PHOTOSYNTHETIC MEMBRANES
III: INFLUENCE OF PHOTO-CROSS-LINKING ON PERMEATION AND DIFFUSION COEFFICIENTS OF HYDROGEN AND CARBON MONOXIDE THROUGH ASYMMETRIC MEMBRANES PREPARED BY PHOTOGRAFTING OF 1,6-HEXANEDIOL DIACRYLATE ONTO CELLULOSE

IGNAZIO RENATO BELLOBONO, ELENA SELLI, BRUNO MARCANDALLI and DINO COMI

Cattedra di Chimica, Department of Physical Chemistry and Electrochemistry, University of Milan, I-20133 Milano (Italy)

ENOS RASTELLI

SORI S.p.A., I-20070 Guardamiglio (Milano) (Italy)

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Summary

Asymmetric membranes were prepared by photochemical grafting of 28.1 μmol cm^{-2} of 1,6-hexanediol diacrylate onto cellulose in the form of filter paper, in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as a photoinitiator, the molar ratio of photoinitiator to acrylated monomer being fixed at 0.086. A fixed polychromatic irradiation flux of 20.2×10^{-8} einsteins s^{-1} cm^{-2} was used. After 10 min irradiation, a nearly quantitative graft yield was reached. By multiple internal reflection IR analysis, a structure with one pendant acrylate group per monomer unit was assigned to the grafted polymer; at longer irradiation times, a further decrease in unsaturation resulting from photo-cross-linking between pendant acrylate groups was observed. Permeabilities P and diffusivities D at 25 °C for hydrogen and carbon monoxide were measured for membrane specimens obtained at different irradiation times. An increase in P reflects a decrease in unsaturation, while the D are independent of irradiation time. The selectivity of the membranes is not influenced by photo-cross-linking.

1. Introduction

The possibility of obtaining systems which behave as asymmetric membranes for gas separation, by photoinduced grafting of ultrathin layers of acrylic copolymers onto a macroporous substrate, was first demonstrated in a previous paper [1]. The kinetics of photoinitiated grafting of single acrylic monomers onto cellulose has since been studied systematically [2] under

experimental conditions suitable for the preparation of asymmetric membranes.

In the present work the influence of irradiation time on membrane performance was investigated, both by examining kinetic variations in the permeabilities and diffusivities of hydrogen and carbon monoxide through the grafted polymer layer and by analysing the percentage of double bonds as a function of the length of irradiation. This model study has been carried out on membranes prepared by photografting of 1,6-hexanediol diacrylate onto cellulose, a monomer on which the most important kinetic information has already been obtained [2]. Hydrogen and carbon monoxide were chosen as the permeating gases because of the satisfactory selectivity of the photochemically prepared acrylic membranes towards them.

2. Experimental details

The sources of cellulose, 1,6-hexanediol diacrylate and 1,2-diphenyl-2,2-dimethoxyethanone were those given in ref. 2.

1 ml of a solution of dry acetone containing 0.795 ± 0.002 M 1,6-hexanediol diacrylate and photoinitiator (molar ratio of the photoinitiator to the photoreactive monomer fixed at 0.0860 ± 0.0003) was uniformly deposited, as described in ref. 2, on a cellulose disk of diameter 6 cm. After evaporation of the solvent under vacuum (0.1 mbar), the sample was irradiated in an inert atmosphere, as described in ref. 2, with a fixed polychromatic flux of $(20.2 \pm 0.7) \times 10^{-8}$ einsteins s^{-1} cm^{-2}. After irradiation for 10 min under the experimental conditions employed in the present work, grafting with a yield of $97\% \pm 2\%$ occurred. Membranes obtained with different irradiation times, ranging between 10 and 280 min, after extraction and drying under vacuum as described in ref. 2, were subjected to two different types of measurement.

