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KINETIC STUDY OF PHOTO-GRAFTING AND PHOTO-CROSS-LINKING OF A CIS-POLYBUTADIENE ONTO CELLULOSE FROM ASSIMETRIC MEMBRANES

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Summary

Photochemical grafting onto cellulose and sucessive photo-cross-linking of 2,00-12,00 $mg.cm^{-2}$ of a cis-polybutadiene, containing 80% cis groups, were investigated kinetically at 30°C in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as a photoinitiator with the weight concentration ratio of photoinitiator to polymer varied between 0,070 and 1,115. Irradiations were carried out polychromatilly, in air or under a stream of nitrogen, with incident radiation of flux I of $2,1.10^{-8}$ $einstein.s^{-1}.cm^{-2}$. Two consecutive kinetic process were observed wich had rates linearly dependent on I. The quantum yields of the first constant-rate period showed a linear dependence on photoinitiator concentration, while the quantum yield for the second constant rate process showed an inverse dependence on n/S (moles of polymer initially deposited per unit apparent cellulose surface). At longer irradiation times, further decrease in insaturation resulting from photo-cross-linking was observed. In light of this information, the mechanism of photo-grafting and photo-cross-linking of cis-polybutadiene on cellulose surface is discussed.

Introduction

The interesting material properties of cis-polybutadiene (their excellent elastomeric characteristics and their impact resistence), make them particularly attrative in radiation-

curable systems(1). Photo-cross-linking of polybutadiene has been investigated (2). During the course of our experiments to prepare membranes by photochemical grafting and cross-linking, we first examined technical methods for preparation and the transport properties of the photosynthetic layers, in order to gain preliminary mechanistic information.

In this work, we have extended our investigations by studying the kinetics of the process to a commercial cis-polybutadiene with a photoinitiator to obtain higher photochemical rates and consider in detail the influence of irradiation on photo-cross-linking in this sistem(3).

Experimental part

Cellulose in form of filter paper ("blue band")was employed as the substrate. A commercial cis-polybutadiene(Coperbo BR-22), wich consisted of a mixture containing 80% cis forms, 12% trans - forms and 8% 1,2-units. 1,2-diphenyl-2,2-dimetoxyethanone(Irgacure, Fratelli Lamberti-Italy) was the photoinitiator, and this was used as received without further purification.

1-2 ml of a solution of dry cloroform containing 5-20 $g.l^{-1}$ cis-plybutadiene, and photoinitiator with the ratio R_w (its weight concentration with respect to that of the polymer, corresponding to the molar ratio R if calculated from the mean molecular weight of polymer) varied between 0,070 and 0.115, was uniformly deposited by a standard procedure, described previously (4),on a cellulose disk 6 cm in diameter. After evaporation of the solvent under vacunn at room temperature, irradiation and gravimetric determination of the graft yelds as a function of irradiation time were performed as described in ref.4, with the only difference being that Soxhlet extraction for the removal of non reacted polymer and ungrafted homocopolymer was carried ou with cloroform as the solvent.

Results and discussion

Photochemical grafting of cis-polybutadiene onto cellulose, in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as the photoiniator, was investigated kinetically at 30°C. Irradiation was carried out polychromatically with incident radiation fluxes in the range $(2,1 \pm 0,2) \times 10^{-8}$ - $(20,5 \pm 0,8) \times 10^{-8}$ einstein.s^{-1}.cm^{-2}, by operating under a stream of nitrogen or in air. The mass m of cis-polybutadiene adsorbed per unit apparent surface S of cellulose was varied between 1,0 and 12,0 mg.cm^{-2}, the ratio R_w of the weight per cent of photoinitiator to that of polymer was varied between 0,070 and 1,115. Graft yield as a function of irradiation time were determined gravimetrically. Some typical experimental curves are reported in Fig.1. In some cases, and particularly for $m/S \leqslant 4$ mg.cm^{-2}, only a single constant rate porcess was observed. With $m/S > 4$ mg.cm^{-2}, a second rate process, of much lower rate, followed up to high graft yields, as determined gravimetrically. In each case, the rates in air were relatively low compared with those obtained when irradiation was effected under a stream of nitrogen (it is well know that oxygen inhibits proccedings by a free radical mechanism).

Further irradiation of the grafted polymer, for wich a practically quantitative graft yield, as determined gravimetrically, had already been reached, reduced the residual insaturation, determined by IR analysis, have a linear correlation with the reduction of the 1,2-pendant vinyl groups (Fig.2.).

