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Holographic grating formation in poly(methacrylate) containing pendant xanthene dyes

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Poly[3′-(m-methacryloyloxyalkyloxy)-2′,4′,5′,7′-tetrabromofluorescein] and poly[3′-(m-metha cryloyloxyalkyloxy)-2′,4′,5′,7′-tetraiodofluorescein] were synthesized by free radical addition polymerization method. Thermal properties of the polymers such as T_g and thermal stability of the polymers were studied by DSC and TGA. Holographic grating formation was formed on the polymeric film using Ar^+ ion laser. Substituent effect on diffraction efficiency of the polymers was investigated. The diffraction efficiency of the polymers was studied with varying concentration of the film and writing beam intensities.

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Keywords: Xanthene dyes, Poly(acrylates), Thermal properties, Holography, Diffraction efficiency

1. Introduction

Photopolymers have been of attraction over the past two decades because of their photonic applications such as holographic data storage, optical information processing and communication technology, etc [1-3]. The potential application of photopolymers for optical data storage was first demonstrated by Todorov et al [4]. Many reports were discussed for optical data storage on the polymer films using Ar^+ ion laser [5-7]. Several methods of film formation have also been investigated such as spin coating [8], Langmuir-Blodgett deposition [9] and sol-gel [10] thin film process to control the thickness and composition of the films to achieve optical quality film for holographic grating formation. Natansohn et al discussed that liquid crystallinity is not an essential criteria for reversible data storage but amorphous polymers are also good candidate for data storage [11]. Ramanujan et al reported that high diffraction efficiency achieved in side chain polymer films by means of biphotonic processes [12]. Min Gu et al reported that two photon excitation of PMMA based photorefractive polymers provides a rewritable 3D bit optical data storage [13]. In general, the xanthenes possess intense and narrow absorption band [14]. Manivannan et al reported that xanthene dyes having holographic data storage property in which electron transfer mechanism involved [15]. The gratings are produced with an interference pattern created from coherent laser light at a wavelength absorbed by the material.

The present work describes hitherto unreported covalently linked eosin yellow and erythrosin-B containing polymethacrylates. They were synthesized and characterized; further their thermal, holographic grating formation and diffraction efficiency have been investigated.

2. Experimental

2.1 Materials and method

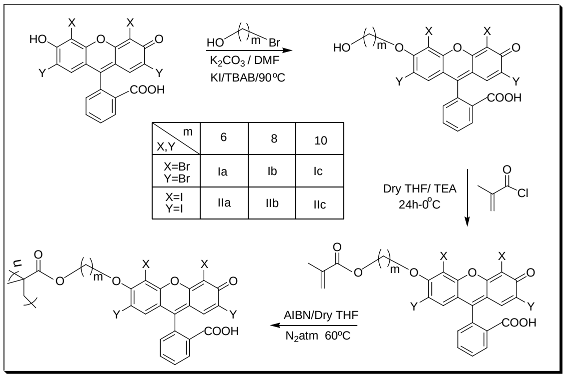
2′,4′,5′,7′-tetrabromofluorescein (Eosin yellow acid), 2′,4′,5′,7′-tetraiodofluorescein (Erythrosin-B acid), potassium carbonate, potassium iodide (KI), tetrabutylammonium bromide (TBAB) (s.d.fine, India), methacrylic acid, benzoyl chloride, 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol (E-Merck, Germany), hydrobromic acid (40%) (Spectrochem, India) were used as received. Dimethyl formamide (DMF), methanol, acetone and tetrahydrofuran (THF), triethylamine (TEA) (SRL, India) were purified by the usual procedure [16] and dried before use. Three m-bromoalkanols (m = 6, 8, 10) were prepared by using reported procedure [17]. Methacryloyl chloride was prepared by the procedure reported elsewhere [18]. 2, 2′-Azobisisobutyronitrile (AIBN) was recrystallized in chloroform-methanol (1:1).

