The Effect of Photo-initiator /Co-initiator Combinations on the Optical Properties of HPDLC

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Abstract

When irradiated with visible light in HPDLC, photoinitiator and coinitiator produce a radical for photopolymerization. According to the kinds of photoinitiator and coinitiator, quantity and rate of produced a radical is different. It is influence on photopolymerization rate relate on diffraction efficiency. Thus, this paper is about the effect of photoinitiator/coinitiator combinations in terms of diffraction efficiency and real-time first order diffraction efficiency.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) have been extensively studied for various electro-optical applications.[1] A modification of PDLC is the holographically formed PDLC or HPDLC. HPDLC gratings are formed by polymerization-induced anisotropic phase separation of liquid crystals from a polymer matrix created through free-radical photopolymerization. When the material is illuminated with a wavelength 514nm a photoreduction reaction is produced, yielding radicals that initiate a radical polymerization reaction. The excited dye can act as an electron acceptor. Electron transfer from a suitable coinitiator, often occurring in an exciple, produces an oxidized radical species which can initiate the polymerization.

Holographic imaging of laser radiation onto a homogeneous mixture of photopolymerizable monomer(s) and liquid crystal results in spatially modulated polymerization kinetics that generates alternating layers of polymer and liquid crystal rich lamellae.

The photoreducible dyes which may be used as components of the photo-initiator in the present invention are those dyes which are capable of forming a stable system with an electron donor in the absence of light and which will undergo reduction when irradiated with visible light in the presence of the electron donating component. Such photoreducible dyes includes rose bengal, erythrosine, eosin, fluorescein, acriflavine, thionin, methylene blue, and the like. The dyes may be used individually or in admixture to increase sensitivity over a wider range of the visible spectrum.

A wide variety of activator was reported in the literature to be reactive in combination with a suitable photoreducible dye. Tertiary amine coinitiators, such as N-phenylglycine, triethanolamine are one of the most important classes of reductants used in combination with photoreducible dye. Photophysical studies revealed that dye triplets interact with amines leading to dye quenching via electron transfer. Enolates of 1,3-diketones, such as acetylacetone or dimedone, are effective reductants for excited state dyes. Electron transfer from the enolate to the dye occurs in an exciplex. It is the semi-oxidised enolate radical which acts as the initiating species, although evidence of direct interaction of monomers with the exciplex has been obtained. The presence of a strong oxidising agent, such as sodium periodate, was reported[2] considerably to increase the polymerization rates of these systems.

The influences of photoinitiator/coinitiator combinations were studied in terms of diffraction efficiency and polymerization rate by measuring real-time first order diffraction efficiency.

2. Experimental

The formulations used in this study for the preparation of HPDLC gratings consisted of a multi-funtional monomer, a reactive diluent, a photoinitiator dye, a coinitiator, and a LC is prepared. PUA is segmented urethane oligomer tipped with acrylic functionality. Polyol (1000g/mol) were reacted with molar excess of diisocyanated to obtain NCO-terminated prepolymer, than hydroxy ethyl acrylate was added to obtain acrylic functionality-capped urethane acrylate oligomers.[3] A eutectic mixture of cyanobiphenyl and cyanoterphenyl compounds was used as LC(E7). The LC content was 35wt.%. The reactive diluents used in the present experiments are N-vinylpyrrollidone(NVP) and trimethylol propane triacrylate(TMPTA). Rose bengal(R.B), methylene

blue(M.B), acriflavine and RBMB were used as photoinitiator. An ion pair (RBMB) isolated from rose bengal and methylene blue has been used as photoinitiator in formulations of photopolymers tested as HPDLC. The ion pair RBMB was obtained as follows: the commercial dyes rose bengal and methylene blue were mixed in aqueous solutions, and the precipitated dark blue solid was purified by crystallization from ethanol and dried.[4] RBMB(1:1) and RBMB(1:2) is mole ratio difference of Rose bengal and methylene blue. Coinitiator used included N-phenylglycine(NPG), triethanolamine(TEA) and Acetylacetone(AA). Oxidizing agent used sodium periodate(SP). Basic formation to prepare photoinitiator/coinitiator combinations is given in Table 1. The cell was constructed by sandwiching the prepolymer syrup/LC mixtures between the two indium-tin-oxide(ITO) coated glass plates, with a gap of 14μm, adjusted by a bead spacer.[5]

The prepolymer mixtures have been irradiated with Ar-ion laser (514nm) at 100mW/Cm^2 intensity, with exposure times of typically 600s.