This mechanism implies photochemical reactivity of one out of two insaturations extended to grafting in the cellulose surface and may be observed at higher cross-linking in the polymer network photografted.

This assimetric membranes are an important structure for separation process for eletrolitic solutions.

Acknowledgments

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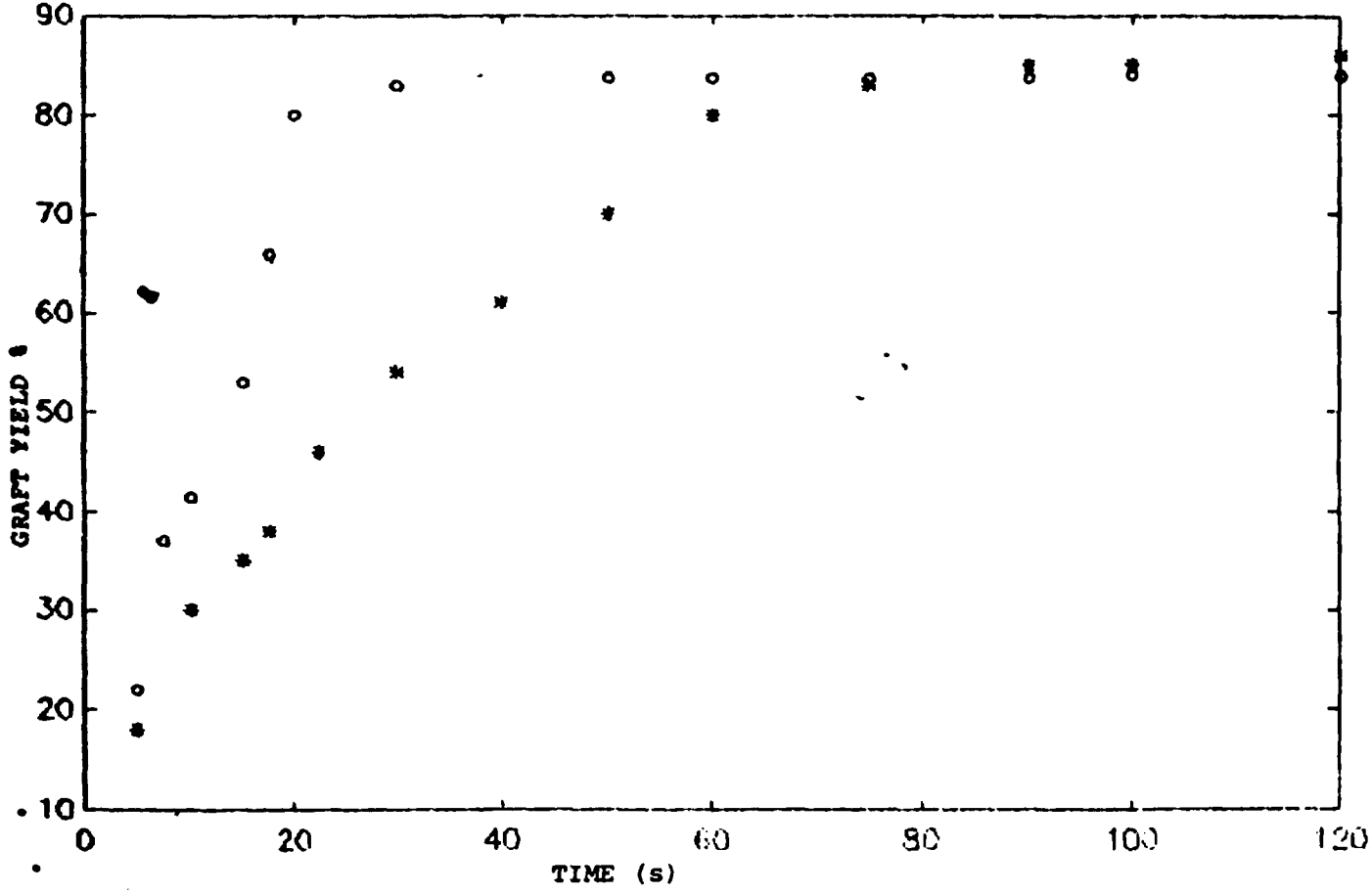

FIG.1- Per cent graft yield(gravimetric analysis)of cis-polybutadiene onto cellulose as a function of irradiation time t in presence of 7wt/wt% Irgacure (o 2,44 mg.cm^{-2} and * 4,49 mg.cm^{-2}).