The permeation coefficients P and diffusion coefficients D for hydrogen and carbon monoxide at 25 °C were measured following the same technique and employing the same instrumentation as described previously [3]. The mean thickness of the supported membrane layer, excluding the cellulose support, was evaluated on the basis of its mass and density, the latter being determined experimentally for monomer samples photopolymerized on glass plates as a function of irradiation time. The thicknesses (62 - 86 μm) obtained in this way were employed in calculations as the effective membrane thicknesses. The results are reported in Table 1; the $- \log P$ are plotted as a function of membrane irradiation time in Fig. 1.

In a parallel series of runs, grafted acrylate membranes were analysed, both during the grafting period and during the successive irradiation, by multiple internal reflection (MIR) IR spectroscopy, in order to evaluate the percentage of original double bonds that remained at each irradiation time. The sharp peak at 810 cm^{-1} corresponding to the CH_2=CH— out-of-plane vibration of the acrylate group was used. For this band the penetration

TABLE 1

Permeabilities P, diffusivities D and solubilities S of hydrogen and carbon monoxide at 25 °C in photografted and photo-cross-linked poly(1,6-hexanediol diacrylate) membrane prepared by irradiation of 28.1 μmol cm^{-2} of monomer supported onto cellulose at various times t of irradiation with a flux of $(20.2 \pm 0.7) \times 10^{-8}$ einsteins s^{-1} cm^{-2}

t (min)	P (cm^2 cmHg^{-1} s^{-1})	D (cm^2 s^{-1})	S (cmHg^{-1})
Hydrogen			
10[a]	$(1.7 \pm 0.3) \times 10^{-10}$ [b]	$(3.8 \pm 0.9) \times 10^{-9}$ [b]	$(4.5 \pm 0.8) \times 10^{-2}$
64	$(3.6 \pm 0.7) \times 10^{-10}$	$(4.1 \pm 1.2) \times 10^{-9}$	$(8.8 \pm 1.7) \times 10^{-2}$
115	$(3.7 \pm 0.7) \times 10^{-10}$	$(3.7 \pm 0.8) \times 10^{-9}$	$(1.0 \pm 0.2) \times 10^{-1}$
176	$(4.6 \pm 0.7) \times 10^{-10}$	$(4.6 \pm 1.3) \times 10^{-9}$	$(1.0 \pm 0.2) \times 10^{-1}$
210	$(5.4 \pm 1.2) \times 10^{-10}$	$(3.9 \pm 0.9) \times 10^{-9}$	$(1.4 \pm 0.3) \times 10^{-1}$
242	$(5.2 \pm 0.6) \times 10^{-10}$	$(3.5 \pm 1.0) \times 10^{-9}$	$(1.5 \pm 0.2) \times 10^{-1}$
280	$(5.0 \pm 0.5) \times 10^{-10}$	$(4.3 \pm 1.0) \times 10^{-9}$	$(1.2 \pm 0.1) \times 10^{-1}$
Carbon monoxide			
10	$(3.6 \pm 0.4) \times 10^{-11}$	$(2.6 \pm 0.8) \times 10^{-9}$	$(1.4 \pm 0.2) \times 10^{-2}$
20	$(4.4 \pm 0.4) \times 10^{-11}$	$(3.4 \pm 1.0) \times 10^{-9}$	$(1.3 \pm 0.1) \times 10^{-2}$
35	$(5.9 \pm 1.3) \times 10^{-11}$	$(3.1 \pm 0.7) \times 10^{-9}$	$(1.9 \pm 0.4) \times 10^{-2}$
50	$(6.1 \pm 0.7) \times 10^{-11}$	$(2.9 \pm 0.5) \times 10^{-9}$	$(2.1 \pm 0.2) \times 10^{-2}$
72	$(6.1 \pm 1.1) \times 10^{-11}$	$(3.3 \pm 0.8) \times 10^{-9}$	$(1.8 \pm 0.3) \times 10^{-2}$
90	$(7.6 \pm 0.7) \times 10^{-11}$	$(3.0 \pm 0.6) \times 10^{-9}$	$(2.5 \pm 0.2) \times 10^{-2}$
142	$(1.1 \pm 0.2) \times 10^{-10}$	$(2.3 \pm 0.9) \times 10^{-9}$	$(4.8 \pm 0.9) \times 10^{-2}$
200	$(9.3 \pm 1.6) \times 10^{-11}$	$(2.6 \pm 0.8) \times 10^{-9}$	$(3.6 \pm 0.6) \times 10^{-2}$
240	$(1.0 \pm 0.2) \times 10^{-10}$	$(2.9 \pm 0.7) \times 10^{-9}$	$(3.4 \pm 0.5) \times 10^{-2}$
276	$(1.1 \pm 0.1) \times 10^{-10}$	$(3.2 \pm 0.9) \times 10^{-9}$	$(3.3 \pm 0.2) \times 10^{-2}$