Table 1. Formulation of PUA with Photoinitiator /Coinitiator Combinations

PU acrylate oligomer/Diluent	Photo-initiator	Co-initiator	Oxidising agent
PUA/NVP/ TMPTA	Rose Bengal	TEA	
	Methylene Blue		
	Acriflavine		
	RBMB(1:1)		
	RBMB(1:2)		
	Rose Bengal	NPG	
	Methylene Blue		
	Acriflavine		
	RBMB(1:1)		
	RBMB(1:2)		

PU acrylate oligomer/Diluent	Photo-initiator	Co-initiator	Oxidising agent
PUA/NVP/ TMPTA	Rose Bengal	AA	
	Methylene Blue		
	Acriflavine		
	RBMB(1:1)		
	RBMB(1:2)		
	Rose Bengal	AA	Sodium periodate
	Methylene Blue		
	Acriflavine		
	RBMB(1:1)		
	RBMB(1:2)		

3. Results and discussion

The diffraction efficiency of the films prepared as a function of photoinitiator/coinitiator combination is shown in Fig. 1. It is seen that the NPG gives much higher diffraction efficiency as compared with TEA and AA as coinitiator used films. This implies that NPG's fragmentation is a unimolecular reaction and is less influenced by such factors, such as pH. NPG is indeed one of the most efficient amine activators for a variety of photoreducible dyes.[6] Also, it is seen that rose bengal and acriflavine give much higher diffraction efficiency as compared with methylene blue and RBMB photoinitiator used films. This is because maximum absorption wavelength of rose bengal and acriflavine is closer to 514nm than methylene blue or RBMB. Due to the fact that maximum absorption wavelength of methylene blue is very far from 514nm, the grating has not been successfully built up, thus diffraction efficiency is near zero. The most efficient results are obtained when at least 90% of the incident light is absorbed at the wavelength corresponding to the absorption maximum of the particular dye employed.

Fig. 2 shows the first order diffraction efficiency of films having coinitiator with rose bengal as a function of the irradiation time. It is seen that photoreaction rate increases along TEA<AA<AA+SP<NPG. The reaction of TEA is slower than the others. Due to differences in the proton exchange reaction, initiating system exhibit a pH dependent reactivity. In this case, the

