Molecular Crystals and Liquid Crystals

Comparative Study of Photomechanical Effects in Linear and Star Azo-Polymers

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We investigated the influence of the polymer macromolecular geometry and chain length in azobenzene containing polymeric liquid crystals (azo-PLC). In particular we studied the photomechanical effects (photoinduced expansion and shrinking) on monodispersed azo-PLCs (polydispersity index 1.08–1.17) prepared from the same monomer and different molecular weights, both in linear and 3-arm star conformation.

The characterization has been carried out in thin films by high resolution null ellipsometry for a simultaneous and independent determination of both mechanical and optical properties (e.g., thickness and refractive index). The measurement system has been set up in a pump probe configuration for a real time characterization of the photoinduced dynamics. The effect of coupling introduced by the polymer star configuration is discussed.

1. INTRODUCTION

Azobenzene containing polymeric liquid crystals in the standard linear conformation have been subject of intense research in the last

two decades [1,2] for the possibility they offer of an external optical control of many physical properties such as optical absorption, birefringence, viscosity [3–5] or volume [6]. More recently the attention on these materials has been focused on their photomechanical properties (for reviews see [7,8]) namely their ability to expand and contract under the action of light. Such phenomenon may find application as photoactuators; for example recently a light driven plastic motor has been realized [9] and the possibility of developing nanoactuators even at single molecule level has been demonstrated [10]. The photoinduced volume variation is a property exhibited by various azobenzene containing systems [7], such as gels, elastomers, cross-linked polymers or dendrites, which possess as common feature the network structure with different degree of coupling between the network elements or "branches." Our study aimed to investigate the influence on the photomechanical effects of the network elements length and their coupling. We studied therefore linear polymers with different chain lengths and the related star polymers where a defined coupling element is introduced by the central core, instead of the statistical links present in gel, dendrites or cross-linked polymers.

For these investigations it appears that polymeric samples with a well-defined structure are needed for a better understanding of the structure-properties correlation; hence, derivatives with a carefully selected molecular mass and low polydispersity are required. This goal can be achieved by using a controlled polymerisation procedure such as atom transfer radical polymerisation (ATRP) [11–13]. Herein, we report a comparison between the different behaviour of linear and star shaped liquid crystalline polymers under optical pumping of the azobenzene photoisomerisation, aimed at a better understanding of the role played by the macromolecular structure in the photomechanical effects of side-chain LC polymers.

In particular, we have considered the two series of homopolymers depicted in Figure 1: four linear, poly(4-ω-methacryloyloxy-hexyloxy-4'-ethoxyazobenzene) {Poly(**M6A**)-2 through Poly(**M6A**)-24} [14], and four related three-arms branched macromolecular derivatives with controlled average molecular weight, star(4-ω-methacryloyloxy-hexyloxy-4'-ethoxyazobenzene) {Star(**M6A**)-2 through Star(**M6A**)-24} [15], obtained by ATRP of monomer 4-ω-methacryloyloxy-hexyloxy-4'-ethoxyazobenzene (**M6A**) (Fig. 1) in the presence of allyl 2-bromo-isobutyrate (**ABIB**), or 1,3,5-(2'-bromo-2'-methylpropionato)benzene (**BMPB**), as the mono- or trifunctional initiator, respectively, having variable average chain length with low polydispersity just by varying the process duration.
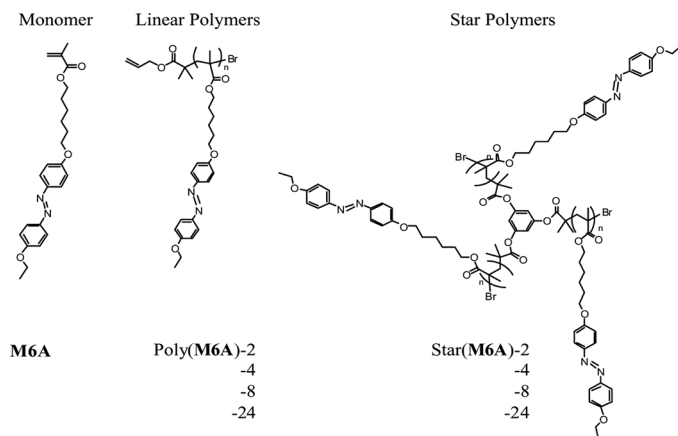
FIGURE 1 Structural formulas of the investigated polymeric samples and of related monomer **M6A**.

These polymeric materials display LC behaviour and the photomechanical properties of the films after irradiation with both visible and ultraviolet light were investigated in detail by high resolution null ellipsometry and their dependence on the macromolecular structure discussed.

