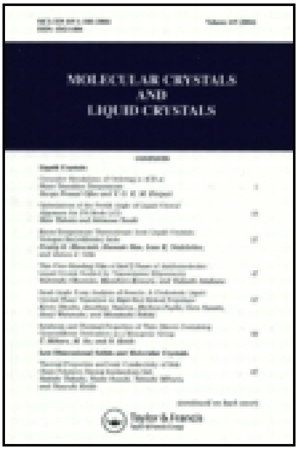

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Influence of the Molecular Weight of Azopolymers on the Photo-Induced Formation of Surface Relief Gratings

Volker Börger [a], Henning Menzel [a] & Marco R. Huber [b]

[a] Technical University Braunschweig, Institute for Technical Chemistry, Braunschweig, Germany
[b] Physikalisches Institut und Bayreuther Institut für Makromolekülforschung, Universität Bayreuth, Bayreuth, Germany

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Volker Börger
Henning Menzel
Technical University Braunschweig, Institute for Technical Chemistry, Braunschweig, Germany

Marco R. Huber
Physikalisches Institut und Bayreuther Institut für Makromolekülforschung, Universität Bayreuth, Bayreuth, Germany

Surface relief grating formation was investigated for a series of azobenzene containing polymers with varying molecular weight. The polymers were obtained by a combination of an atom transfer radical polymerization of trimethylsilylethyl methacrylate and subsequent polymeranalogous introduction of the azobenzene chromophore. Irradiation of the polymers with interfering polarized laser beams resulted in the formation of surface relief gratings. The modulation depth of the gratings as measured by AFM decreases with increasing molecular weight, however, the effect is much smaller than expected.

Keywords: atom transfer radical polymerization; molecular weight dependence; surface relief gratings

INTRODUCTION

It is well known that azobenzene chromophores undergo trans-cis-trans-isomerization cycles upon irradiation with light of appropriate wavelength. Employing polarized light for excitation, these isomerization cycles may result in a reorientation of the chromophores. This effect can be used for optical data storage, as first reported by Todorov et al. in 1984 [1]. In particular holographic storage via refractive index patterns in the film volume has been investigated in

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Address correspondence to Henning Menzel, Technical University Braunschweig, Institute for Technical Chemistry, Hans-Sommer-Straße 10, D-38106 Braunschweig, Germany. E-mail: h.menzel@tu-bs.de

recent years [2–6]. These holographic gratings, depending on the birefringence of the film, can be inscribed into films with azobenzene either added to an amorphous or liquid-crystalline polymer or with the azobenzene bonded covalently to the polymer chain, respectively [7,8].

In 1995 it was discovered that under some conditions the writing of such refractive index gratings for holographic data storage can result in an additional surface relief grating (SRG), which scatters the light even more efficiently [9,10]. These SRGs are characterized by modulation depths, which can be in the order of the film thickness (up 1 μm). Thus irradiation of azobenzene containing polymer films with interfering laser beams causes not only a reorientation of the chromophores but also a massive photo-induced mass transport in the film on a micrometer scale. This material transport takes place well below the glass transition temperature of the polymer. So far several mechanisms have been proposed to explain this process, but none can explain all observed phenomena completely [11–14].

The influence of the polymers molecular weight on the efficiency of the SRG-formation so far has been investigated only by employing mixtures of an azobenzene containing polymer with non-functionalized poly (methyl methacrylate) (PMMA) samples of different molecular weights [15,12]. It was found that increasing the molecular weight of the PMMA from 4000 g/mol ($P_n = 40$) to 11 700 g/mol ($P_n = 117$) decreased the inscription rate significantly. At molecular weights higher than 11 700 g/mol mol no modulation of the surface was observed. This was reasoned by the entanglement of the PMMA above at higher molecular weights [12]. In contrast Tripathy et al. reported that SRGs can be inscribed in polymers with very high molecular weight of more than 500 000 g/mol, but which is less efficient than for the low molecular weight polymers [13].

Here we report on a series of azopolymers in which molecular weight has been varied systematically to elucidate its influence on the SRG formation. The polymers were prepared by living radical polymerization of a protected 2-hydroxyethyl methacrylate (HEMA) and subsequent deprotection and polymer analogous introduction of the azobenzene chromophore as a side chain. Surface relief gratings were written in films of these polymers and the SRG characterized by their diffraction efficiency and the modulation depth, which can be determined by AFM.