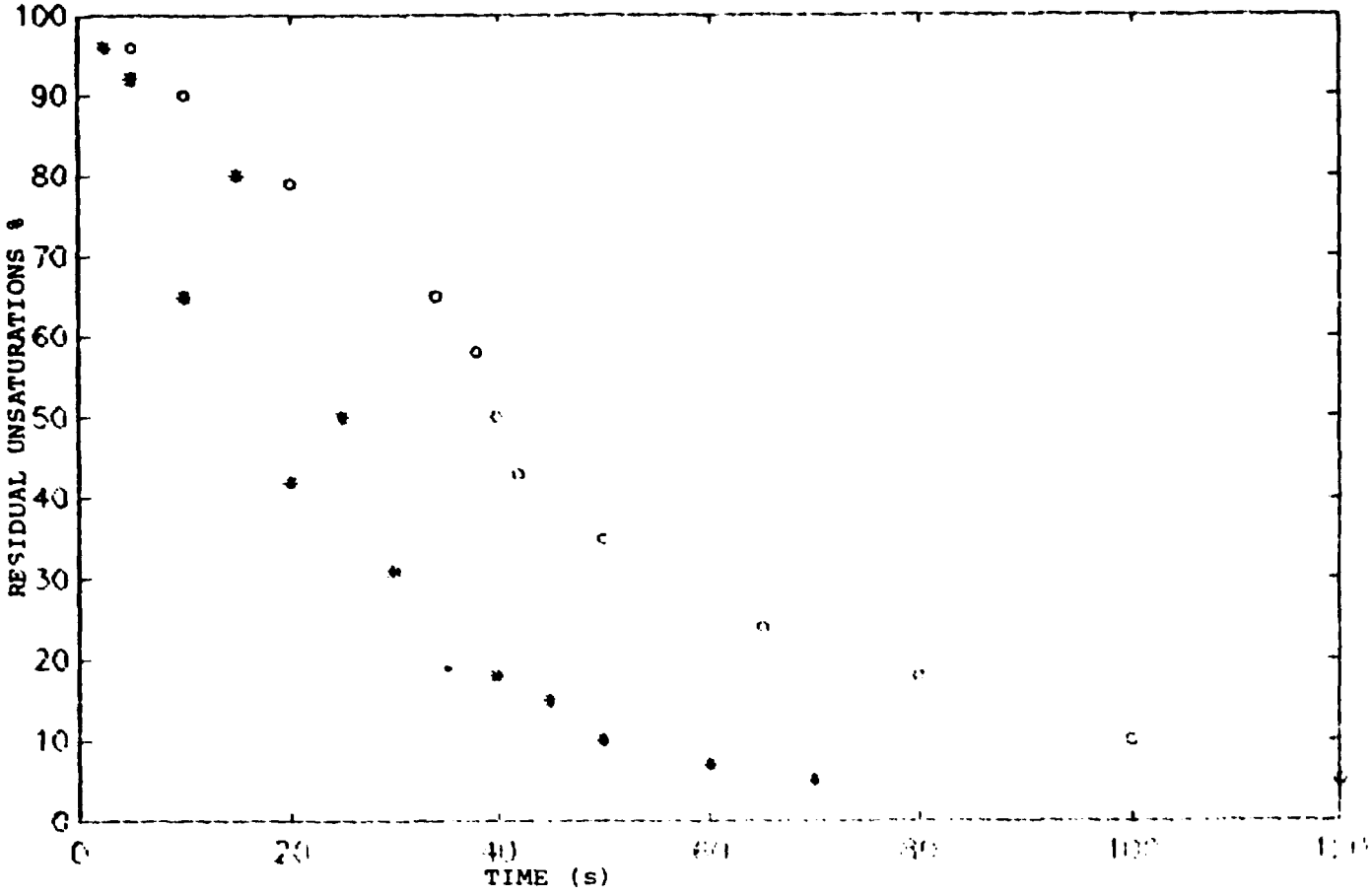

FIG.2-Per cent residual unsaturation (1,2-vinyl groups,by IR analysis) of cis-polybutadiene onto cellulose as a function of irradiation time t, in presence 7 wt/wt% Irgacure(a 2,44 mg.cm^{-2}and o in air * in N_2 stream).