2.2 Synthesis of polymer

2′,4′,5′,7′-tetrabromofluorescein (0.09 mol) was dissolved in dry DMF(20 mL). Anhydrous potassium carbonate (6 mol), catalytic amount of KI and TBAB were added to it. The reaction mixture was heated to 90ºC with stirring; 6-bromo-1-hexanol (0.1mol) was added drop wise to the reaction mixture and heating continued at that temperature for 3 days. The reaction mixture was cooled to room temperature and poured into ice-cold dilute hydrochloric acid solution. The precipitated 3′-(6-hydroxyhexyloxy)-2′,4′,5′,7′-tetrabromofluorescein was filtered, washed with water until neutral and then dried. 3′-(6-hydroxyhexyloxy)-2′,4′,5′,7′-tetrabromofluorescein (0.01 mole) was dissolved in dry THF (20 ml) and dry

TEA (0.01 mol) was added under nitrogen atmosphere. Methacryloyl chloride (0. 012 mol) was added drop wise at ice-cold condition (0ºC) and then, the reaction mixture stirred for 12 h. The amine hydrochloride thus formed was filtered and THF evaporated to dryness under reduced pressure. The monomer obtained was used for polymerization immediately. The monomer 3′-(6-methacryloyloxyhexyloxy)-2′,4′,5′,7′-tetrabromofluorescein was dissolved in dry THF and AIBN (5 mole percentage of monomer) were taken in a 100 ml standard reaction tube and purged with nitrogen gas for 30 min, closed and kept in a thermostat at 60ºC for 24 h and cooled. Then the reaction mixture was poured into excess of methanol and precipitated poly[3′-(6-methacryloyloxyhexyloxy)-2′,4′,5′,7′-tetrabromofluorescein] (Ia) filtered, washed with methanol and purified by dissolving in THF and reprecipitated with excess methanol. The purified polymer was dried in vacuo at 50ºC for constant weight. The remaining polymers (Ib, Ic and IIa-IIc) were prepared in a similar manner.

All the polymers were prepared with an even number of side-chain methylene spacers by a free radical addition polymerization method shown in Scheme I. The structure of the polymers was confirmed spectroscopically. In the FT-IR spectrum of monomer, two bands are vanished during the polymerization such as the absorption band at 920 cm^{-1} corresponding to C-H bending of geminal $=CH_2$ and the stretching vibration band of C=C at 1600 cm^{-1}. Similarly, in the ^{1}H-NMR spectrum, the formation of the polymer is clearly evident from the disappearance of the two singlets at 5.7 and 6.3 ppm of the vinyl protons in the methacrylate moiety. The first series of polymers (Ia-Ic) have absorption maxima of 544 ± 1 nm (Fig.1.) and second series of the polymers (IIa-IIc) have absorption maxima dwelling in the range of 540-552 nm.



Scheme I. Synthesis of polymers.

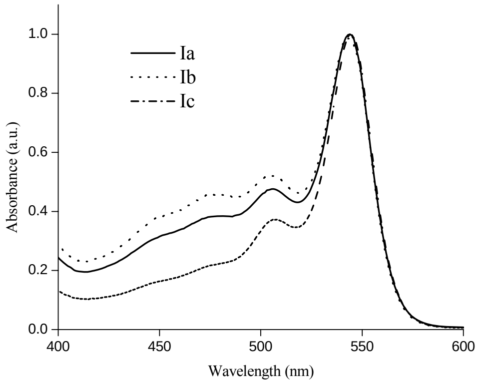


Fig. 1. Absorption spectra of the polymers Ia-Ic

These polymers are soluble in high polar solvents such as DMF, DMSO, THF and DMAc, insoluble in methanol, ethanol, benzene, toluene, n-hexane and chloroform. Table 1 shows the yield and intrinsic viscosity of the polymers. The intrinsic viscosity (η_{in}) was obtained by extrapolating, $\eta_{sp/c}$ to zero concentration. All the polymers were obtained in good yield with moderately high molecular weight.