EXPERIMENTAL SECTION

Materials

All chemicals were used as purchased without any further purification unless noted otherwise. 2-Hydroxyethyl methacrylate (HEMA) was dissolved in water (1:3, v/v) extracted three times with light petroleum and salted out with sodium chloride. The organic phase was dried over Na_2SO_4, the solvent evaporated, and the monomer destilled under reduced pressure. HEMA was converted into the trimethylsilyl-protected species according to Ref. 16. 4,4′-Dinonyl-2,2′-bipyridine was synthesized according to Ref. 17. The synthesis of 2-(4-(4-cyanophenylazo)phenoxy)acetic acid has been described in a previous paper [18].

Polymerizations

In a Schlenk-tube, 15 mL (68.80 mmol) of the protected HEMA-monomer, 37.44 mg (0.26 mmol) CuBr and 213,08 mg (0.52 mmol) 4,4′-dinonyl-2,2′-bipyridine were combined, the solids were dissolved, and the solution degassed for 45 minutes with argon. Subsequently 38.7 μL (0.26 mmol) 2-bromo-2-methyl-propionic acid ethyl ester was added as initiator and the mixture was heated to 90°C. After 45 minutes the green polymer solution was diluted with methanol and passed over an aluminia-column to remove the Cu-ions. Stirring the sample in methanol under acidic conditions resulted in deprotection of the HEMA-groups. The polymer is purified by precipitation in diethylether.

Polymer Analogous Reaction (General Procedure)

All reactions were performed in Schlenk-tubes under nitrogen. 0,25 g Poly-(2-hydroxyethyl methacrylate) was dissolved in 2 mL dimethylformamide (DMF) and cooled down to 0°C. In a second Schlenk-tube 0.65 g 2-(4-(4-cyanophenylazo)phenoxy)acetic acid was dissolved in 4 mL (DMF) and 0.38 g of N,N′-carbonyldiimidazole dissolved in 2 mL DMF are added. Within 45 min a clear, red solution of the intermediate forms, which was transferred slowly via a syringe into the polymer solution. After 1 hour the mixture was allowed to come to room temperature and was stirred for another 72 hours. Subsequently the mixture was poured in 300 mL methanol for precipitation. For further purification the resulting polymer was dissolved in DMF and precipitated from methanol again.

Methods

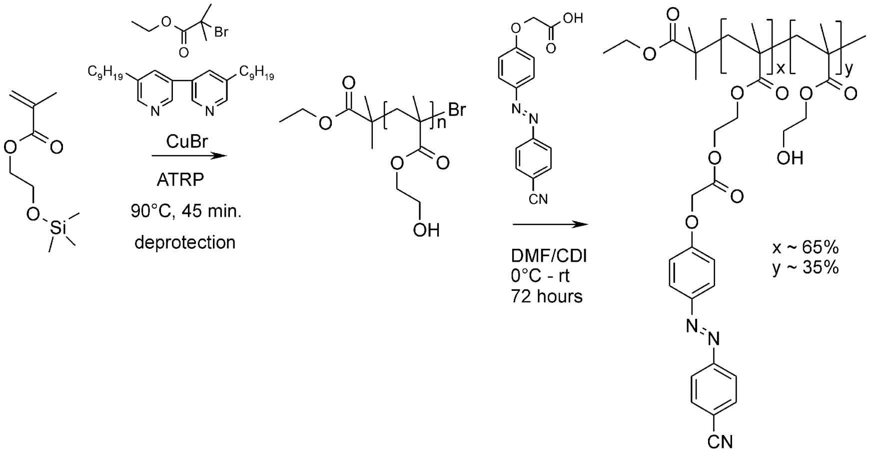
Size Exclusion chromatography (SEC-MALS) was carried out in DMF containing 0,5 Mol/L LiBr using PL Mixed-C columns at a flow rate of 0,5 mL/min (80°C). The polymers were detected by a Wyatt Mini-Dawn light-scattering detector and Schambeck RI detector RI2000F.

