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Improving the performance of PVA/AA photopolymers for holographic recording

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ABSTRACT

Photopolymers have proven to be useful recording material for applications such as holographic data storage or holographic optical elements. In this work, the performance of a 900 μm thick polyvinyl alcohol/acrylamide photopolymer (PVA/AA) developed in our laboratory is improved by means of 4,4′ azo-bis-(4-cyanopentanoic acid), ACPA. We minimizing the initiator effect of ACPA working at low recording intensity of 5 mW/cm^2. The improved photopolymer presents low scattering and diffraction efficiencies as high as 85%. This result is related to the chain transfer effect produced by ACPA.

1. Introduction

Photopolymers are versatile holographic recording materials for use in the development of new optical elements as well as in data storage devices. For these ongoing applications the recording materials must be optimized to obtain maximum diffraction efficiency with low scattering. Photopolymers with a hydrophilic matrix such as polyvinyl alcohol (PVA) are adequate materials for use in hologram recording experiments. They use water as the solvent and can be made in layers of different thicknesses [1–4]. One of the photopolymers most widely used is composed of acrylamide (AA) as polymerizable monomer, triethanolamine (TEA) as radical initiator, yellowish eosin (YE) as dye and PVA and water as binder [5–10]. TEA is the initiator most often used with dyes derived from fluorescein because they can generate a radical in a redox reaction under excitation by light. The dye is bleached in this reaction because it is decomposed in the photoinitiation reaction [11–14].

The use of a redox initiation is not possible for other compounds such as pyrromethene derived dyes because they are not photoreducible and thus another initiation system is necessary in these cases. 4,4′ azo-bis-(4-cyanopentanoic acid), ACPA, is a water soluble radical initiator used in solution polymerization with thermal initiation. The molecule produces two radicals and one nitrogen molecule when it reacts with the excited dye in the initiation and the radicals generated react with the monomer in the propagation step. We used this initiator with a dye derived from pyrromethene in a solid layer polymerization and in a previous study we developed a holographic recording material that contains ACPA and pyrromethene dye in a PVA matrix [15]. ACPA is an interesting initiator for this kind of dyes which cannot react with TEA in a redox reaction.

In this work, we use ACPA as a chain transfer agent (CTA) and not as initiator, due to its capacity to generate two identical radicals. TEA/YE is the redox system with TEA as initiator. It is necessary to adjust the recording intensity conditions of the chain transfer experiments to minimize the initiation capacity of the ACPA molecule. The inclusion of CTA's into PVA/AA photopolymers in order to improve their holographic performance through a reduction of the molecular weight of polymer chains grown during the recording of holographic optical elements, was introduced and developed by Gleeson et al. [16–19].

When a diffraction grating is recorded in a photopolymer, a radical polymerization initiated by light takes place in the exposed zones. The basic mechanism in a radical polymerization involves the following reactions:

Initiation

$$I \xrightarrow{k_d} 2R^{\cdot} \tag{1}$$

$$R^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot} \tag{2}$$

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Propagation

$$
\begin{aligned}
&M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}\\
&M_2^{\cdot} + M \xrightarrow{k_p} M_3^{\cdot}\\
&\vdots\\
&M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot}
\end{aligned}
\qquad (3)
$$

Termination

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{k_{tc}} M_{x+y} \qquad (4)$$

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{k_{td}} M_x + M_y \qquad (5)$$

In a photopolymerization, the mechanism of initiation is more complex that those indicated by Eqs. (1) and (2). A more detailed scheme is included in Refs. [11,12,20]. For this work we consider only the propagation reactions (3).

The radicals **R.** derived from the initiator molecule (TEA), Eq. (1), react with the monomer M (AA), Eq. (2), generating a growing macroradical M_n**.** in the propagation reaction system (3). Two growing macroradicals are deactivated by combination or disproportionation in the (4) and (5) termination reactions. Kinetic constants are denoted by letter 'k', with a subscript for each reaction.

1.1. Chain transfer mechanism

Adding a chain transfer agent *XA* to the photopolymer composition introduces a new reaction in the propagation reaction system (3) of the kinetic scheme:

$$M_n^{\cdot} + \mathrm{XA} \xrightarrow{k_{tr}} M_n - X + A^{\cdot} \qquad (6)$$

where $M_{n^{\cdot}}$ is a growing macroradical that reacts with the chain transfer agent XA producing deactivation of the growing macroradical. The new radical $A^{\cdot}$ can start a new polymer chain according to the following reaction:

$$A^{\cdot} + M \xrightarrow{k_a} M_1^{\cdot} \qquad (7)$$

The chain transfer has two effects on the polymerization reaction. The main effect is the decrease in polymer chain molecular weight due to the presence of XA molecules, which deactivate the growing macroradicals $M_{n^{\cdot}}$. Another possible effect may be seen in the kinetics. The reaction velocity may decrease or remain the same as in the case of no chain transfer depending on the values of the kinetic constants k_{tr}, k_a and k_p. The usual situation is when $k_p \gg k_{tr}$ and $k_a \approx k_p$ and therefore the velocity of polymerization does not change. On the other hand, if $k_a < k_p$ the polymer chain molecular weight and polymerization velocity decrease [11,12,20–22].

