Azobenzene-Containing Polymers for Surface Relief Gratings

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Summary: Well defined azobenzene containing (co)polymers have been synthesized by atom transfer radical polymerization and subsequent polymeranalogeous reaction for introduction of the chromophores. Four different series were prepared varying only one of the following material parameters at a time, while keeping the others constant. Varied were the molecular weight, the azobenzene content, the glass transition temperature and the molecular architecture of the copolymers. With these four series of (co)polymers the influence of the molecular parameters on the photoinduced formation of surface relief gratings was investigated.

Keywords: atom transfer radical polymerization; chromophore content; glass transition temperature; molecular weight; photoinduced mass transport; star shaped polymer; surface relief grating

Introduction

Azobenzene-containing polymers have attracted much interest in applications for data storage and other optical technologies.[1] This wide range of applications arises from the unique phenomena found for these materials: Upon exposure to polarized light dichroism and birefringence can be induced. When azobenzene containing polymer films are irradiated with interference patterns of polarized light formation of surface relief gratings (SRG) on the micrometer-scale can be observed.

The formation of SRGs was first reported in 1995 by NATANSOHN et al.[2] and TRIPATHY et al. [3] but the mechanism of this effect which involves a massive transport of the polymer material well below the glass transition temperature is not yet clarified. Various models have been proposed to explain the formation of SRGs, but none can explain all observations.[1] While the physical conditions for the SRG formation have been optimized to some extent, the influence of polymer structure and properties on the efficiency of the SRG formation has not yet been investigated in detail. Parameters like molecular weight, glass transition temperature, azobenzene content, and others are believed to influence this process. For the investigation of a single of these molecular parameters, it is necessary to synthesize model polymers in which one parameter can be varied separately, while all others are kept constant.

We developed a synthetic route in which prepolymers of protected 2-hydroxyethyl methacrylate (HEMA) and comonomers are synthesized via Atom Transfer Radical Polymerization (ATRP). This polymerization method gives an excellent control over the degree of polymerization, the composition and architecture of the (co)polymers. Subsequently the prepolymers are modified in a polymeranalogous reaction with azobenzene chromophores. In this way the chromophore content, type, and linking can be adjusted. With this method well defined azobenzene-containing (co)polymers were

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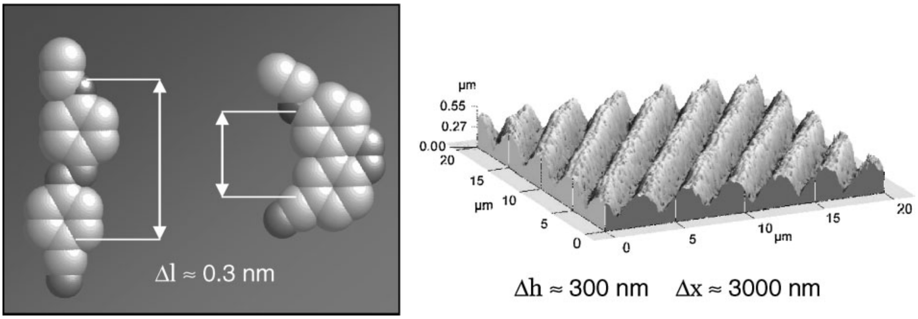

Figure 1.
Comparison of the length scale of the change in dimension of the azobenzene moiety upon isomerization (ca. 0.3 nm) and the change in the film topography during the SRG formation (300–3000 nm).

obtained, varying only in the molecular weight,[4] the chromophore content,[5] the glass transition temperature or the architecture (branched or linear)[6] and the influence of these parameters on the formation of SRG was studied.

Experimental Part

Materials

The synthesis of the prepolymers and the polymeranalogous introduction of the chromophores has been described in details previously.[4,5] For preparation of branched prepolymers 4-, 6- and 12-arm initiators have been used in the ATRP according to a literature procedure.[6–8] The copolymerization of HEMA with n-butyl methacrylate and isobornyl methacrylate for adjusting the glass transition temperature was performed in a similar manner as the copolymerisation with methyl methacrylate.[4,5]

Characterization

Molecular weights and molecular weight distributions were measured by SEC/MALLS combination in THF (membrane filtered and degassed) containing LiBr (0.1 mol/L) on two PL-gel 5µm mixed-C columns (Polymer Laboratories, VARIAN) at 80 °C and a flow rate of 0.5 mL/min. Detection was performed with a Shodex RI-101 differential refractive-index detector set at 45 °C and a TriStar MiniDawn light scattering (LS) detector from Wyatt Technology (angles at 30, 90, and 120°). Data acquisition and processing were performed using the ASTRA software (Wyatt). Glass transition temperatures (Tg) were determined by differential scanning calorimetry (DSC) with a Netzsch DSC 204 Phoenix thermal analyzer (scanning rate of 10 K min^{-1}). UV-vis spectra were recorded on a Perkin Elmer Lambda 5 instrument in tetrahydrofurane (THF) as solvent. The spectra were analyzed with the UV WinLab software (Perkin-Elmer).

