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Chemical mechanism of photobleaching of poly-3BCMU film

Xiang-yang Zhang [a], Qu Li [b], Ju-zheng Liu [a], S. Sottini [c]

[a] *Department of Chemistry, National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, China*
[b] *Department of Applied Physics, Shanghai Jiaotong University, Shanghai 200030, China*
[c] *IROE–CNR, Via Panciatichi 64, Firenze, Italy*

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Abstract

The experimental results of photobleaching of poly[4,6-decadiyne-1,10-diolbis(*n*-butoxycarbonylmethylurethane)] (poly-3BCMU) film are given in this paper. From changes in the UV spectra of the films before and after photobleaching and effects of oxygen and a laser on photobleaching, we might conclude that poly-3BCMU films undergo the degradation layer by layer from the surface to the inner region and that in every layer poly-3BCMU molecules decompose step by step and finally form small soluble molecules. Also, we studied in detail the effect of oxygen on photobleaching and concluded that the decomposition of the films is a zero-order reaction with respect to oxygen in air. The experimental results could be of use to the photobleaching technique and waveguide manufacture.

Keywords: Photobleaching; Poly-3BCMU

1. Introduction

Organic and polymeric compounds have now been the focus of research into non-linear optical (NLO) materials because of their promise of large values of the second-order and third-order NLO susceptibilities, ultrafast response time, high optical damage thresholds and better architectural flexibility and ease of fabrication, and they have potential and widespread applications in the areas of all-optical switching, planar and channel waveguides, signal processing, optical computing and optical fibre telecommunications [1]. Polydiacetylenes (PDAs) are promising compounds among these organic and polymeric materials. Poly[4,6-decadiyne-1,10-diolbis(*n*-butoxycarbonylmethylurethane)] (poly-3BCMU) is a typical representative and is also an organic NLO material which is likely to be applied in future devices. It has been reported that [2] the non-resonant χ^3 value of poly-3BCMU is -2×10^{-10} e.s.u., and the response time is of the order of picoseconds. Poly-3BCMU is a linear π-conjugated polymer prepared by solid state polymerization of diacetylene monomers. In the polymeric system, the conjugated carbon backbone holds the main origin of the NLO properties, while side groups provide structure control and facilitate materials processing. The long alkyl chain side groups attached to the conjugated backbone of diacetylene monomers, such as the urethane parts (–OCONH–), have two advantages: the first that they participate in the van der Waals interactions between monomers, and the second that the incorporated urethane groups lead to a planar structure on polymerization by forming hydrogen bonds between adjacent side groups. The architectural flexibility resulting from the modification of the chemical structures of substituted side groups allows PDAs to be prepared in the form of single crystals, Langmuir–Blodgett (LB) films, thin films and solutions. In particular, they are suitable for making waveguide devices. Recently Westlan et al. reported that PDAs were made as optical waveguides which had been applied in signal processing [3]. To produce waveguide devices made of organic films, fabrication techniques for waveguide devices must be developed. Spin coating, evaporation, sputtering, LB technique, photoetching and photobleaching are possible ways of making planar and channel waveguides. Photobleaching can greatly after the refractive index of organic films and therefore can be used to fabricate optical waveguides, such as lens, gratings, and planar and channel waveguides [4–6]. This article will give in detail the experimental results for the photobleaching processes of poly-3BCMU films and thus put forward a possible chemical mechanism for the process.

2. Experimental section

The average molecular weight of poly-3BCMU in the experiment was 375 000. Poly-3BCMU films were prepared

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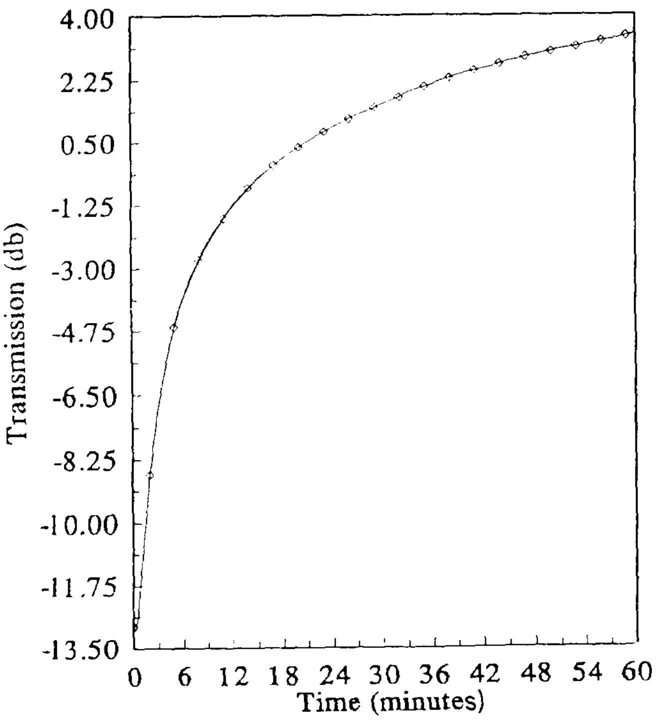