photopolymerisable system can be reversibly activated or deactived by changing the pH of the medium.[7] Acetylacetone is effective reductants for excited state dyes. Polymerization show a pH dependence which points to the anions being active compounds, with the enolate anions being better quenchers of the triplet state of the dyes than the conjugated acids. NPG of initiation mechanism is a unimolecular reaction and is less influenced by such factors, such as pH. So photopolymerization of NPG is the fastest than the others.
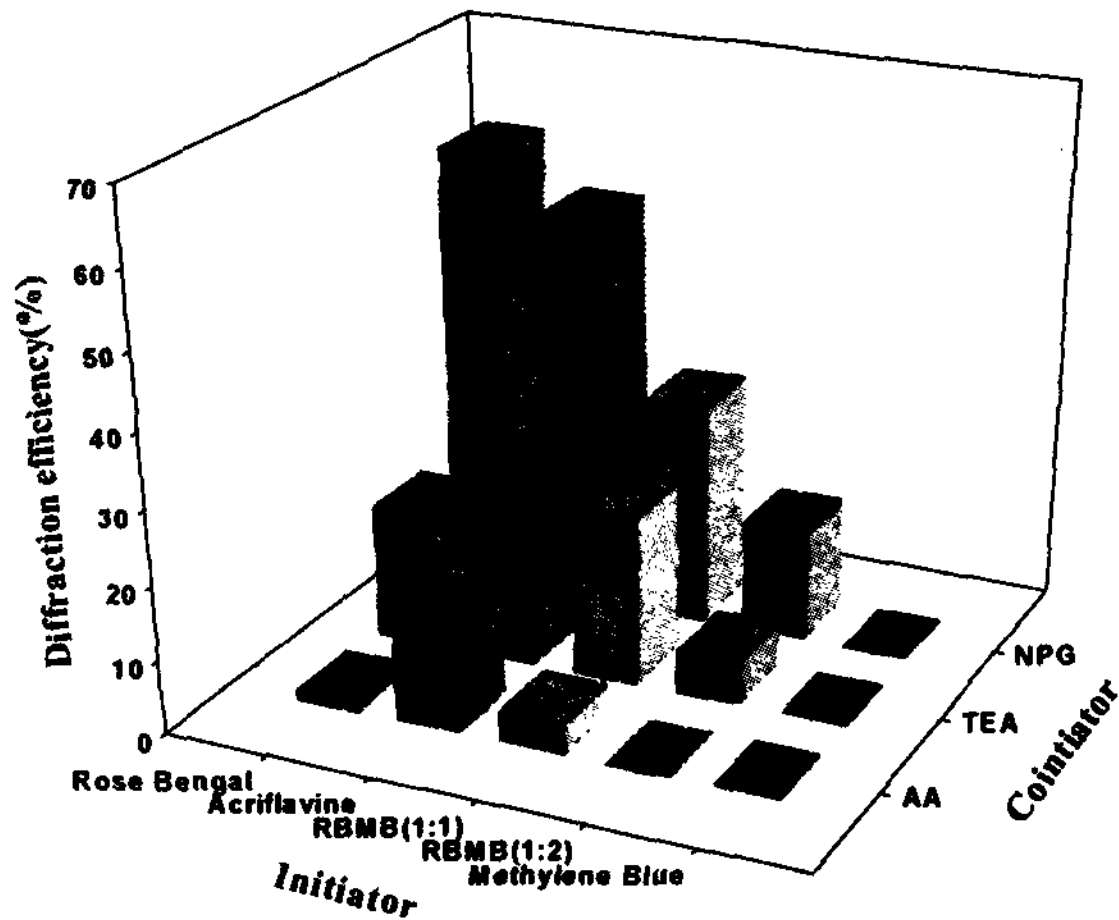
Fig. 1. Diffraction efficiency-initiator-coinitiator relationships of HPDLC films.
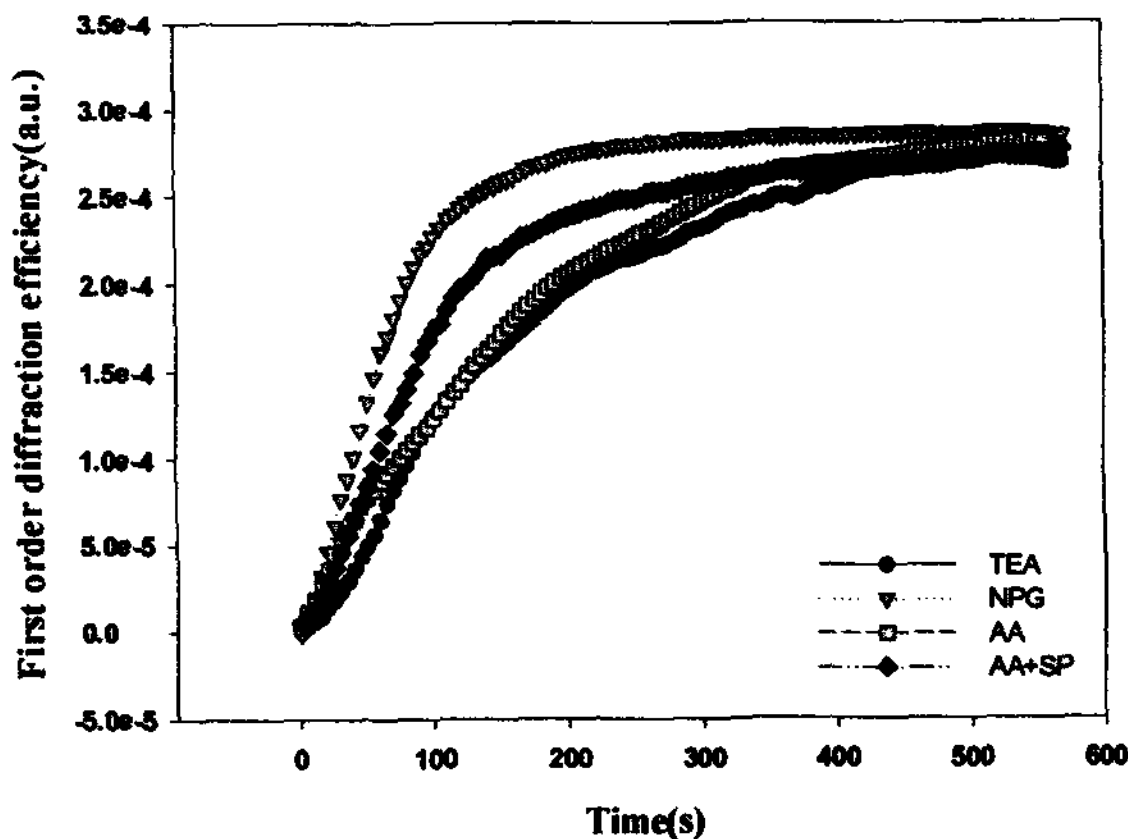

Fig. 2. The first order diffraction efficiency of the probe beam for the samples having TEA, NPG, AA and AA+SP with rose bengal.