Data aquisition and processing were performed using the ASTRA-software (Wyatt). Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) with a Netzsch DSC 204 Phoenix thermal analyzer (scanning rate of 10 K/min). The azobenzene content of the polymers was determined by UV/vis absorption spectroscopy employing the π-π^*-band (365 nm). The spectra were recorded on a Perkin Elmer Lambda 5 instrument in tetrahydrofurane (THF) as solvent. 2-(4-(4-Cyanophenylazo)phenoxy)acetic acid ethyl ester was used for calibration. To ensure 100% trans-isomer, the solutions were stored in the dark for several days and handled under red light before recording the spectra.

Thin films were prepared by spin coating on fused silica or glass substrates from THF solutions; they were annealed to remove any residual solvent and were checked by profilometry measurements (Dektak 3030ST). Diffraction gratings were recorded by using a previously described holographic set-up for four-wave mixing experiments [5]. A set of polarizers and wave plates was used to control intensities and polarization states of the interfering beams. In these experiments orthogonal linearly polarized beams in a pp-geometry were used. Typically, a ‘pump-on’ writing period of 300 s was used and followed by another ‘pump-off’ period of 50 s, in order to check that the grating was permanent (see Fig. 2). The read-out was performed with a diode laser ($\lambda = 685$ nm) outside the absorption band of the sample in order to prevent perturbations. The surface relief depth was examined by AFM measurements.

RESULTS AND DISCUSSION

To investigate the role of the molecular weight in the formation of surface relief gratings in azopolymers it is necessary to vary this parameter but to keep all other parameters (e.g., azobenzene content, glass transition temperature, polydispersity) constant. The synthesis of polymers with a controlled molecular weight from monomers having azobenzene moieties is difficult because of the retarding effect of the azobenzene group [19–22]. For the controlled variation of the molecular weight therefore a prepolymer approach was applied. The prepolymers have been prepared by ATRP of the trimethylsilyl protected HEMA monomer with 2-bromo-2-methyl-propionic acid ethyl ester as initiator and CuBr/dinonylbipyridine as catalyst. This method gives excellent control over the degree of polymerization and molecular weight distribution. After deprotection a series of hydroxy functionalized prepolymers with narrow polydispersity was obtained. Subsequently the chromophores are introduced by a polymer



SCHEME 1 ATRP-Polymerization of (2-trimethylsiloxyethyl methacrylate), deprotection and subsequent polymer analogous esterification for introduction of the azobenzene side chain.

analogous esterification with 2-(4-(4-cyanophenylazo)phenoxy)acetic acid (see Scheme 1).

The esterification of the HEMA was done employing N, N′-carbonyldiimidazole (CDI) as activating reagent. CDI reacts with the carboxylic acid group by formation of an imidazolide, which subsequently reacts with the hydroxy group yielding the ester. This reaction is sterically demanding. The already established side chains shield remaining hydroxy groups from reaction with the bulky imidazolide. Therefore the maximum side chain density is restricted to approximately 65% (see Table 1 and Fig. 1). It is impossible to obtain a very high degree of substitution by this method, however, it gives easy access to polymers with constant composition. This is of particular importance because the degree of azobenzene substitution has a strong influence on the SRG formation [23]. The polydispersity of the polymers is in all cases very low.

The glass transition temperature is another important parameter for the SRG formation [24]. As can be seen from Table 1 and Figure 1 within the error of the method the glass transition temperature does not vary for the polymers (Tg = 97.5°C ± 2), but only the very low molecular weight polymers have a somewhat lower Tg as expected. Thus employing the prepolymer approach it is possible to obtain a series of polymers which vary in the molecular weight but not in parameters like azobenzene content, Tg, or polydispersity.