2. MATERIAL AND METHODS

The monomer 4-ω-methacryloyloxy-hexyloxy-4′-ethoxyazobenzene (**M6A**) was synthesized as previously reported [16]. Structures of the investigated azobenzene liquid crystalline polymers are shown in Figure 1. They were synthesized by ATRP procedures, as described previously, using a monofunctional ATRP initiator (**ABIB**) for the linear polymeric derivatives [14], or a trifunctional initiator (**BMPB**) for the three-arms star polymers [15], in the presence of CuBr and hexamethyltriethylentetramine (HMTETA).

Relevant data for the investigated polymeric products, Poly(**M6A**) and Star(**M6A**), are reported in Table 1.

The living character of the ATRP process of monomer **M6A** yields polymers with well defined structures, average molecular weight and low values of polydispersity index (Table 1), which was determined in THF solution by Size Extrusion Chromatography (SEC) using HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5-micron MXL column, a UV-VIS detector Linear Instrument model UVIS-200, working at 254 nm,

TABLE 1 Structural and Thermal Characteristics of the Polymeric Materials

Sample	Structural properties			Thermal transition[c]		
	$\overline{M}_n^a$ (g/mol)	$\overline{M}_w/\overline{M}_n^a$	$\overline{X}_n^b$	T_g (°C)	$T_{S\rightarrow N}$ (°C)	T_I (°C)
Poly(**M6A**)-2	4600	1.13	11.2	57	66	116
Poly(**M6A**)-4	6000	1.12	14.6	63	76	129
Poly(**M6A**)-8	9700	1.13	23.6	69	79	129
Poly(**M6A**)-24	14800	1.17	36.0	76	92	148
Star(**M6A**)-2	5600[d]	1.21	4.5	57	78	124
Star(**M6A**)-4	8600[d]	1.12	7.0	57	80	127
Star(**M6A**)-8	19000[d]	1.08	15.4	71	87	142
Star(**M6A**)-24	43700[d]	1.14	35.5	85	94	150

[a]Determined by SEC in THF at 25°C.

[b]Average polymerisation degree ($\overline{X}_n$) for linear macromolecules and for each branch of the star shaped derivatives calculated by $\overline{M}_n$ values.

[c]Obtained from the second DSC heating cycle under nitrogen at 10°C/min heating rate. g (glass), S (smectic A1), N (nematic), I (isotropic) phases.

[d]Calculated by $\overline{M}_n = \text{Conversion} \cdot (M_{M6A}/M_{BMPB}) \cdot MW_{M6A} + MW_{BMPB}$, where M_{M6A} and M_{BMPB} are the initial amounts in moles of monomer and trifunctional initiator and MW_{M6A} and MW_{BMPB} are their molecular weights, respectively.

and a calibration curve for MXL column, obtained by using mono-disperse polystyrene standards in the range 800–35000 g/mol.

The phase transition temperatures and relevant textures were determined by a combination of differential scanning calorimetry (DSC) on a TA Instrument DSC 2920 Modulated apparatus at a heating/cooling rate of 10 K/min under nitrogen atmosphere on samples weighing 5–9 mg and Polarising Optical Microscopy (POM) observations on polymer films obtained by casting on glass slides with a Zeiss Axioscope 2 polarising microscope through crossed polarisers fitted with a Linkam THMS 600 hot stage.

All the macromolecules display on heating a glass-transition temperature (T_g), a smectic liquid-crystal-phase melting endotherm with a consequent nematic liquid-crystal-phase melting endotherm and finally an isotropization temperature (T_I) (Table 1).

The LC texture and the thermal properties of the synthesized linear and star polymers of **M6A** are in agreement with those of Poly(**M6A**) with $M_w = 74000$ mg/mol and polydispersity index = 1.9 ($T_g = 70$°C, $T_{S\rightarrow N} = 97$°C and $T_I = 152$°C), obtained by AIBN-initiated free radical polymerisation, extensively studied by DSC, POM, and X-ray diffraction [16]; with the expected differences in the transition temperatures values that appear strongly dependent on the polymeric architecture, polymerisation degree and on the molecular weight distribution.

The samples of the eight synthesised polymers for the ellipsometric study have been prepared on silicon substrates by spin coating technique. The compounds have been dissolved in chloroform at 5 mg/ml concentration and cast on the substrates spinning at 2000 rpm, yielding film thicknesses in the range of 35–60 nm. The thickness has been adjusted in such range in order to study thin samples required for a uniform optical pumping without self screening effects due to the high optical extinction coefficient of the azobenzene chromophore and at the same time sufficiently thick to neglect surface effects. As a matter of facts, such surface interactions, due to the change of hydrophilicity between trans/cis isomers, become dominant for ultrathin or single molecular layer [17].