Fig. 3 shows the first order diffraction efficiency of films having photoinitiator with NPG as a function of the irradiation time. Dyes with high triplet quantum yield and longer triplet lifetime and high reactivity in the triplet state generally satisfy these requirements. It is seen that photoreaction rate

increases along RBMB(1:2)<RBMB(1:1)<acriflavine<rose bengal. As maximum absorption wavelength is close to 514nm, triplet quantum yield is higher.
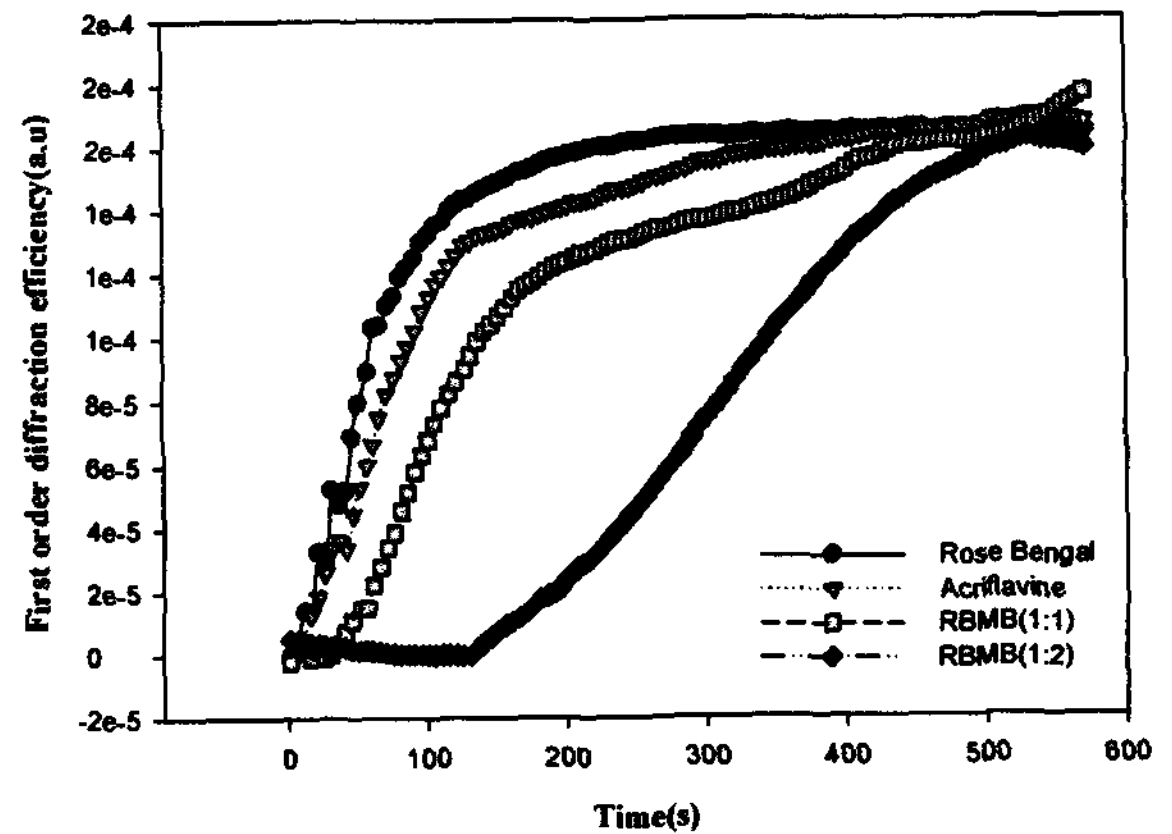

