

UV-Light Induced Crosslinking Reaction of Cinnamate Natural Rubbers: Effect of the Spacer Length, Counter-Ion Nature, and Content

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ABSTRACT: Maleated natural rubber was modified by introducing different contents of cinnamate groups, separated from the main chain by $-(CH_2)_n-$ spacers ($n = 2$ to 6). Residual carboxylic acid groups were neutralized as Li, Na, and K-salts. The kinetic behavior of these materials towards ultraviolet-induced crosslinking reaction was investigated and correlated with T_g . © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 907–910, 1998

Key words: cinnamoylated rubbers; photocrosslinking reactions; glass transition temperature; effect of the counter-ion; effect of the spacer length

INTRODUCTION

Polymers sensitive to ultraviolet (UV) irradiation are widely used as photoresists, applied onto Cu-covered plates in the manufacture of printed circuits. In the case of negative photoresists, irradiation promotes crosslinking of the photosensitive polymers. By using a mask, the nonirradiated part, still soluble, may be easily removed by soaking the whole system in an appropriate solvent. However, as environment restrictions increase worldwide, efforts have been made to minimize the emission of pollutants, mainly from chemical industries. From this standpoint, water-based systems have become increasingly interesting.^{1,2}

Along with this tendency, the search for materials with better performance still remains. Several investigations have tried to correlate kinetic behavior with chemical structure.^{3–5} One of the features required to improve reactivity seems to be chain mobility. In this regard, polydienes have

been extensively studied, and some general remarks could be drawn.^{4,6} To begin with, a continuous increase in the concentration of reactive groups improves reactivity only up to a certain value, after which any further increment does not usually have a positive effect, due to mobility restrictions imposed by the crosslinks already formed.^{7,8} This, in turn, leads to inhomogeneities in the reactive groups distribution within the polymer matrix. To overcome this situation, several articles have reported the preparation of polymers with very flexible backbones, in which the unreacted groups, trapped inside the network, could be reached by irradiation and still would have enough mobility to assume the ideal conformation, required for the reaction to take place.^{9–12}

In this work, natural rubber was modified by introducing different contents of maleic anhydride. The maleic residues were then esterified with glycol cinnamates, giving rise to half-esters, in which the cinnamate groups were separated from the main chain by segments of different lengths. The remaining acid residues in these polymers were neutralized with lithium, sodium, and potassium methoxide. The kinetic behavior of the crosslinking reaction of the resulting polymers in the salt form was investigated.

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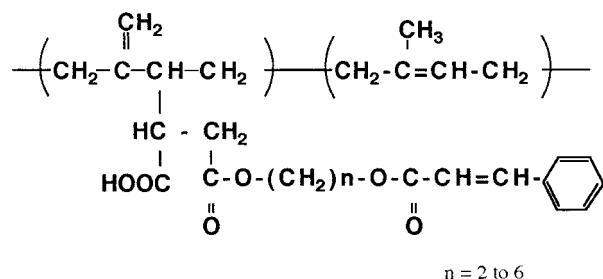
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EXPERIMENTAL

Natural rubber, supplied as type I latex by Instituto Agronômico do Norte, was recovered by coagulation and purified, as described before.¹³ Maleic anhydride, cinnamic acid, and thionyl chloride from Riedel-de-Haën and ethylene glycol from Carlo Erba do Brasil, were reagent grade and used without purification. 1,3-Propylene glycol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol, from Aldrich Chemical Co., were vacuum-distilled. Sodium methoxide supplied by Harshaw Chemical, lithium from Riedel-de-Haën, and potassium from E. Merck Darmstadt were used as received.

Maleated poliisoprenes with various degrees of maleate incorporation were prepared according to a previous article.¹³ Through ring-opening esterification of the maleic anhydride residue with oxyalkylcinnamate esters, each of the maleated polyisoprenes gave rise to a set of compounds in which the alkyl moiety had a number of $-\text{CH}_2-$ groups varying from 2 to 6, with the following structure¹³:



These products were kept as chloroformic solutions, under nitrogen, in a refrigerator.

The remaining carboxylic groups were neutralized with appropriate amounts of standard sodium, lithium, or potassium methoxide solutions. The correct amount necessary for neutralization was calculated by preliminarily titrating duplicate samples of each product in the presence of phenolphthalein. A third sample was then neutralized in absence of the indicator and diluted to about 1% (w/v) for kinetic measurements.

Glass transition temperatures were obtained from a Perkin-Elmer DSC-2 Calorimeter, calibrated with indium. Samples of each polymer film of about 20 mg were heated and cooled twice at 10°/min. Instrument sensitivity was 1 mcal/s.