In this paper, the performance of a 900 μm PVA/AA photopolymer, developed in our laboratory, is improved thanks to a chain transfer effect. We use ACPA as chain transfer agent XA in a photopolymer with TEA/YE as initiator system. We analyze the influence of the chain transfer effect on the holographic characteristics of the photopolymer.

2. Holographic set-up

To study the behavior of the photopolymer as a holographic recording material, we obtained unslanted diffraction gratings using the holographic set-up shown in Fig. 1. A 514 nm beam from an Argon ion laser was used to store diffraction gratings by means of continuous laser exposure. The laser beam was split into two secondary beams with an intensity ratio of 1:1. The diameter of these beams was increased to 1.5 cm with an expander, while spatial filtering was ensured. The object and reference beams were recombined at the sample at an angle $\theta = 16.8°$ to the normal with an appropriate set of mirrors, and the spatial frequency obtained was 1125 lines/mm. The working intensity at 514 nm was 5 mW/cm^2. The diffracted and transmitted intensity were monitored in real time with a He–Ne laser positioned at Bragg's angle ($\theta' = 20.8°$) tuned to 633 nm, where the material is not sensitive. The diffraction efficiency (DE) was calculated as the ratio of the diffracted beam to the incident power. The transmission efficiency (TE) was calculated as the ratio of the transmitted beam to the incident power. The Fresnel losses are not considered in the calculation and therefore the DE$_{\max}$ values obtained in the angular scan will be 10–15% higher [9].

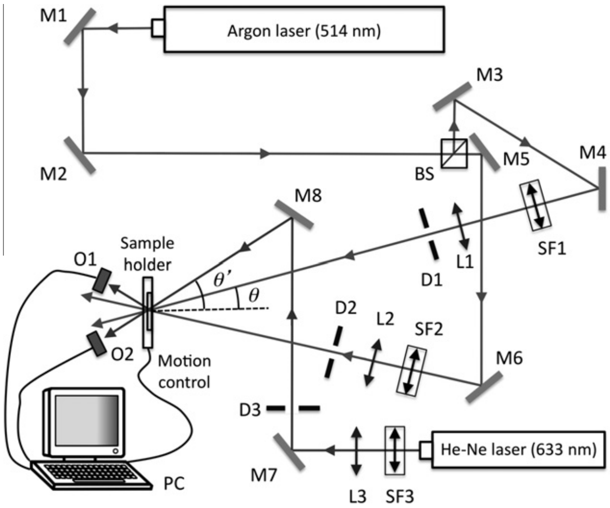

Fig. 1. Experimental set-up: BS, beamsplitter, M_i, mirror, SF_i, spatial filter, L_i, lens, D_i, diaphragm, PC, data recorder.

3. Preparation of the photopolymers

In holographic recording materials based on PVA/AA, a solution of PVA in water forms the matrix and this was used to prepare the solution of the acrylamide monomer, ACPA and the photopolymerization initiator system: yellowish eosin and triethanolamine. The PVA was supplied by Fluka, AA, TEA and ACPA by Aldrich and YE by Panreac. The solutions were prepared using a conventional magnetic stirrer, under red light, and left in a climatic chamber (Fisher Scientific Climacell 222) to allow the water to evaporate in controlled conditions ($T = 20 \pm 1$ °C, relative humidity = 45 ± 5%). The concentrations of the components in the optimized photopolymer solution can be seen in Table 1. The solution was deposited by gravity in circular polystyrene molds to avoid strain and distortion in the material during the water evaporation process and left in the dark to allow the water to evaporate. During this time the laboratory conditions (temperature, T, and relative humidity, RH) were recorded. When part of the water had evaporated, the "dry" mate-

Table 1
Component concentrations in the prepolymer syrup.

Component	Photopolymer A	Photopolymer B	Photopolymer C
AA	0.34 M	0.34 M	0.34 M
TEA	–	0.15 M	0.15 M
YE	9.1×10^{-5} M	9.1×10^{-5} M	9.1×10^{-5} M
ACPA	9.0×10^{-3} M	$(0–9.0)\times 10^{-3}$ M	–
PVA Fluka 18-88			
M_w = 130,000 u	13.4% m/v	13.4% m/v	13.4% m/v