2.3 Film preparation

The polymer Ia was dissolved in THF (3 wt %, 6 wt % and 9 wt %) and centrifuged for about 15 minutes, the supernated solution decanted, filtered through a 0.2 μm syringe filter and then spin coated onto precleaned (dilute chromic acid washed) glass slides and annealed at 50ºC in vacuum for 2 h. The remaining polymers Ib, Ic and IIa-IIc films were prepared in a similar manner.

2.4 Measurements

Infrared spectra were recorded on a Nicolet IR (Impact 440) spectrophotometer using KBr pellets. High-resolution ^{1}H-NMR spectra were recorded on a Brucker spectrometer (300 MHz). In general, deutrated DMSO was used as a solvent for ^{1}H-NMR spectra. The absorbance of the polymers were measured on a Shimadzu UV–260 UV-spectrophotometer using the polymer solution (in DMSO solvent) of 0.1g in 10mL standard flask taken in a 1cm quartz cuvette. The inherent viscosity of the polymers 1% (w/v) was determined in THF at 30ºC using an Ubbelohde viscometer. TGA studies were carried out on a Mettler Toledo STAR^e system under nitrogen atmosphere. The heating rate of TGA analysis was done at 20ºC min^{-1}, with a nitrogen flow of 20 mL min^{-1}.

2.4.1 Experimental set-up for grating formation

Since absorption spectra of these polymer films show absorption peak (λ_{max}) around 540-552 nm, the 514.5 nm output of the Argon ion laser (Stabilite 2017, Spectra-

Physics) is used as light source for the writing beam for investigation. The output wavelength from this laser at 514.5 nm is very close to the center of the absorption band of these polymers. The output from the laser is divided into two beams of equal intensity (70 mW each) using a dielectric coated beam splitter and are allowed to interfere on the film. The experimental set-up is shown in Fig. 2. To monitor the progress in the grating formation, a beam from He-Ne laser of power 12 mW at 632.8 nm is used as probe beam. The intensity of the first order-diffracted beam is measured by a photo detector connected to the power meter. The experiment is executed on a vibration isolation table.