Films were prepared by coating each solution onto quartz plates. Irradiation was carried out with a 200-W high-pressure mercury lamp, model UI-501, from Ushio Electric. Photocrosslinking re-

action was followed in a Varian spectrophotometer model Cary 17, and the reaction progress was followed, as described previously.¹⁴

RESULTS AND DISCUSSION

The introduction of maleic anhydride to natural rubber gave rise to products with different degrees of incorporation: 7, 15, 19, 26, and 29 mol %. Each one of these products was reacted with the appropriate glycol monocinnamate to give polymers with the photosensitive group separated from the main chain by a number of $-\text{CH}_2-$ groups varying from 2 to 6. Finally, each polymer was obtained in the form of Li-, Na-, and K-salts.

Photoreaction was monitored by measuring the decrease in the 278-nm absorption, after irradiation during different periods of time. Kinetic treatment of the obtained data followed the procedure described before.¹⁴ The observed rate constant, k_{obs} , for each product was calculated according to the following equation:

$$k_{\text{obs}} = 4.60 \frac{1}{6.023 \times 10^{23} h \nu} \varepsilon I_0 \frac{k_2}{k_3 + k_4}$$

where h and ν are the Planck's constant and the wave number, respectively; ε is the molar absorptivity; I_0 is the intensity of incident light; and k_2 , k_3 , and k_4 are the dimerization, isomerization, and deactivation rate constants, respectively, corresponding to the most important reactions pathways occurring in photochemical processes.

Figure 1 shows the k_{obs} dependence on the number of methylene groups in the spacer and different degrees of cinnamate incorporation for the polymers in the salt form.

From the curves in Figure 1, it can be observed that k_{obs} values are strongly dependent on n only for small amounts of incorporated cinnamate groups (7 mol %). However, a common behavior is not found for all 3 salt forms. The Li- and K-salts show a decrease in k_{obs} as the spacer length is increased, whereas for Na-salts, there is a minimum value for $n = 3$. These dissimilarities become less evident as the cinnamate content, or the ion concentration, increases.

It is well documented in the literature that the photodimerization of cinnamate groups is a reaction that depends on some characteristics.^{15,16} For the reaction to take place, a particular spacial conformation is required so that cyclobutane rings can be formed. As the photoreaction is carried out

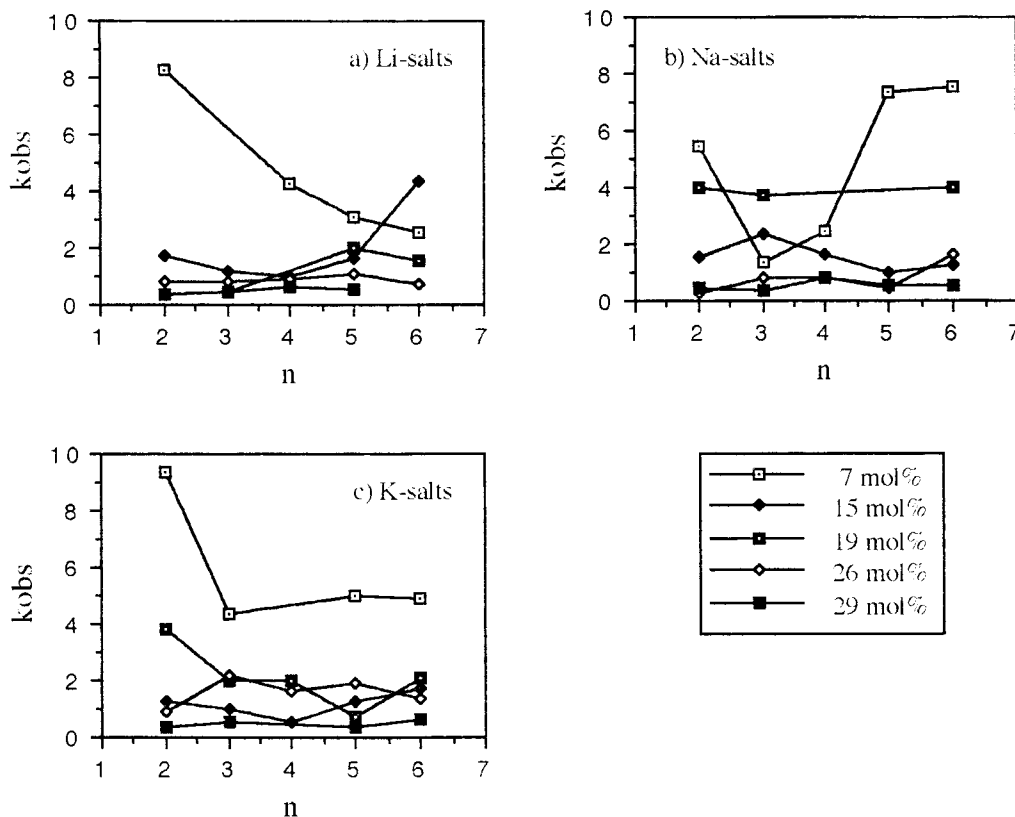


Figure 1 K_{obs} as a function of spacer length for polymers with different degrees of cinnamate incorporation, where n is the number of methylene groups in the spacer.

in the solid state, it is assumed that the molecules have a certain degree of mobility and that a high flexibility would facilitate the reaction.^{17,18} According to this, it would be expected that, in our system, as the spacer length varies from 2 to 6, k_{obs} would increase. However, it has been found that in the polymers with 7 mol % cinnamate incorporation, in the form of Li- or K-salts, the opposite behavior is observed, which leads to the conclusion that mobility alone is not the driving force for network formation.