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. Diffraction gratings were recorded by using a previously described holographic set-up.[5,9]

Influence of the Molecular Weight

To investigate the influence of the molecular weight on the formation of surface relief gratings a series of polymers was synthesized. Within this series the molecular weight of the prepolymer was adjusted using ATRP. The prepolymers were then reacted with an azobenzene containing carboxylic acid employing N,N-carbonyl-diimidazole for activation (s. Figure 2). 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

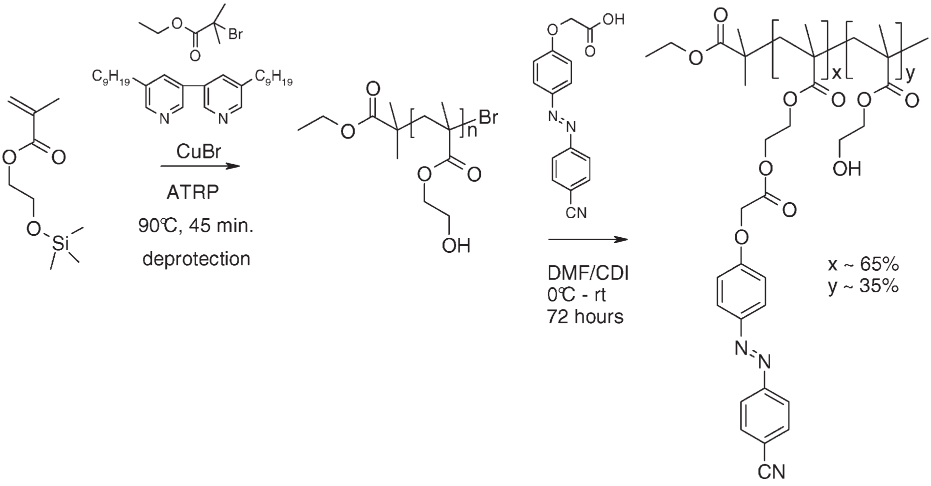

Figure 2.
Synthesis of azobenzene containing polymers varying only in the molecular weight.[4]

from reaction with the bulky imidazolide. Therefore the maximum side chain density is restricted to approximately 65% (Figure 3). Furthermore the glass transition temperature proved to be almost identical within this series, but only the very low molecular weight polymers have a somewhat lower Tg.

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.[4] 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. 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 data are compiled in Figure 4. A general trend is noticeable: The higher the molecular weight the lower the

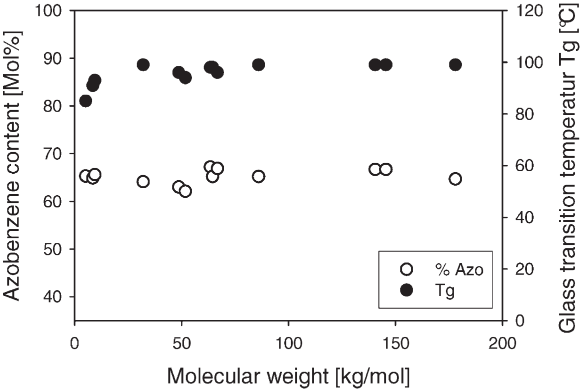

Figure 3.
Azobenzene content and glass transition temperature plotted for the polymers with different molecular weight.[4]

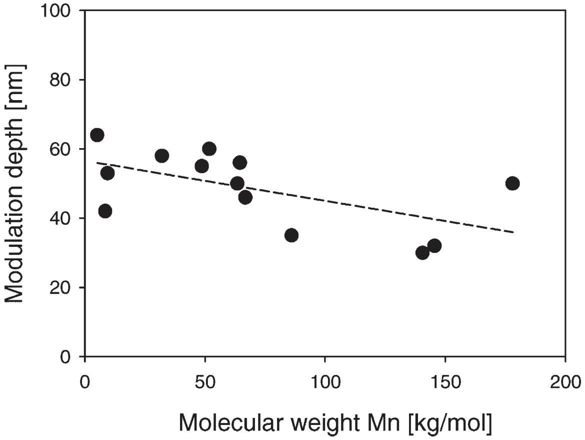

Figure 4.
Modulation depth determined by AFM as function of the molecular weight. The dashed line was drawn to visualize the general trend.[4]

modulation depth. However the influence is much less than expected from the report of Barret et al.[10]. The results therefore supports the general idea that a higher molecular weight slows down the process somewhat, but does not inhibit it completely.