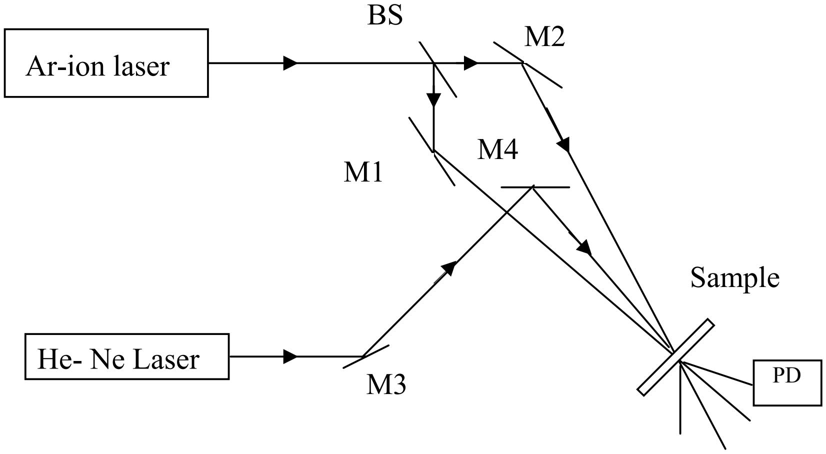


Fig. 2. Experimental set-up for grating formation

3. Results and discussion

3.1. Thermal studies

The TGA thermograms of all the polymers are shown in Fig. 3 and the data are presented in Table 1. The thermal stability was evaluated by 2% weight loss at minimum temperature. The TGA data revealed that all the polymers were stable up to 284-331ºC and single stage decomposition was observed. The decomposition of the polymer was almost complete at 500ºC; after that no weight loss was noticed. The eosin yellow containing polymers (Ia-Ic) were stable in the range of 284-315ºC. The hexamethylene spacer containing eosin blue polymers were stable up to 315ºC while, decamethylene spacer containing polymers were in the range of 284ºC. The lower methylene chain containing polymers were more stable than the higher methylene chain containing polymers [19]. Erythrosin-B containing polymers (IIa-IIc) were in the range of 291-331ºC. The thermal stability of the polymers was increased by increasing the size of the substituent on the side chain containing the dye of the polymers. This adopts the following order:

Erythrosin-B > Eosin yellow

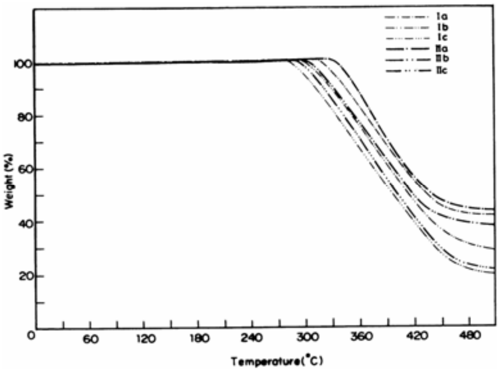


Fig. 3. TGA thermograms of polymers Ia-IIc.

The erythrosin-B series of polymers (IIa-IIc) was more stable than the eosin yellow containing polymers (Ia-Ic). The 50% weight loss of all the polymers was observed in the range of 399-438ºC. Here again, the weight loss took place in a regularly decreasing manner with increasing methylene chain. The char yield was measured at 500ºC. All the polymers showed char yield in between 19-43%. The maximum char yield was noticed for polymer IIa (43%) and minimum for polymer Ic (19%). The TGA data suggests that the char yield decreases, when the chain length between the main chain methacrylate unit and the side chain xanthene dye pendant unit increases [20] may be ascribed to oxidation.

Table 1. Yield, λ_{max}, intrinsic viscosity and TGA data of polymers Ia-IIc

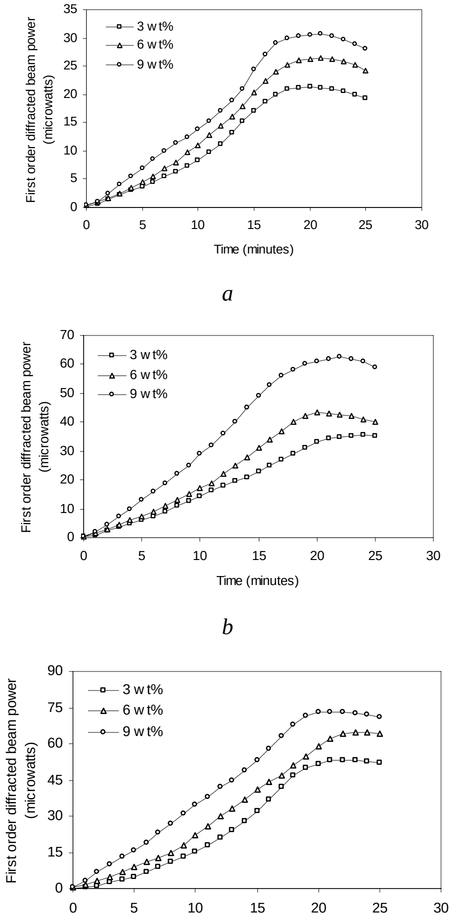
Polymer	Yield (%)	λ_{max} (nm)	Intrinsic Viscosity [η] (dLg^{-1})	TGA			
				Wt. Loss corresponds to		Weight loss at 500°C	Char yield at 500°C
				2%	50%		
Ia	72	544	0.89	315	428	59	41
Ib	75	545	0.82	298	405	72	28
Ic	70	544	0.87	284	396	81	19
IIa	82	540	0.88	331	438	57	43
IIb	85	543	0.89	300	418	62	38
IIc	80	552	0.82	291	399	79	21

3.2 Holographic grating efficiency of the polymers

The diffraction efficiency of grating formation in Ia-Ic and IIa-IIc polymers are investigated. The diffraction efficiency of the grating is found to depend on the concentration of the polymers and the intensity of the interfering beams.

