

Nitroxide radicals reduce shrinkage in acrylate-based holographic gratings

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Abstract

High resolution holographic polymer dispersed liquid crystal gratings are photo-induced periodic structures commonly affected by shrinkage. This phenomenon represents a problem in several application fields such as in high density optical storage. In this work we observed that, by directly monitoring the blue-shift of the reflection peak of the periodic structure, an evident shrinkage reduction occurs using the nitroxide radical Tinuvin770-*N*-yloxy [(bis(2,2,6,6-tetramethyl-piperidine-1-yloxy-4-yl)-sebacate)] as inhibitor of polymerization. This compound is a stable hindered amine light stabilizer-derived free radical, which plays a significant role in the photo-polymerization dynamics.

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1. Introduction

Several papers, in various contexts of biology and medicine, are focused on the use of photo-polymerizable acrylates in the chemistry of polymers and in other research fields of science [1–3]. Shrinkage phenomena, which mainly consist of changes in the intermolecular distances [4] during polymerization, are a common and well known problem in polymers and in particular in acrylate materials [5–8]. The shrinkage could depend on several factors such as: the nature of monomers, the structure of forming polymer chains,

and the type of polymerization (generally free radical polymerization causes a shrinkage higher than cationic polymerization) [9]. The final shrinkage is the superimposition of each single contribution connected with the photo-polymerization processes. Besides the usual and well known shrinkage measurements [10–12], several experimental techniques have been developed to measure shrinkage in photo-polymerizable systems. A very sensitive technique has been applied to study holographic polymer dispersed liquid crystals gratings (HPDLCs) [13–15] in different experimental configurations in order to distinguish the different contributions to the shrinkage of the material [16,17]. HPDLCs are composite materials used in several contexts of science and technology since high resolution holograms can be easily written by using conventional interferometric techniques. Reviews on these materials

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and their applications can be found in Refs. [18–20]. In this work we used some of the experimental methods reported in Refs. [16] and [17] to measure shrinkage in acrylate-based holographic gratings systems. In particular, we investigated the use of a nitroxide radical TINUVIN770-*N*-yloxy, [bis(2,2,6,6-tetramethyl-piperidine-1-oxyl-4-yl)-sebacate free radical] corresponding to the Tinuvin770, [bis(2,2,6,6-tetramethyl-piperidine-4-yl)-sebacate], an hindered amine light stabilizer (HALS) with aim of reducing shrinkage in HPDLC gratings. This important feature allows the use of holographic gratings in several application fields (i.e. high density holographic data storage) in which the polymerized surfaces can be directly exposed to the effect of the environmental light. Many papers have been published in the field of photo-stabilization in polymers via HALS [21–23]. These compounds are a class of amines hindered due to the presence of sp^3 carbons in vicinal position to the amine function. This hindrance is at the basis of the stability of the derived nitroxide radical, intermediate in the protection mechanism by HALS [21,24], as described by the Denisov cycle [21,25]. Nitroxide radicals can react directly with carbon centered radicals to inhibit [26] and to control polymerizations [27].

2. Experimental

2.1. Materials

The basic materials used in our investigations are described as follows: di-penta-erythritol-hydroxy-penta/hexa-acrylate (DPHPA) monomer, 1-vinyl-2-pyrrolidone (NVP), *N*-phenyl-glycine (NPG) purchased from Aldrich and BL038 liquid crystal (LC) mixture from Merck. Genocure (CQ*), a racemic mixture of camphore–quinone, was purchased from Rahn. Tinuvin770, Tinuvin770-*N*-yloxy nitroxide radical come from Ciba Specialty Chemicals (Basel, Switzerland). Tempest-8 (2,2,6,6-tetramethyl-piperidine-4-octanoyloxy-1-oxyl free radical) was synthesized by us with the procedure explained below in the text. The homogeneous mixture was composed of DPHPA, BL038 and NVP and placed by capillarity between two small rectangular glasses (1 mm thickness) separated by 50 μ m mylar stripes. DPHPA was previously heated for 10 min at 100 °C, in order to increase the transparency and to reduce the viscosity. The mixture was optimized for blue light irradiation (457.9 nm) by adding CQ* (0.6% final concentration) and NPG, at the final concentration of 1%, dissolved in NVP at concentration of 10%. NVP acts as a solvent for the photo-initiators and as a cross-linker [13]. The mass ratio of monomer, LC, and photo-initiators solution is 65:25:10. Tinuvin770-*N*-yloxy nitroxide radical was added to have the following final concentrations: 0.2%, 0.4%, 0.6%, and 0.8%. The Tempest-8 and Tinuvin770 were used in final concentrations of 0.7% and 0.6%, respectively. The nitroxide Tempest-8 was synthesized by reacting 4-hydroxy-TEMPO (2,2,6,6-tetramethyl-piperidine-4-hydroxy-1-oxyl free radical) with octanoyl-chloride and tri-

ethylamine. 4-Hydroxy-TEMPO (0.4 mmoles) was reacted with 1.8 mmoles of octanoyl-chloride and 1.8 mmoles of triethylamine in 18 ml of toluene under magnetic stirring at room temperature. After 1.5 h the reaction was complete. The reaction mixture was then washed 10 times with distilled water, extracted with 50 ml of dichloromethane and dried over anhydrous sodium sulphate and concentrated. The identity and purity of the compound were checked by thin-layer chromatography, mass spectroscopy, on a Carlo Erba QMD 1000 spectrometer (Milan, Italy) in EI mode, and electron spin resonance spectroscopy on an ESR spectrometer (E4; Varian, Sunnyvale, CA, USA). The ESR spectrum, as recorded in chloroform, showed the three typical bands of the nitrogen with constant coupling $a_N(\text{NO}\cdot) = 1.58$ mT and g -factor = 2.00610. Tempest-8, Mass Spectroscopy: molecular weight calculated for $\text{C}_{17}\text{H}_{32}\text{NO}_3 = 298.45$; found: m/e (relative intensity), 298 (M , 42), 284 (15). All the reagents and solvents used for the synthesis of Tempest-8 were purchased from Aldrich Chemical Co. (Milwaukee, WI, US).

The molecular structures of the compounds used in this study are reported in Fig. 1.

2.2. Methods

The holographic recording system is illustrated in Fig. 2 with the spectroscopic system used for dynamic characterization of the grating during and after the recording process. The writing wavelength was $\lambda = 457.9$ nm. The experimental technique for measuring shrinkage determination consists of the real-time monitoring of the optical shrinkage by using a spectrometer connected to a data acquisition system. In particular, during irradiation, a periodic pattern of light impinges on the glass surfaces containing the polymerizing material causing the inducing of the photo-polymerization process only in the illuminated areas. In this way, a periodic one-dimensional modulation of the optical and mechanical properties of the material is obtained. During irradiation, the low power incoherent white light of the spectrometer light source impinges on the sample as reported in Fig. 2. In this way, the growths of the reflection peak and its displacement in wavelength can be monitored in real-time. A typical result is shown in Fig. 3. The depth of the peak gives information on the optical properties of the structure whereas its position in wavelength reflects the real-time modifications of the periodicity of the one-dimensional polymeric structure connected with the shrinkage of the polymeric material. The periodicity of the polymeric structure was expressed by the grating pitch $A = \lambda/2 \sin(\theta/2)$, where λ is the writing wavelength measured inside the sample and θ the angle between the two writing beams, as reported in Ref. [13].

3. Results

Fig. 3 represents the dynamic of the peak formation without nitroxides into the mixture. The induction time,

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