reaction conversions versus time for the photocrosslinkable polymer samples.

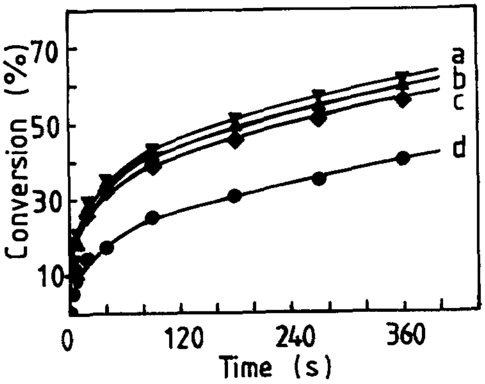


Figure 6: Time conversion for the dimerization reaction of cinnamate groups of A-1,6-HM films of different thicknesses
(a) 0.747 x 10^{-2} mm,
(b) 0.825 x 10^{-2} mm,
(c) 1.600 x 10^{-2} mm,
(d) 3.018 x 10^{-2} mm, by UV irradiation at 30°C.

The kinetic equation for the photodimerization of the cinnamate group can be derived after assuming that: (a) the

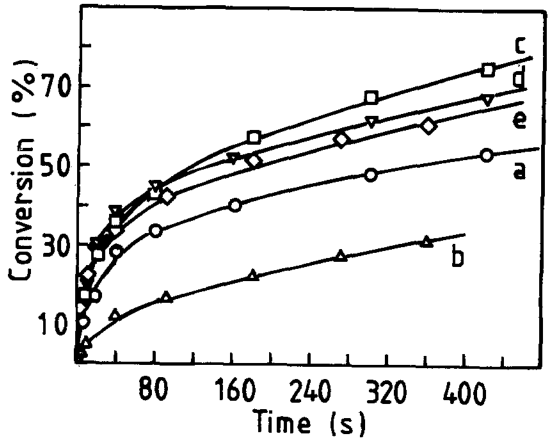


Figure 7: Time conversion for the dimerization reaction of cinnamate groups of (a) A-1,2-EM, (b) A-1,3-PpM, (c) A-1,4-BM, (d) A-1,5-PtM, (e) A-1,6-HM by UV irradiation at 30°C.

steady state is reached by the excited species, (b) the deactivation rate is much higher than the dimerization rate, and (c) for thin films, the intensity of the transmitted light is practically the same as the intensity of the incident light. Taking these hypotheses into account, a second order kinetics (Equation 1) (5) was applied in this work.

$$\frac{1}{[C]} - \frac{1}{[C_o]} = k_{obs} \cdot t \qquad \text{Equation 1}$$

where $k_{obs} = 4.60 \cdot \frac{1}{6.023 \times 10^{23}\ h\nu}\ \epsilon I_o\ \frac{k_2}{k_3 + k_4}$,

h and ν denote Planck's constant and wave number, respectively, ϵ is the molar absortivity, I_o is the intensity of the incident light, k_2, k_3 and k_4 are the dimerization, isomerization and deactivation constants, respectively.

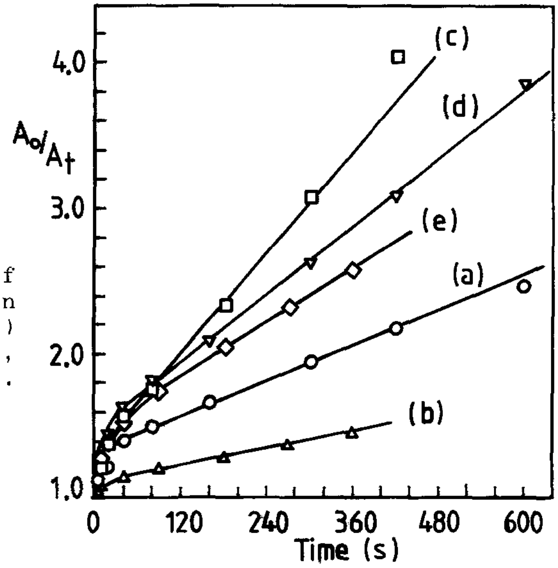


Figure 8: Dependence of $[C_o] / [C]$ on UV irradiation time for (a) A-1,2-EM, (b) A-1,3-PpM, (c) A-1,4-BM , d) A-1,5-PtM, (e)A-1,6-HM.

Figure 8 shows values of A_o/A_t as function of reaction time. After a short isomerization period, straight lines are obtained. The angular coefficients of the linear portion of those curves can be used to calculate k_{obs} values.

It might be expected a certain relationship between T_g and the dimerization efficiency, quantified by k_{obs}. In fact, this relation was observed for products A-1,4-BM, which has the lowest T_g and was the one to react more rapidly, and A-1,3-PpM, which showed the highest T_g and the lowest k_{obs}; the two products of markedly different T_g values.

Acknowledgments: The authors thank FAPERJ for financial assistance.

References

1. Azuma C, Sanui K, Ogata N (1982) J Appl Polym Sci 27: 2065
2. Le Bras J, Pinazzi C, Milbert G (1959) Rev Gen Caoutchouc 36:215
3. Le Bras J, Pantrat R, Pinazzi P (1964) Reagents with multiple bonds. In: Fettes E M (ed.) Chemical reactions of polymers, Interscience Publishers, New York London Sydney (High Polymers, vol 19, pp (194-233)
4. Azuma C, Hashizuma N, Sanui K, Ogata N (1983) J Appl Polym Sci 28: 543
5. Azuma C, Mitsuboshi T, Sanui K, Ogata N (1980) J Polym Sci, Polym Chem Ed 18: 781

Accepted November 26, 1990 K