3.4 Formation of grating as a function of the concentration

Different concentration of polymer films (3 wt%, 6 wt% and 9 wt%) are exposed to interference pattern and the intensity of first order-diffracted beam is measured continuously for 25 min, maintaining the power of the writing beams at 70 mW each. The variation of the intensity of the first order diffracted beam for different concentrations of Ia-Ic polymer films are graphically presented in Fig. 4. When increasing the polymer concentration from 3 wt% to 9 wt%, the rate of formation as well as diffracted intensity increases for Ia, Ib and Ic polymers [21]. The polymer Ic has more diffraction efficiency of the grating than polymer Ia and Ib. The diffraction efficiency of the gratings thus written reaches a maximum value and then start decreasing. This may be due to degradation of the grating construction after reaching saturation value. Similar behaviour is observed in IIa-IIc polymers as shown in Fig. 5.

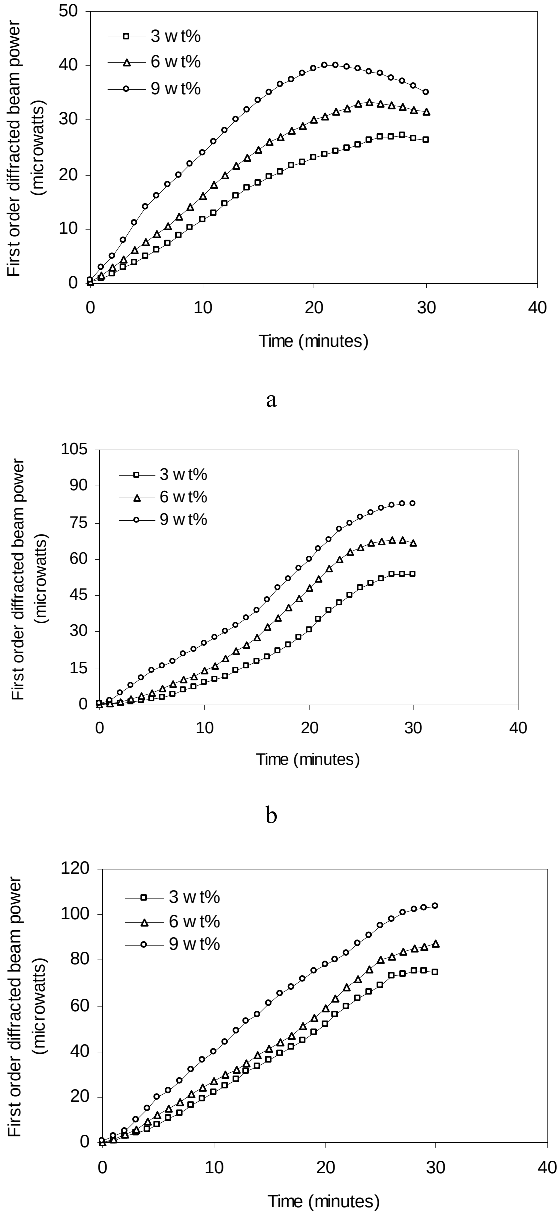


a

b

c

Fig. 4. Variation of first order diffracted beam power with time for different concentrations of (a) Ia (b) Ib and (c) Ic polymers for writing beam power 70 mW.