TABLE 1 Molecular Weight Determined by SEC-MALLS (Mn), Degree of Polymerization (P_n) Polydispersity (PD), Composition (azo), Glass Transition Temperature (Tg) and Modulation Depth as Measured by AFM for the Polymers

Sample	M_n [g/mol]	P_n	PD [M_w/M_n]	Azo [Mol%]	Tg [°C]	Depth [nm]
1	5 200	17	1.21	65.2	85	>64*
2	8 500	28	1.31	64,9	91	42
3	9 500	31	1.32	65.6	93	53
4	32 100	105	1.40	64.1	99	58
5	48 700	160	1.36	63.0	96	55
6	51 800	170	1.30	62.1	94	60
7	63 500	210	1.21	67.2	98	50
8	64 500	215	1.33	65.2	98	56
9	66 800	220	1.36	66.9	96	46
10	86 000	285	1.33	65.2	99	35
11	140 500	460	1.46	66.7	99	30
12	145 500	480	1.65	66.7	99	32
13	178 000	590	1.44	64.7	99	50

*shorter exposure time for sample 1 (ca. 260 sec).

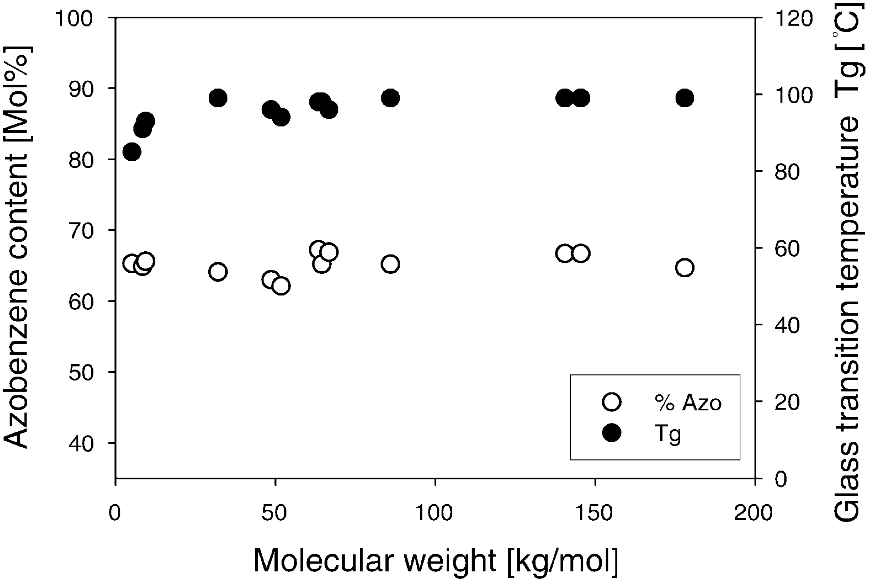


FIGURE 1 Azobenzene content and glass transition temperature for the polymers depicted as function of the molecular weight.

Thin films of these polymers were prepared by spin coating from THF solution (~0.5 µm thickness). Surface relief gratings have been inscribed on polymer films at identical recording conditions as described the experimental section above. The grating formation process was monitored by the growth of the first order diffraction of a low-intensity laser beam. In a typical experiment the diffraction efficiency increases almost linearly in the first minutes, then the increase slows down and the diffraction efficiency approaches a maximum value. However, this saturation value was not reached within the exposure time used in the experiments. Figure 2 shows three typical examples of the "growth curves" recorded for polymers with different molecular weight. The diffraction efficiencies of all polymers show a similar behavior, however the grating inscription rates are different.

The modulation depth i.e. the amplitude of the grating after 300 s was used as a measure for the efficiency of the SRG formation in the polymer film. The amplitude can be measured by AFM. The results for the polymers are compiled in Table 1 and are depicted as function of the molecular weight in Figure 2. A general trend is noticeable: The