[a]Time corresponding to a practically quantitative graft yield (95% or above), as measured by gravimetric analysis and to nearly 50% residual acrylate groups in the grafted layer, as measured by MIR IR.
[b]Uncertainties are expressed as standard deviations from the mean value of 4 - 6 permeametric determinations on different samples.

depth, under the experimental conditions, was about 6.5 μm, a depth statistically corresponding in the great majority of cases to about one tenth of the mean grafted polymer thickness in the membrane. The MIR penetration depth, however, exceeded the mean thickness of the dense skin layer, which was fairly low in most cases (see Fig. 2). No interference by the cellulose substrate was noticed for the 810 cm^{-1} band. MIR spectra were measured on a Perkin–Elmer spectrophotometer, using an MIR accessory with a KRS-5 crystal and a single incident angle of 45°. Analytical values of residual acrylate groups were corrected for the apparent thickness increase obtained from the accompanying density variations during photo-cross-linking of the grafted layer.
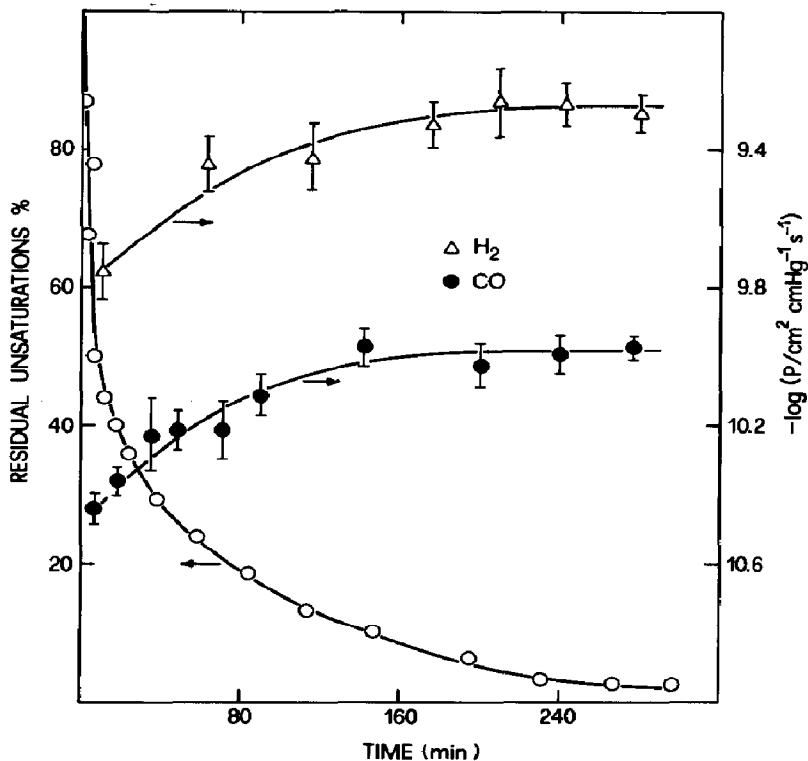
Fig. 1. Left ordinate: per cent residual unsaturation (acrylate groups, by MIR IR spectroscopic analysis) during photografting and successive photo-cross-linking of 1,6-hexanediol diacrylate onto cellulose, as a function of irradiation time (in minutes). Right ordinate: negative logarithm of the permeabilities P (cm^2 $cmHg^{-1}$ s^{-1}) of hydrogen and carbon monoxide through the membranes prepared in this work as a function of irradiation time (in minutes).