a

b

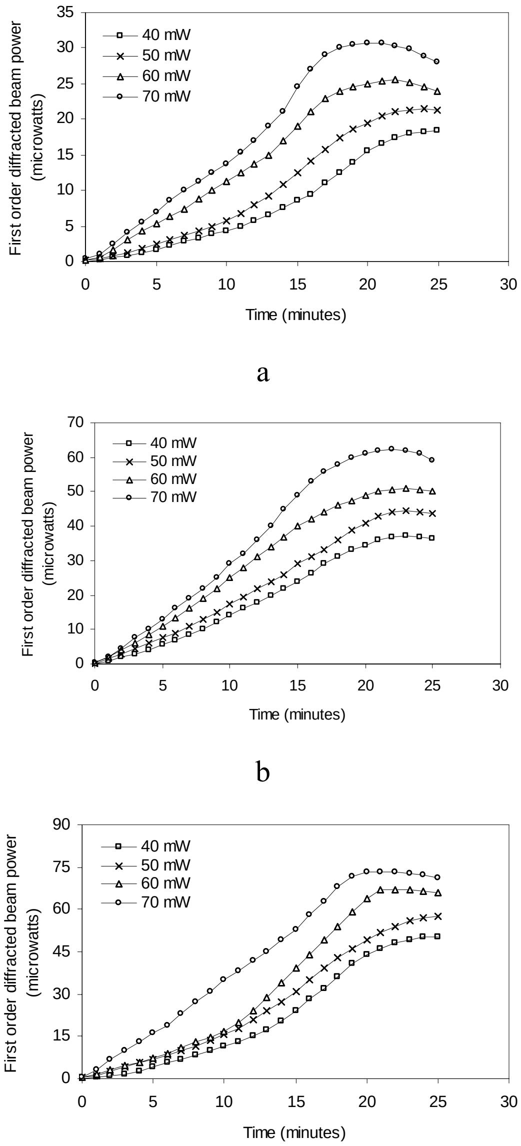
c

Fig. 5. Variation of first order diffracted beam power with time for different concentrations of (a) IIa (b) IIb and (c) IIc polymers for writing beam power 70 mW

The efficiency of the grating is dependent on polymer concentration and the maximum achieved efficiency is 1.6% for 9 wt% concentration of IIc films.

3.5 Formation of grating as a function of intensity of the writing beams

The formation of grating is studied for 40, 50, 60 and 70 mW powers of each writing beam by monitoring the intensity of the first order diffracted beam. The writing beam powers of 40, 50, 60 and 70 mW powers of each correspond to the intensities 0.67, 0.84, 1.02 and 1.18 W/cm^2 respectively. With increase in the powers of the writing beams, the rate of formation as well as diffracted intensity increases [22] for Ia-Ic polymer for 9 wt% concentration as shown in Fig. 6. The polymer Ic shows more diffraction intensity with increasing writing beam power than polymer Ia and Ib. In the case of polymer Ib having diffraction intensity in between polymer Ia and Ic. The polymer Ia appeared the least diffraction intensity than the others. Similar behaviour is observed in IIa-IIc polymers as shown in Fig. 7.



a

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Fig. 6. Variation in the first order diffracted beam power with time for different writing beam powers in (a) Ia (b) Ib and (c) Ic polymers for concentration ***9 wt%***