Fig. 1. Transmission of 488 nm bleaching light through 1 μm thick poly-3BCMU film during the photoinduced bleaching process. The power density of the beam was 7 W cm^{-2}.

from poly-3BCMU solution by the spin coating method and their thickness was about 1 μm. The bleaching light in the experiment was irradiation from an Ar ion laser. The laser beam was split into two beams with a beam splitter, one as the photobleaching beam and the other as the reference beam. We described the course of photobleaching of poly-3BCMU films by the ratio between the power of transmitted beam through the films and the power of reference beam. Fig. 1 is for a typical photobleaching process. The variations in T (transmissivity) with time reflected changes in some properties of the films. To clarify the deeply photobleaching process of poly-3BCMU films, we measured the absorptive spectra of the films in different stages and in different conditions.

3. Results and discussion

Fig. 1 is a typical photobleaching curve. The variations in T with time indicated some changes in physical or chemical properties of the films in the process of bleaching, and these changes in properties resulted in the alteration of the refractive index of thin films. For instance, the refractive index of poly-3BCMU films is 1.67 before bleaching and 1.51 after complete bleaching ($\lambda = 849$ nm) [7].

3.1. UV spectrum

Fig. 2 gives the absorptive spectra of poly-3BCMU films in different stages of photobleaching. Fig. 2(a) shows complete photobleaching absorptive curves of poly-3BCMU films at different bleaching stages. There were stronger absorptive peaks in the regions with $\lambda = 400$ nm–700 nm for the unbleached film. The two strong peaks broadened and gradually became weak with bleaching time; at the same time, some weak peaks appeared in the far UV region (220–320 nm). The peaks finally disappeared when the films were completely bleached. For unbleached films, there were two strong peaks ($\lambda_{max} = 550$ nm, $\lambda_{max} = 620$ nm) which corresponded to the π–π^* transition of the long conjugated backbone of the poly-3BCMU molecules. The broad peaks (400 nm–700 nm) became weaker and weaker and finally disappeared with the bleaching time, but the peaks did not shift to the blue region. This indicates that the bleaching process first took place on the surface layer of the films and then gradually moved into the interior of the films. Fig. 2(b) is an expanded view of the 200 nm–400 nm region of Fig. 2(a). At 30–45 min the UV spectrum of bleaching films was similar to that of the monomer. At the end of bleaching the weak peaks disappeared, indicating that monomer-like molecules underwent further changes. This is a subject of further research. Fig. 2(c) shows an absorptive curve of poly-3BCMU monomer and there were only a few weak absorptive peaks in the far UV region (220 nm–320 nm). These peaks corresponded to the π–π^* transition of the conjugated diacetylene backbone and the n–π^* transition of carbonyl groups of side chains of the monomer. The strong absorption ($\lambda \leq 220$ nm) corresponded to n–σ^* or σ–σ^* transitions of monomer molecules. The absorptive curves of polymer films at different bleaching times showed that long conjugated chains undergo two interlacing processes: (a) the process of degradation from the surface to the interior of film layer by layer and (b) the process of degradation from long conjugated chain to short conjugated chain, to monomer-like compounds, and to small molecules, with the conjugated unsaturated bonds finally being broken completely.