3. Results and discussion

Asymmetric membranes were prepared by photochemical grafting of 28.1 μmol cm^{-2} of 1,6-hexanediol diacrylate onto cellulose in the form of filter paper, with a polychromatic irradiation flux of $(20.2 \pm 0.7) \times 10^{-8}$ einsteins s^{-1} cm^{-2} for 10 min at 30 ± 2 °C in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as the photoinitiator (with a molar ratio of 0.086 between photoinitiator and monomer). During the grafting period, the percentage of double bonds, as determined by MIR IR spectroscopy, decreased from an initial 100% to about 50% (see Fig. 1). Owing to the kinetics conditions, this corresponded to grafting of a homopolymer chain onto the substrate with a quantum yield of 46 ± 4 monomer molecules per quantum and a nearly quantitative graft yield (97% ± 2%). The results of MIR IR analysis thus clearly show that a structure with one pendant acrylate group per monomer unit may be assigned to grafted polymer.
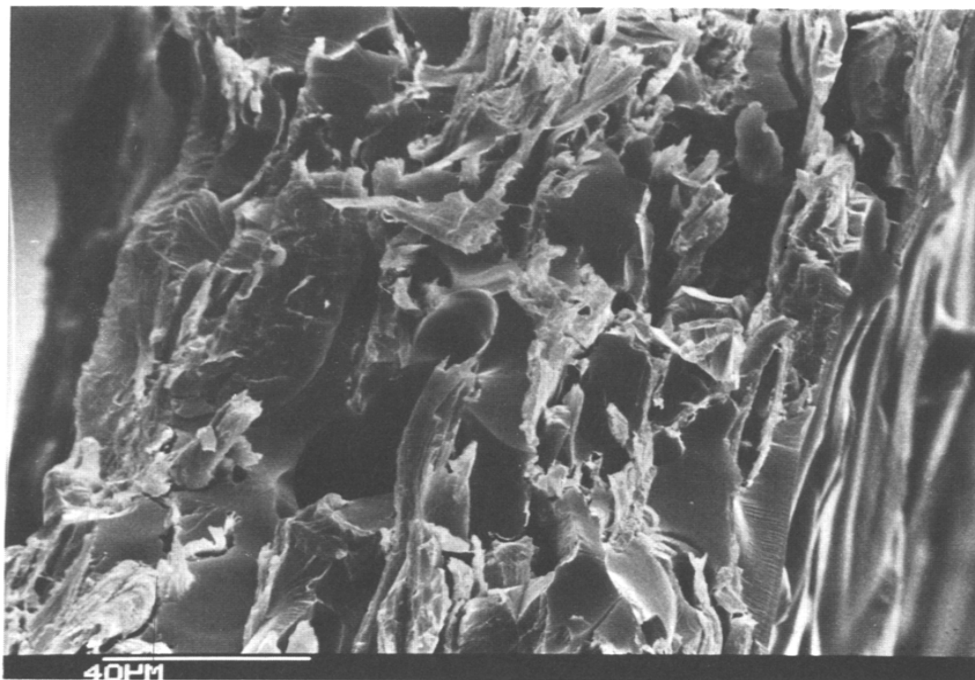
(a)
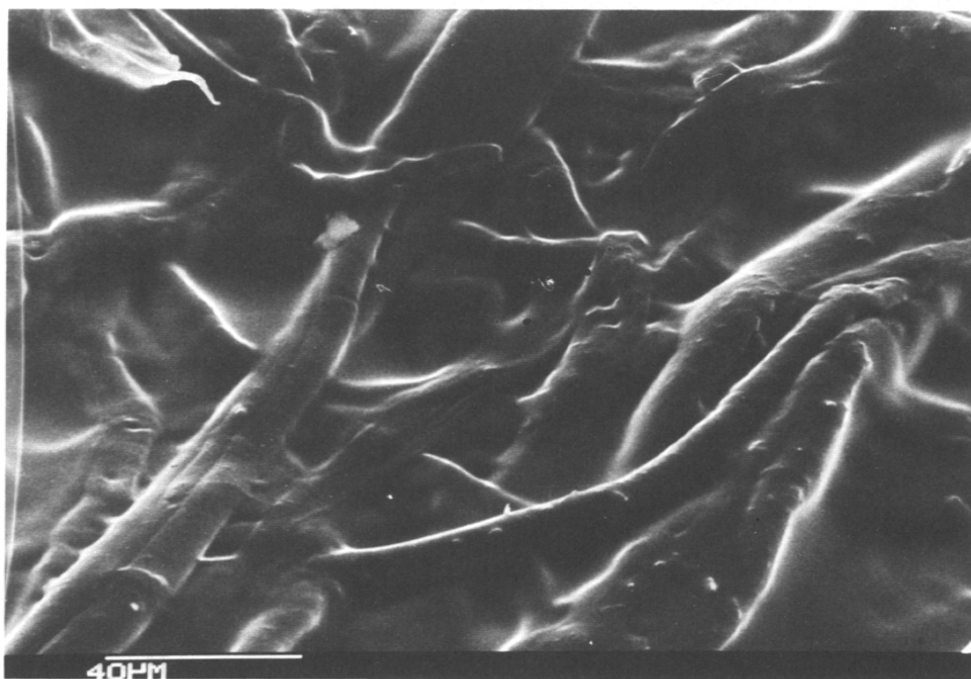
(b)