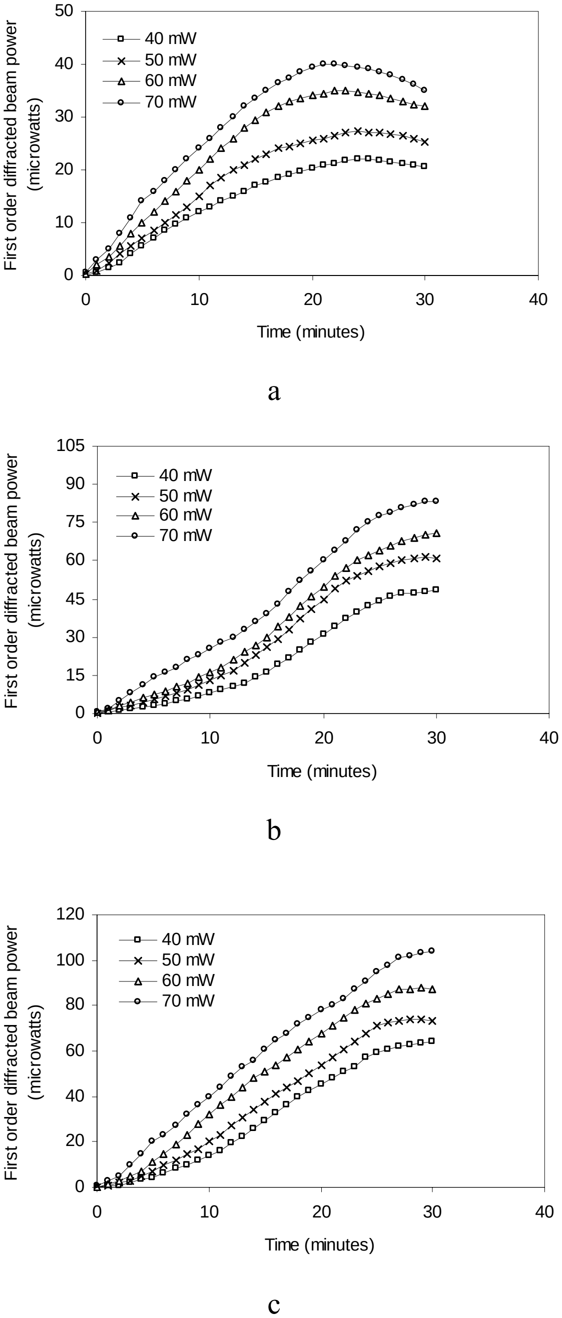


Fig. 7. Variation in the first order diffracted beam power with time for different writing beam powers in (a) IIa (b) IIb and (c) IIc polymers for concentration 9 wt%

The results displayed in the previous section indicated the relationship between diffraction efficiency and other parameters such as concentration and intensity of the writing beams for both the dye systems, viz. eosin yellow and erythrosin-B dyes based poly(methacrylate) films. The polymer Ic has better diffraction efficiency than Ia and Ib for the same recording parameters. As well the polymer IIc has more diffraction efficiency than IIa and IIb for the same recording parameters**.** Hence polymer Ic and IIc are chosen to compare the efficiency of the eosin yellow and erythrosin-B dyes based poly(methacrylate) films. It has been found that IIc polymer is more efficient than the Ic polymer as shown in Fig. 8 for 9 wt% concentration of the samples and for the writing beam power 70 mW each.

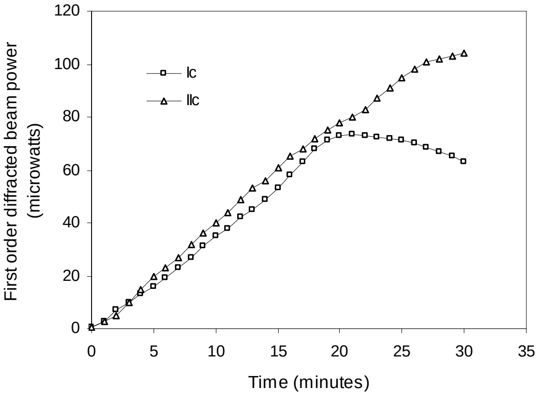


Fig. 8. Comparison between Ic and IIc polymer for writing beam intensity 70 mW and 9 wt% concentration