Influence of the Azobenzene Content

The influence of the azobenzene content on the SRG writing efficiency is discussed controversial in literature. T. Fukuda et al. found an increase of the writing efficiency with azobenzene content,[11] while L. Andruzzi et al. suggested that there is an optimum azobenzene content beyond which the efficiency decreases again.[12] In order to keep all other parameters like molecular weight, glass transition temperature, and degree of substitution constant, a series of polymers were synthesized having two different side chains in varying compositions. In this case the esterification was carried out using the acid chloride method

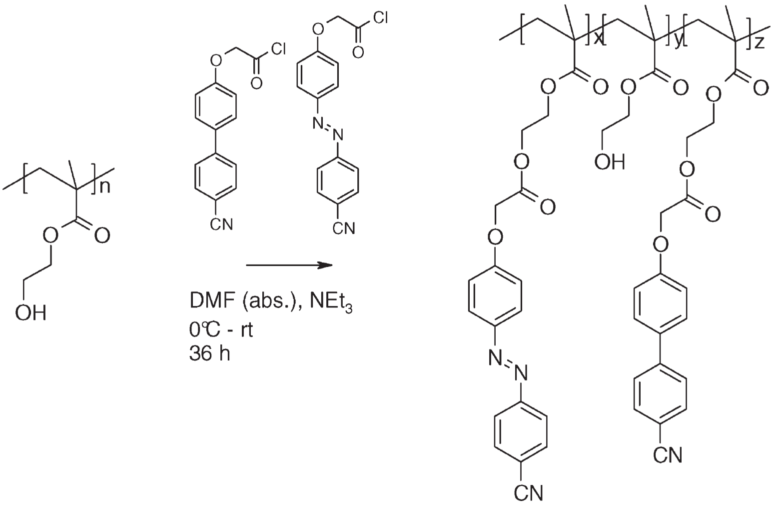

Figure 5.
Synthesis of polymers varying only in the azobenzene content.[5]

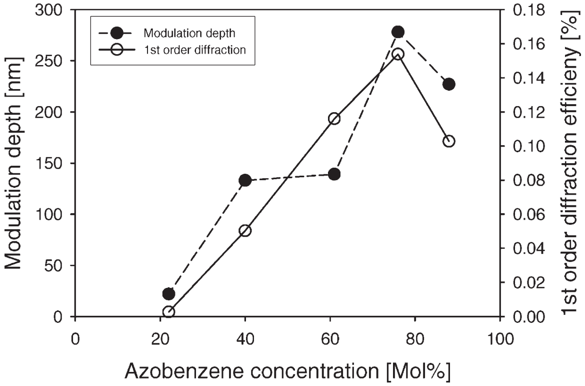

Figure 6.
Modulation depth and 1st order diffraction efficiency as function of the azobenzene content (writing time = 10 min, geometry = lcp – rcp, film thickness = 260–450 nm, grating amplitude $\Lambda = 2.4$ μm).

in order to obtain higher degrees of substitution.

Employing one prepolymer for all polymeranalogous reactions and the approach of replacing more and more of the photoactive side chains by non-photoactive but structurally similar biphenyl groups, the glass transition temperature of the polymers in this series could be kept constant within the error of the measurements.[5]

Again thin films of these polymers were prepared and used in SRG writing experiments. Both the first order diffraction efficiency and the modulation depth were determined after 10 min writing time. Both are measures for the writing efficiency. The higher the modulation depth the higher is the 1st order diffraction of the surface relief grating. The results (s. Figure 6) clearly indicate that there is an optimum azobenzene concentration. This effect can be rationalized with the tendency of azobenzene for π-π-stacking.[5,13] Such an aggregation was proven by a shift of the π-π^*-band in the UV/vis spectrum.[5,13] The aggregates may be thought as a kind of a soft physical crosslinking obstructing the translational motions necessary for efficient SRG formation.[5,14]

Influence of the Polymer Architecture

The effect of the polymer architecture on the writing efficiency is another subject of the ongoing discussion about the parameters influencing the SRG writing efficiency. Barret et al. have reported that for polymers with molecular weights beyond the entanglement limit there is no SRG formation.[10] Going from a linear to branched polymer should decrease the tendency for entanglement and therefore increase the writing efficiency. Indeed it has been reported that dendrimers show a high writing efficiency.[15] However, so far no comparison of polymers differing only in the architecture has been carried out. To obtain a polymer series for such an investigation prepolymers were synthesized having the same molecular weight but being linear, 4-, 6- or 12 arm stars. Atom transfer radical polymerisation (ATRP) allows adjustment of the molecular weight and can yield star-shaped polymers when multifunctional initiators are used. The dendritic initiators depicted in Scheme 1 have been prepared according to an already published procedure.[7,8]