3.2. Effect of oxygen on photobleaching

As we know, photobleaching of films must have two fundamental conditions: photons and oxygen. Rochford et al. [3] reported that poly-4BCMU films cannot be bleached with laser light of wavelength 488 nm in a vacuum chamber because of the lack of oxygen. In our experiment we laid stress on the effect of oxygen on photobleaching when we studied the photobleaching process of poly-3BCMU films. We found that the photobleaching depended on whether molecules of oxygen exist on the surface of the films, not on the time for which the films were exposed in the air (Fig. 3). The results indicated that oxygen required for the photobleaching does not come from oxygen already permeated in the films but directly from the surrounding atmosphere. Further researches showed that with respect to the concentration of oxygen the reaction of the bleaching of poly-3BCMU films is zero-order in conditions of not very high vacuum but, when the vacuum is very high, photobleaching of poly-3BCMU

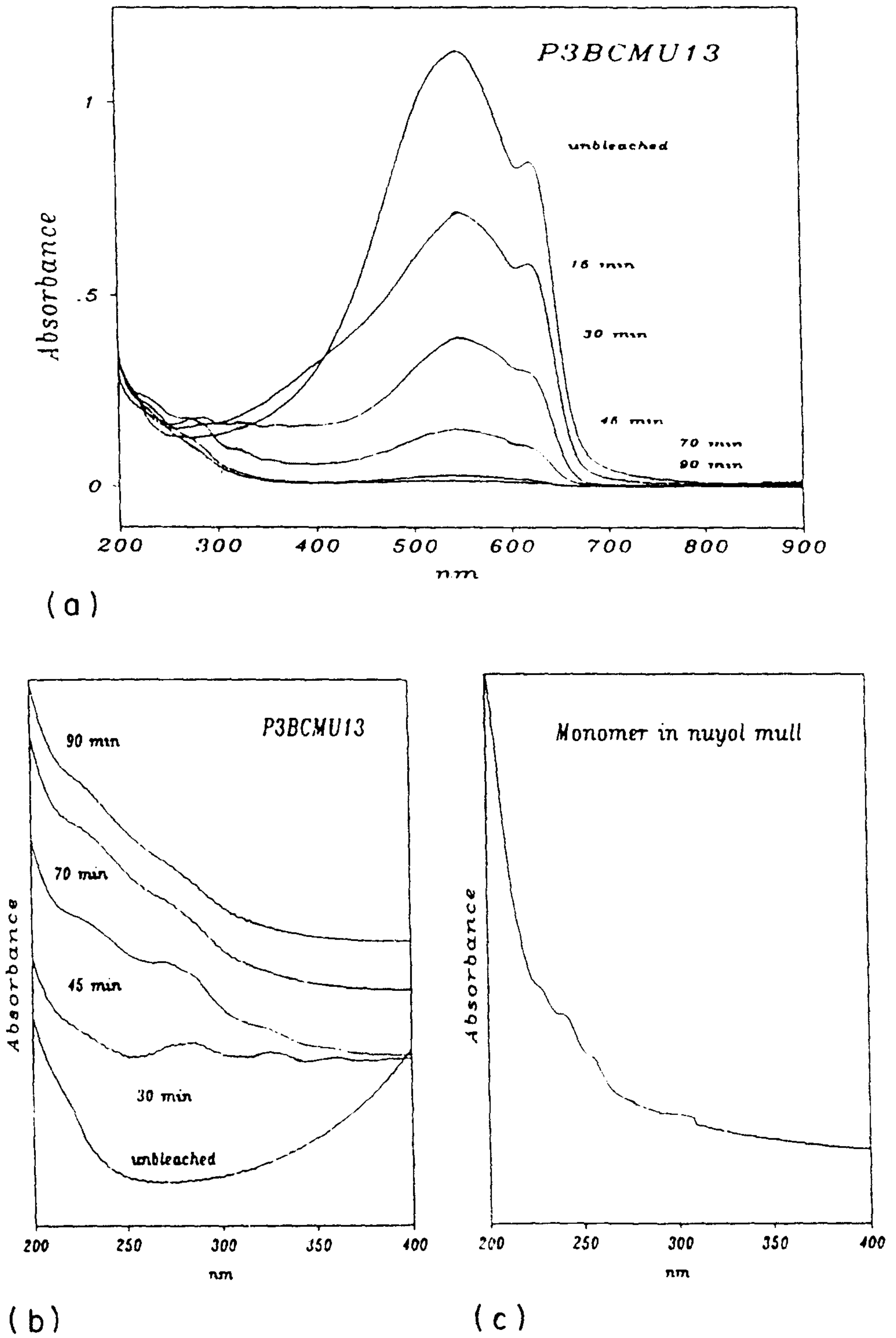


Fig. 2. (a) Spectra of a film during the bleaching. (b) Expanded view of the UV region ($\lambda = 200$–400 nm). (c) Spectrum of the 3BCMU monomer.

films depended strongly on concentration of oxygen–magnitude of vacuum pressure.