3.6 Comparison between eosin yellow and erythrosin-B dyes based poly(methacrylate) films

Erythrosin-B containing polymers have virtually the same diffraction efficiency of eosin yellow containing polymers as shown in Fig. 8. But the erythrosin-B containing polymers were witnessed to be more stable for relatively longer exposure when compared with eosin yellow containing polymers. This may be explained based on the substituent effect on the xanthene molecule and their thermal stability. The eosin yellow has four bromine substitutions at 2′, 4′ and 5′, 7′ positions in the xanthene molecule, while erythrosin-B has four iodine substituents in the similar position. The size and molecular weight of the iodine substituents was higher than the bromine atoms. The bulky iodine atoms (Mol.wt:129.9g) present in the erythrosin-B moiety stabilized the triplet-excited state in the dye molecule more than that of the eosin yellow containing smaller bromine atoms (Mol.wt.79.90g). The thermal stability of the erythrosin-B containing polymers was more than the eosin yellow containing polymer, which were inferred from TGA thermograms. It is in accordance with the results observed.

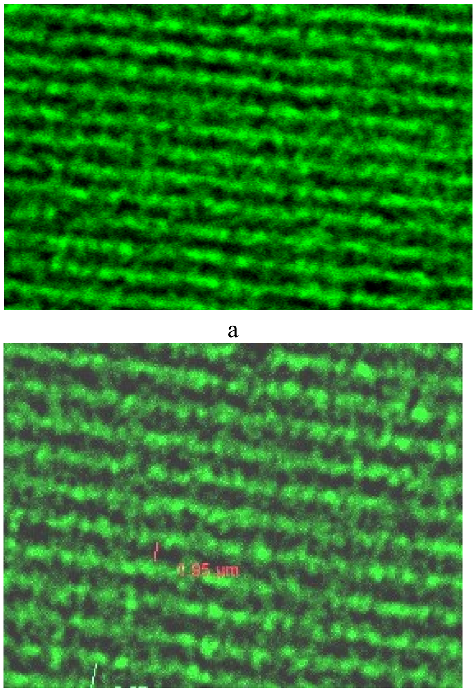
Diffraction efficiency of the grating is stable and remains unchanged even beyond one year in this polymer film. Under optimum conditions, a maximum of three diffraction orders are observed in polymer IIc.

3.7 Permanent surface relief grating formation of xanthene dyes containing polymers

The holographic permanent surface relief grating formation [23] is recorded in polymeric films, following model is proposed: When the films are exposed to interference pattern, in the bright region, the dye molecules absorb the light energy and excited to the singlet state, which decay rapidly to the triplet state. Since the energy is high enough, the molecules in the triplet state are further excited and dissociated carbon-carbon single bond (homolytic fission) into the free radicals of high volatility. Thus the concentration of dye molecules in the bright region decreases lead to reducing the thickness of the film. This results in inscribing of permanent surface relief grating formation on the polymers [24].

3.8 Confocal microscopic observation

Gratings formed in the polymer films are examined using a Lieca SP2 confocal microscope with Ar/Kr and He/Ne laser sources with Photomultiplier tube as the detector. The image was taken in the reflection mode by exciting at 488 nm. Fig. 9 shows the photographs of the samples of Ic and IIc polymer where gratings have been recorded using writing beam power of 70 mW each. These surface relief gratings are permanent and stable remaining as such more than one year.



a

b

Fig. 9. ***Confocal microscopic observation of grating formation on a) polymer Ic and b) polymer IIc***

4. Conclusions

This work has focused on the synthesis of new series of xanthene dye based poly(alkyloxymethacrylate)s with an even number of side-chain methylene spacers by free radical addition polymerization method. Thermal data revealed that the polymers were stable in between 331-284°C. The formation of grating strongly depends on concentration of the polymers and writing intensity of the polymers. The polymer film Ic and IIc show better diffraction efficiency than polymer film Ia-Ib and IIa-IIb respectively. Comparing diffraction efficiency of the polymer films Ic and IIc with same concentration and power, it is found that IIc is more efficient. The grating formation on the polymer samples are stable and remained unchanged beyond one year. The maximum diffraction efficiency of 1.6 % has achieved for polymer IIc.

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