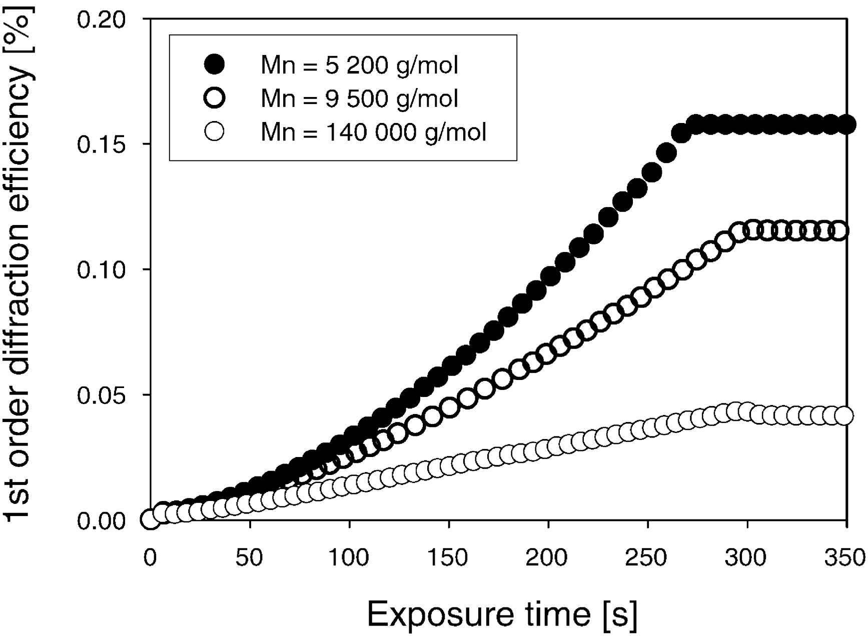


FIGURE 2 Diffraction efficiency of the SRG photofabricated on film of polymers with different molecular weight as function of the exposure time.

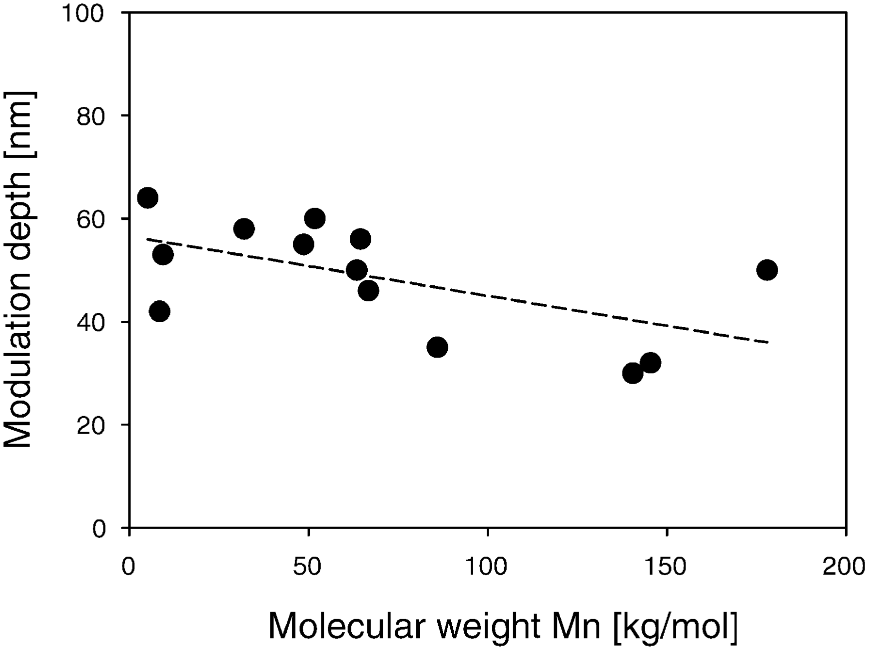


FIGURE 3 Modulation depth determined by AFM as function of the molecular weight. The dashed line was drawn to visualize the general trend.

higher the molecular weight the lower the modulation depth. However, the scattering of the data does not allow a extensive interpretation. Furthermore, the datum for the lowest molecular weight is a lower limit, since the irradiation time was only 260 s. Despite these problems with the data, it is obvious, that the influence of the molecular weight on the SRG formation is less pronounced than expected from the report of Barret et al. [12]. The results therefore supports the general idea that a higher molecular weight slows down the process somewhat, but does not inhibit it completely.

CONCLUSIONS

The dependency of the SRG formation on the molecular weight was investigated with a series of well defined azopolymers. The polymers were obtained by a combination of an atom transfer radical polymerisation of trimethylsilylethyl methacrylate and subsequent polymeranalogous introduction of the azobenzene chromophore. In holographic experiments the different polymers show growth curves for the diffraction efficiency of the first order diffraction which are similar in their shape, but indicate different growth rates. The modulation depth (See Figure 3) of the grating as measured by AFM decreases with increasing molecular weight, however, the effect is much smaller than expected.

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