Nevertheless, mobility restrictions have a deleterious influence on k_{obs} , as seen in Figure 1. Higher ionic concentrations can cause some kind of organization to appear, minimizing potential effects brought about by structural differences. As a result, the curves corresponding to ion concentration higher than 7 mol % show decreasing k_{obs} values that become almost invariable with n for 29 mol %.

Efforts have been made aiming to correlate the efficiency of the photochemical processes with the motion of specific groups.^{4,5} It has been found that small variations in the polymer structure may promote expressive changes in chain mobility,^{17,18}

frequently associated with the glass transition temperature, T_g . Thus, Figure 2 shows how this parameter is influenced by polymer flexibility.

For the polymer with 7 mol % incorporation, k_{obs} varies significantly with the spacer length, whereas T_g remains almost insensitive. As T_g is a measure of chain mobility, this result corroborates the previous suggestion that flexibility alone is not the most important factor affecting the reactivity of cinnamate groups in these systems. For ion concentration higher than 7 mol %, variation of n leads to different behaviors, depending on the particular salt.

Investigations on ionic polymers in the solid state show that there is a critical ion concentration, which determines microstructure and greatly influences physical properties.¹⁹ Two types of aggregates are involved. Below the critical value, there is predominance of multiplets containing a small content of ionic pairs, which act as physical crosslinks. Above this critical value, the aggregates consist not only of ionic pairs but also of parts of the hydrocarbon chains and present some characteristics of microphase separation.

In the solid state, the behavior to be expected

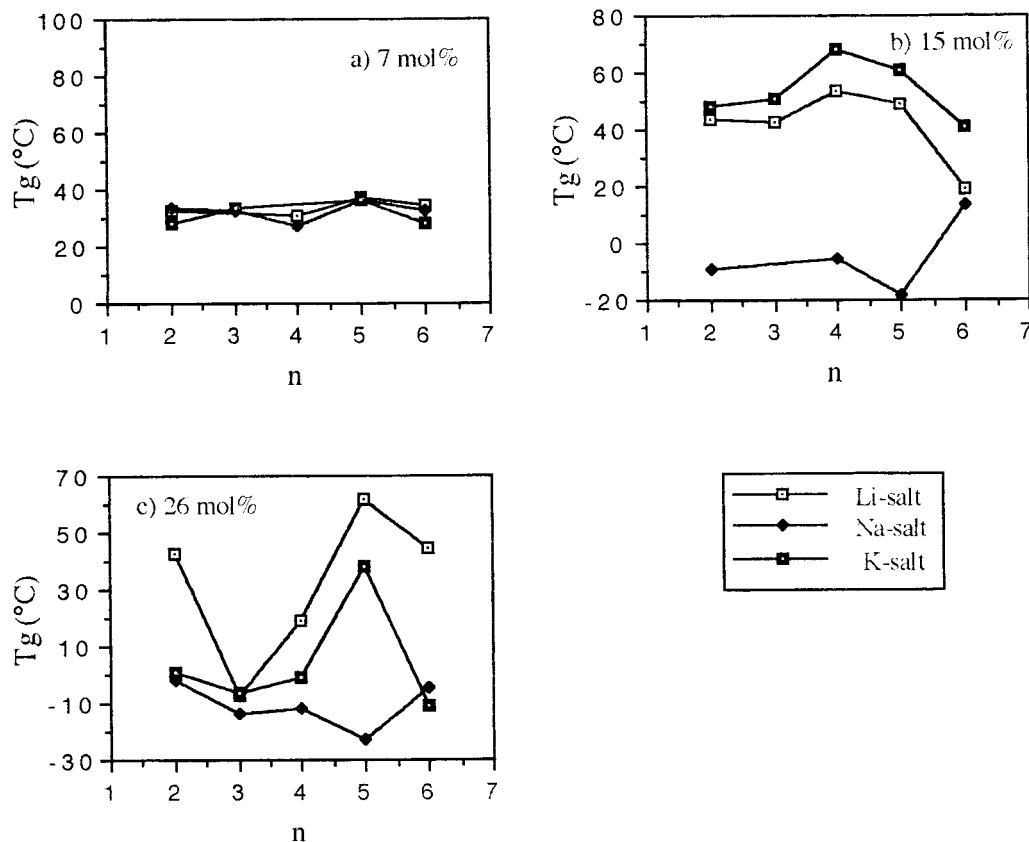


Figure 2 Variation of T_g with spacer length for different amounts of cinnamate incorporation, where n is the number of methylene groups in the spacer.

from the polymers investigated in the present work seems to be extremely susceptible to slight structural differences. Aside from chemical structure, molecular organization and chromophore distribution also play an important role.

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