Fig. 2. Electron micrograph (scale shown on figure) of (a) the cross-section and (b) the surface top layer of a membrane prepared by photoinitiated grafting of 28.1 μmol cm^{-2} of 1,6-hexanediol diacrylate onto cellulose.

Irradiation of the samples was continued after the end of the grafting period. A further decrease in unsaturation was observed and followed by means of MIR IR analysis. Permeametric characterization of membranes was also carried out, consisting in the measurement of P and D for hydrogen and carbon monoxide at 25 °C as a function of irradiation time. The results are reported in Table 1. The P are also reported graphically in Fig. 1, in which the MIR IR experimental data are also shown. The following are clearly observed: (i) the increase in the permeation coefficients as a function of time is paralleled by photo-cross-linking between pendant acrylate groups which brings about a decrease in unsaturation (Fig. 2); (ii) the diffusion coefficients remain unaffected by irradiation of the grafted layer, within the limits of experimental error (see Table 1); (iii) furthermore, the ratio between the permeation coefficients of hydrogen and carbon monoxide is practically constant (in other words the selectivity of the membranes does not appear to be appreciably influenced by photo-cross-linking). As a consequence of (ii) and (iii), the variations in permeation coefficients imply only changes in the solubility S of the gases in the grafted layer after irradiation, as expressed by $S = P/D$ reported in Table 1.

A dense skin layer is obtained in the membranes at the end of the constant-rate grafting period, during which unsaturation decreases linearly with time, as indicated in Fig. 1; its structure, as illustrated by electron micrography (Fig. 2), is fully compatible with that of an oligomolecular layer of homopolymer grafted onto the cellulose substrate either by photoinitiator radical propagation or by a cellulose radical propagation mechanism, as discussed in our previous paper [2]. Further irradiation, after the grafting stage, modifies the grafted polymer, reduces its unsaturation from 50% of the grafted diacrylate to very low values amounting to a few per cent of the initial value. The photo-cross-linking mechanism may possibly involve radical formation from pendant acrylate groups of the grafted chains either by direct excitation in the high energy UV region or via energy transfer by photoinitiator triplets, both processes occurring with quantum yields much lower than those of the first constant-rate grafting period. The main physicochemical effect of photo-cross-linking on the transport properties of the investigated gases appears to be on the solubility. This is not an improbable conclusion, since the presence of double bonds conjugated to carbonyl groups in pendant acrylate groups should strongly affect the adsorption and desorption as well as the absorption characteristics. The solubility generally seems to increase, even if without specificity for the two gases, with a decrease in unsaturation and the progressive cross-linking of grafted chains. The diffusion coefficients, on the contrary, are not perceptibly altered outside the range of experimental uncertainty.

Acknowledgments

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