When practical optical waveguide devices are made by the photoetching method, poly-3BCMU films must be first coated with photoetching adhesives and then exposed to light radiation. It is important to us whether the exposure process causes possible bleaching of poly-3BCMU films and thus alters linear and non-linear properties of poly-3BCMU waveguides. In order to make clear possible unfavourable effects of the exposure process, we studied the photobleaching processes of poly-3BCMU films coated with photoetching adhesives. The thicknesses of two poly-3BCMU films were both 1 μm; one film was coated with 0.4 μm thick photoetching adhesives (photoresist), and the other was used as a reference film. We obtained the experimental results that the rate of bleaching of poly-3BCMU film coated with pho-

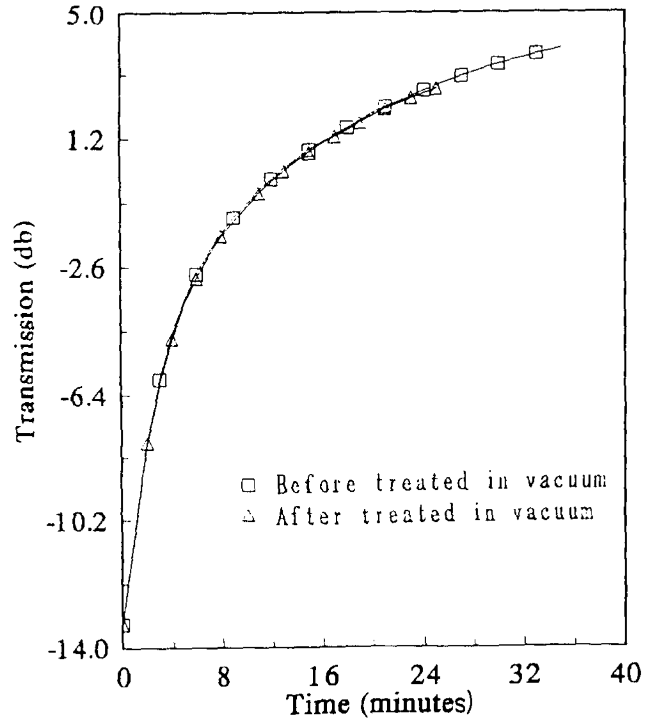


Fig. 3. Photoinduced bleaching processes of poly-3BCMU film before (□) and after (△) it was treated in a vacuum chamber. The power density of the bleaching beam was 7 W cm^{-2}.

toetching adhesive was much lower than that of naked film (Fig. 4). This is because the coating almost isolated the oxygen supply from the surface of the film. Therefore, in such experimental conditions, a few seconds of exposure did not cause obvious photobleaching of the poly-3BCMU film coated with photoetching adhesives. However, subsequent development of the films after exposure could slightly affect the surface structure of the films and thus lead to some unfavourable influence on the quality of slab waveguides because the developing solvent dissolved partly and expanded the surface of poly-3BCMU films. The problem must be solved when the method is applied to fabricate waveguides.

We previously mentioned that photobleaching must have two necessary conditions: photons and oxygen. How exactly does oxygen play a role in the process of bleaching? For most polymer systems, the quantum efficiency of photodegradation is relatively low under light radiation ($\lambda \geqslant 315$ nm) and is still low even for light radiation ($\lambda < 315$ nm) without oxygen because the light radiation cannot effectively and rapidly initiate photodegradation of organic polymers. This is true for poly-3BCMU molecules. Also, the light ($\lambda = 488$ nm) in our experiment cannot be effectively absorbed by poly-3BCMU molecules to produce enough active radicals which initiate degradation of the molecules, and thus no obvious bleaching took place without oxygen. However, in the presence of oxygen molecules, the case was different. At first poly-3BCMU molecules absorbed energy from photons and then interacted with triplet state oxygen molecules ($^3O_2$) (that is, ground state) and transferred energy to oxygen molecules; then singlet state oxygen molecules ($^1O_2$) were generated. The energy difference between the two states of oxygen is about 94.2 kJ mol^{-1}. The light radiation at 849 nm [7] and even at 1.06 μm can satisfy the requirement, but in fact light from 400 nm to 700 nm is more suitable for the process. It could be described as follows:

$$^1\{\text{poly-3BCMU}\} \xrightarrow{h\nu} {}^3\{\text{poly-3BCMU}\}^* \qquad (1)$$

$$^3\{\text{poly-3BCMU}\}^* + {}^3O_2 \longrightarrow {}^1O_2 + {}^1\{\text{poly-3BCMU}\} \qquad (2)$$