Applying appropriate conditions for the ATRP, in particular by choosing the right catalyst system, well defined star copolymers can be obtained and no star-star coupling is observed.[6] Furthermore, copolymerization with methyl methacrylate reduced the density of functional chains and with that the tendency for aggregation. The functionalization of the prepolymers

Table 1.
Molecular parameters for the polymer series with variation of the molecular architecture.[6]

Polymer architecture	MMA content%	HEMA content%	Azobenzene content%	Tg [°C]	Mn [g/mol]	PD
linear	44	14	42	99	138 000	1.09
4-arm	41	16	43	99	128 000	1.23
6-arm	42	15	43	99	129 000	1.25
12-arms	42	16	42	97	124 000	1.18

was accomplished by esterification of the OH-groups using 2-(4-(4-cyanophenylazo)-phenoxy)acetylchloride in a polymeranalogous reaction. This method gives a high degree of substitution of approximately 75% (see Table 1). The four polymers of the series have very similar molecular weights (variation less than 10%), thus its influence on the grating formation may be neglected.[4] Furthermore, the azobenzene content and also the amount of remaining OH-groups are comparable for all polymers of the series. The glass transition temperatures of the polymers are almost identical.[6]

Thin films of the polymers were prepared and surface reliefs were written into the films. The kinetics as well as the modulation depths reached for the polymers of this series were very similar (s. Table 2). Thus no distinct influence of macromolecular architecture on the surface grating formation could be detected for the investigated polymers under applied experimental conditions.

The fact that no influence of the molecular architecture was observed is rather unexpected, since stars have a lower melt viscosity i.e. higher molecular mobility in the case of non entangled systems, however should be significantly higher for entangled systems, since the raptation motion is hindered.[16,17] For our systems we expect a higher mobility for the star-shaped polymers since for the invidual side chains the critical molecular weight for entanglement is not reached while this is the case for the linear polymer.[6] It is difficult to put these results into the context of the existing theories and to judge the role of entanglements in mechanism of the surface relief formation. Probably more experiments are necessary or the theories describing the photoinduced formation of surface relief gratings have to be extended.

Influence of the Glass Transition Temperature

The glass transition temperature has been described to have a strong influence on the efficiency of the SRG writing process.[18] However, the experiments have been carried out with polymers having also different chromophores, thus no clear differentiation of the influence of the glass transition temperature is possible. The copolymerisation of HEMA with various monomers allows adjustment of the glass transition temperature. Thus three different copolymers were prepared by ATRP. Beside methyl methacrylate, which already has been used before, n-butyl methacrylate was used to reduce the glass transition temperature, while isobornyl methacrylate is a monomer which increases Tg.

Table 2.
Modulation depth of the SRG obtained in azobenzene containing polymers (writing time = 30 min, geometry = orthogonal, linearly polarized beams with polarization planes at ± 45°, film thickness = ~ 0,5μm, grating amplitude $\Lambda = 2{,}4$ μm).[6]

Polymer	linear	4-arm	6-arm	12-arm
relief depth ± rms[a)] [nm]	242 ± 30	253,5 ± 32	240 ± 26	248 ± 29

[a)] root mean square.

Table 3.
Molecular parameters of azobenzene containing copolymers having different glass transition temperatures.

	-MMA	-BMA	-IBMA
Degree of polymerization	499	499	473
Mn [g/mol]	997 00	116 100	130 200
Polydispersity	1.12	1.13	1.09
HEMA-content [mol%]	50.0	49.7	53.0
abs. Azobenzene content [mol%]	32.0	31.9	31.2
Tg [°C]	103	72	113

The prepolymers were again esterified by the acid chloride method to obtain azobenzene containing polymers. Upon introduction of the bulky azobenzene moiety the glass transition temperatures change compared to the prepolymers. The copolymer with n-butyl methacrylate becomes more stiffer and the Tg increases, while in the case of the iso-bornyl methacrylate the stiffness of the polymer chain is not changed that much, however, the distance between the chains becomes larger and thus the Tg is somewhat lowered. However, three polymers covering a temperature range of more than 40° difference in the Tg have been prepared by this synthetic approach (s. Table 3).