Fig. 3. The first order diffraction efficiency of the probe beam for the samples having rose bengal, acriflavine, RBMB(1:1) and RBMB(1:2) with NPG.
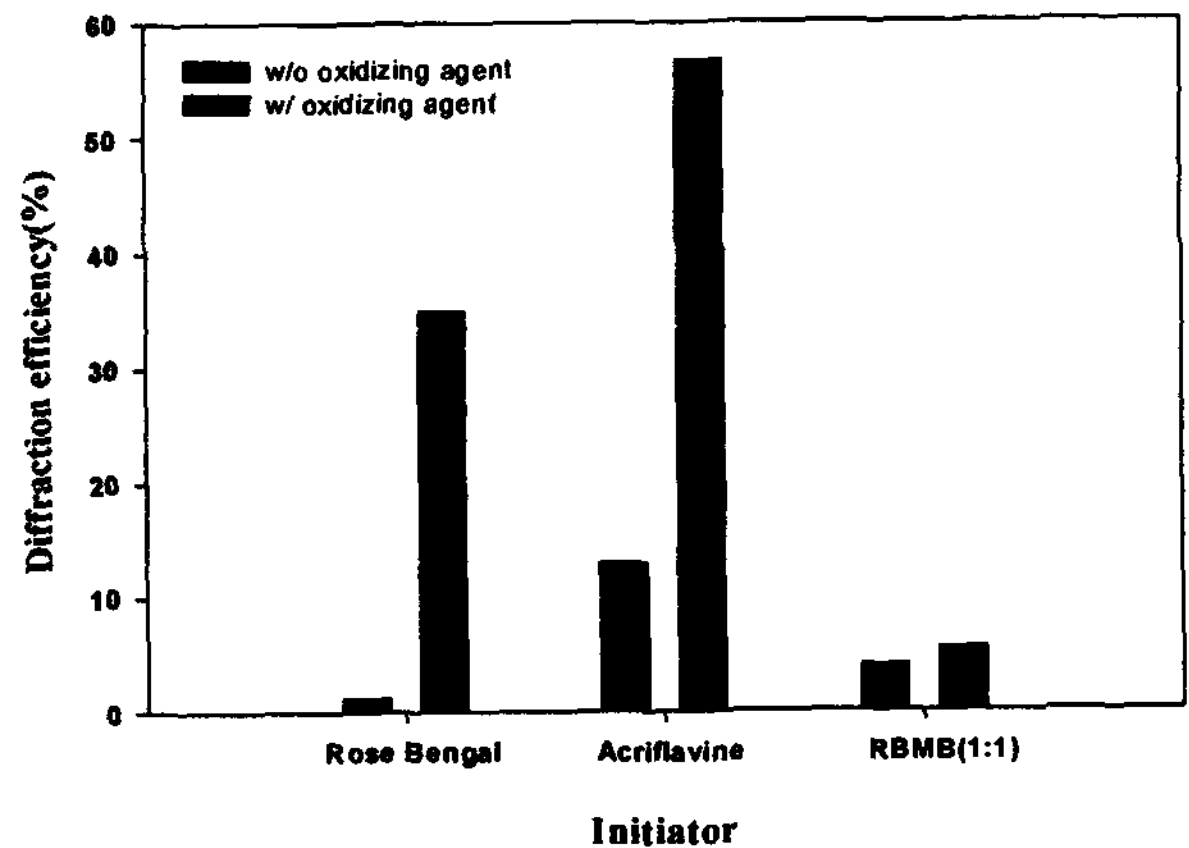

Fig. 4. Diffraction efficiency vs. type of initiator w/ and w/o oxidizing agent.

Diffraction efficiencies of the HPDLC films w/ and w/o sodium periodate are given in Fig. 4. It is seen that the diffraction efficiency increase with the addition of oxidizing agent. It appears that the oxidizing agent functions to oxidize the reduced dye back to its photoreaction state, and thereby perpetuate the polymerization reaction.

4. Conclusion

The relationship between diffraction efficiency and photoreaction in HPDLC has been studied in terms of photoinitiator/coinitiator combinations. As the absorption wavelength of photoinitiator gets

close to 514nm, high diffraction efficiency and fast photopolymeriazation were obtained. This can possibly be interpreted in terms of high triplet quantum yield. Among three of coinitiator being used, NPG gave the highest diffraction efficiency and the fastest photoreaction. Initiation mechanism of NPG is less influenced by surrounding environment, and NPG is one of the most efficient amine activators. When acetylacetone added oxidizing agent, diffraction efficiency and photoreaction increased.

5. References

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