In the action of laser beam large quantities of active singlet oxygen were formed from triplet oxygen owing to the intensity of the laser. In contrast to triplet state oxygen molecules ($^3O_2$), singlet state oxygen molecules ($^1O_2$) are of very high activity and of longer lifetime. Also, singlet state oxygen molecules ($^1O_2$) are very sensitive and active to unsaturated compounds, and thus degradation of poly-3BCMU molecules of surface layer took place rapidly [8,9]. Why do we think that oxygen participates in the degradation in singlet state ($^1O_2$) molecules? Except for higher activity and longer lifetime of singlet state oxygen ($^1O_2$) molecules, there is the experimental fact that no obvious changes take place in the poly-3BCMU film when the film is exposed in air for weeks and even months without radiation of light, that is large quantities of triplet state ($^3O_2$) molecules cannot initiate the degradation of the films. Therefore we concluded that oxygen participates in the degradation in singlet state ($^1O_2$) molecules.

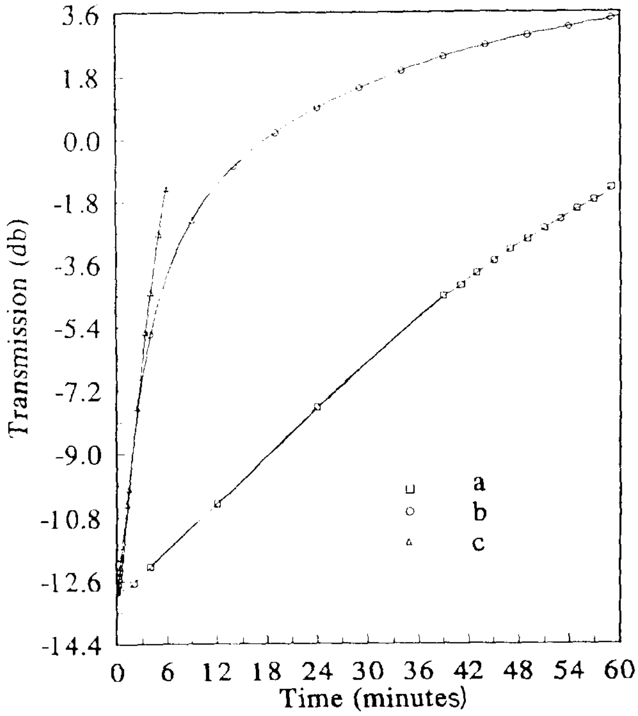


Fig. 4. Photoinduced bleaching processes of poly-3BCMU films before and after it was coated with photoresist: curve a (□), after coating with photoresist; curve b (○), before coating with photoresist; curve c (△), the same as curve a except that the time scale is compressed by a factor of 10.

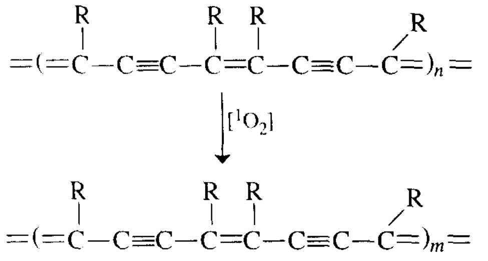
3.3. Mechanism of degradation

Trozzolo and Winslow [10] and Rahby and Rabek [11] studied photodegradation of organic molecules and put forward the mechanism involving singlet state oxygen molecules. From the differences in UV spectra of the films before and after bleaching and effect of oxygen on the bleaching, we concluded that poly-3BCMU molecules underwent reaction according to the following mechanism. Chemical degradations first took place on the surface of films. After the surface structure was broken, oxygen permeated into the next layer of the films accompanied by degradation of second-layer molecules. Thus the degradation went into the interior of the films gradually. Meanwhile, in every layer of the film, the mechanism involving active singlet state oxygen molecules was followed:

(i) from polymeric molecules to oligomer molecules;
(ii) from oligomer molecules to monomer-like molecules;
(iii) from monomer-like molecules to small molecules.