In SRG writing experiments a clear influence of the glass transition temperature can be established. The modulation depth after 30 min writing time decreases from approximately ~250 nm for the copolymer with a Tg of 72 °C to ~120 nm for the copolymer with a Tg of 103 °C. The copolymer with the highest Tg of 113 °C

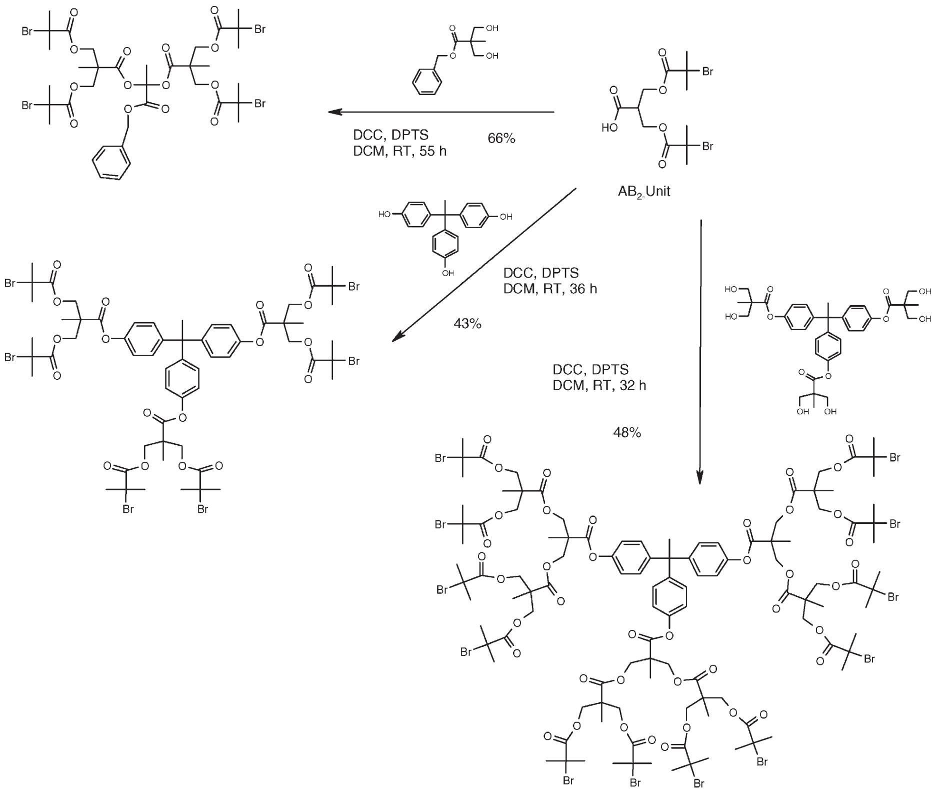

Figure 7.
Dendritic initiators for ATR polymerization yielding 4-, 6- and 12-arm star prepolymers synthesized according to ref. [7]

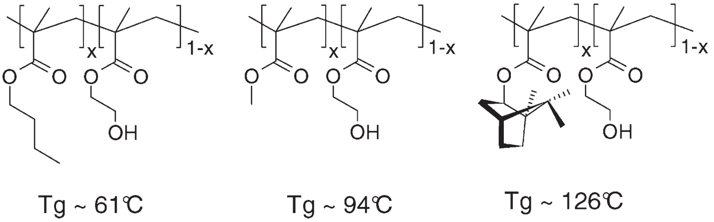

Figure 8.
Prepolymers having different glass transition temperatures.

allowed the formation of SRG with only ~110 nm modulation depth.

Conclusion

Linear and star shaped polymers and copolymers were synthesized for preparation of well defined azobenzene containing materials suited for the investigation of parameters influencing the efficiency of the photoinduced formation of surface relief gratings. Atom transfer radical polymerization (ATRP), which allows adjusting the molecular weight and the architecture of the polymers, was chosen for the preparation of the prepolymers. The prepolymers were subsequently functionalized with azobenzene chromophores by polymeranalogous reaction. The polymers differ only in one parameter at a time, either the molecular weight, or the content of azobenzene moieties, or their architecture or the glass transition temperature. With the respective polymer series it was proven that increasing the molecular weight decreases the writing efficiency, but not as pronounced as expected from previous reports. Furthermore, it was shown that there is an optimum azobenzene content above which the writing efficiency decreases again. The architecture of the copolymers – namely being linear, 4-, 6-, or 12-arms stars – has on the other hand no significant influence on the SRG writing efficiency. This is a somewhat unexpected result if the mechanisms which have been proposed for the photoinduced SRG formation are taken into account. Finally the strong influence of the glass transition was confirmed.

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