It may be described as follows:

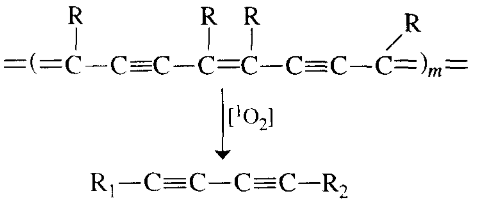
(i)



$$=(=\overset{R}{C}-C\equiv C-\overset{R}{C}=\overset{R}{C}-C\equiv C-\overset{R}{C}=)_n= \xrightarrow{[^1O_2]} =(=\overset{R}{C}-C\equiv C-\overset{R}{C}=\overset{R}{C}-C\equiv C-\overset{R}{C}=)_m=$$

$R = (CH_2)_3OCONHCH_2COO(CH_2)_3CH_3$; $m << n$

(ii)



$$=(=\overset{R}{C}-C\equiv C-\overset{R}{C}=\overset{R}{C}-C\equiv C-\overset{R}{C}=)_m= \xrightarrow{[^1O_2]} R_1-C\equiv C-C\equiv C-R_2$$

(iii) $R_1-C\equiv C-C\equiv C-R_2 \xrightarrow{[^1O_2]} R'-CH_2-R''$

Therefore we concluded that changes in the chemical structure of poly-3BCMU films accompanied the photobleaching process and thus caused variation in refractive index of the films. Research is being carried out to clarify the mechanism further.

3.4. Effect of laser power on degradation

Fig. 5 shows the photobleaching of the films with different power densities. At the same relative energy density, the bleaching efficiency of poly-3BCMU films with bleaching light at low power density is better than that at high power density. This also indicated that the supply of oxygen was important to the bleaching of poly-3BCMU films and that the permeating rate of oxygen into the films had different influences on the bleaching process at different power densities. At lower power density the supply of oxygen is enough to bleach the films; however, at high power density the supply of oxygen is not enough to satisfy the need of the fast bleaching process. Therefore we reached the conclusion that at the same energy density the bleaching efficiency of films depended on the power density of the bleaching light, that is bleaching light with lower power density was more effective in bleaching poly-3BCMU films. This property may be of use for organic waveguide fabrication.

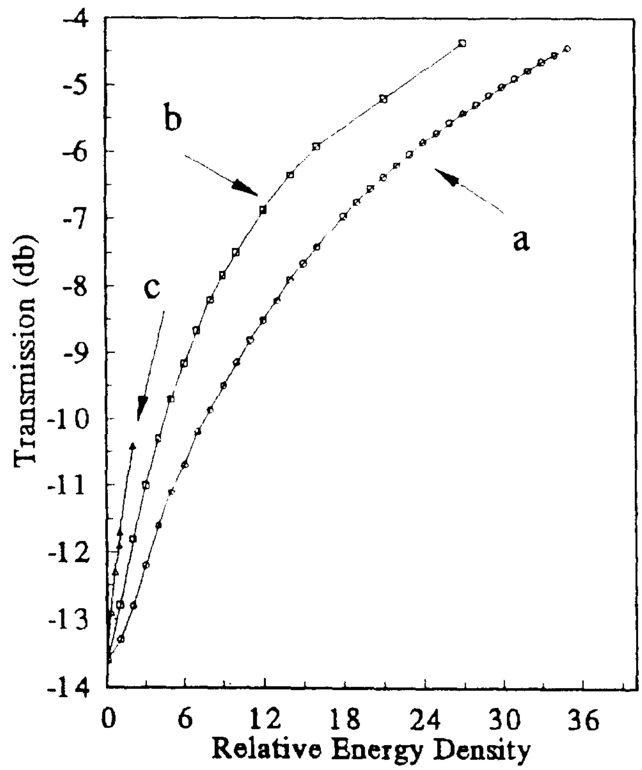


Fig. 5. Photoinduced bleaching processes of poly-3BCMU film for different power densities of the bleaching beam: curve a (○), 0.8 W cm^{-2}; curve b (□), 0.08 W cm^{-2}; curve c (△), 0.008 W cm^{-2}.

4. Conclusions

In this paper, we studied photobleaching of poly-3BCMU films in different conditions, put forward a chemical mechanism for the bleaching process and obtained the following conclusions. (i) The photobleaching of poly-3BCMU films must have two necessary conditions: photons and oxygen. (ii) The photobleaching of poly-3BCMU films involves two interlacing processes: (a) a first process of degradation from the surface to the interior of the film layer by layer and (b) a second process of degradation from long conjugated chain to short conjugated chain to monomer-like compounds to small molecules when the conjugated unsaturated bonds were broken completely. (iii) Oxygen, bleaching time and power density of the laser are the main factors affecting photobleaching. Among these, the effect of oxygen is the most important. (iv) When we made various structures in poly-3BCMU planar waveguides with the photoetching method, the films were relatively stable to exposure and development.

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