Both refractive index and thickness of samples, thermostated on a Peltier plate, were measured by high resolution null ellipsometry using a single wavelength ellipsometer (Multiskop, Optrel Gmbh), set up in a pump probe configuration. The instrument is equipped with a He-Ne laser impinging on the sample with an angle of incidence of $70°$ operating at 632.8 nm, which probes the materials outside the azobenzene absorption region, while the optical pumping has been obtained by means of two Light Emitting Diodes LEDs, positioned above the sample. Two LEDs with emission peaks centered at 390 nm and 470 nm were necessary in order to induce respectively trans->cis and the reverse isomerizations of the azobenzene chromophore which in turn result in a contraction and expansion of film [14,18]. The samples of each compound, before the experiments, have been annealed some hours at $5°C$ above their glass transition temperature (T_g) (see Table 1), in order to remove solvent residues and to obtain a stabilization of the film. The annealing process was monitored by ellipsometry and continued until the achievement of a stable film thickness. The samples cooled to room temperature exhibit an isotropic phase as after their preparation by the spin coating technique as characterised by polarizing optical microscopy. Particular attention has been paid to avoid a smectic crystallization which inhibits the photomechanical effects and can be induced by the annealing process above T_g, therefore before the ellipsometric measurement the isotropic structure of samples or the absence of birefringent islands has been checked through the polarising microscope.

3. RESULTS

The thickness and refractive index variations of samples have been monitored in real time by the ellipsometer during irradiation by measuring the ellipsometric angles Δ and Ψ with 5 second time resolution. An example of photoexpansion at room temperature of samples

previously compacted with UV illumination is reported in Figure 2; where the dynamics of thickness of a linear [Poly(**M6A**)-4] and a star polymer [Star(**M6A**)-4] are reported for comparison.

Generally the photoinduced dynamics in azo-PLC depends on the system viscosity, resulting on slower relaxation times with increasing molecular weight as reported in the case of photoinduced birefringence [19]. Here we observe, as a first remarkable difference between the two macromolecule types, that the branched polymer with a comparable glass transition temperature (even lower see Table 1) and molecular weight displays a higher relaxation time. Such result suggests that the star macromolecular geometry inhibits the photoinduced softening/fluidification effect [5] which allows the molecular reorientation in azo-PLC polymers even well below the glass transition temperature. The coupling introduced by the star geometry influences not only the dynamics but also the overall effect, namely the final volume variation, as it can be deducted from Figure 2. The data obtained for the eight synthesized polymers are summarized in Figure 3.

The measurements were performed below the T_G of each compound at 55°C; this higher temperature was chosen in order to gain a faster dynamics. The final film percentage expansion ($\Delta V/V$) of the compounds, plotted as a function of their molecular weight (Fig. 3), clearly indicates a frustration introduced by the branched geometry in the photo-expansion. The percentage volume expansion increases with
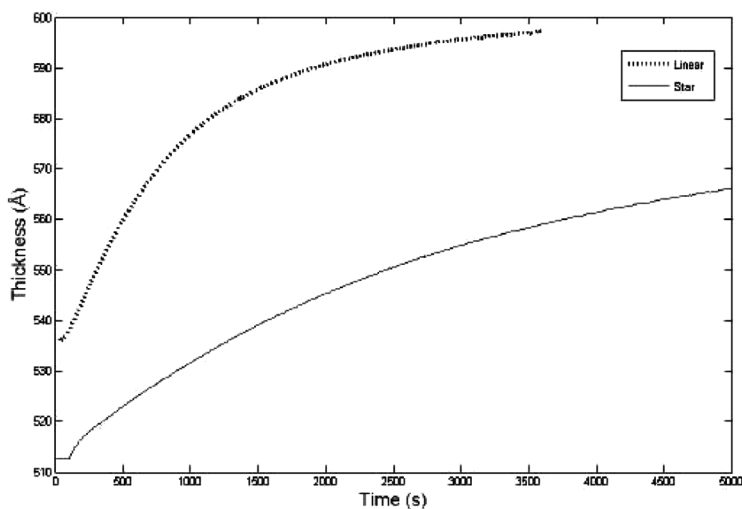

FIGURE 2 Examples of expansion dynamics [Poly(**M6A**)-4 and Star(**M6A**)-4].
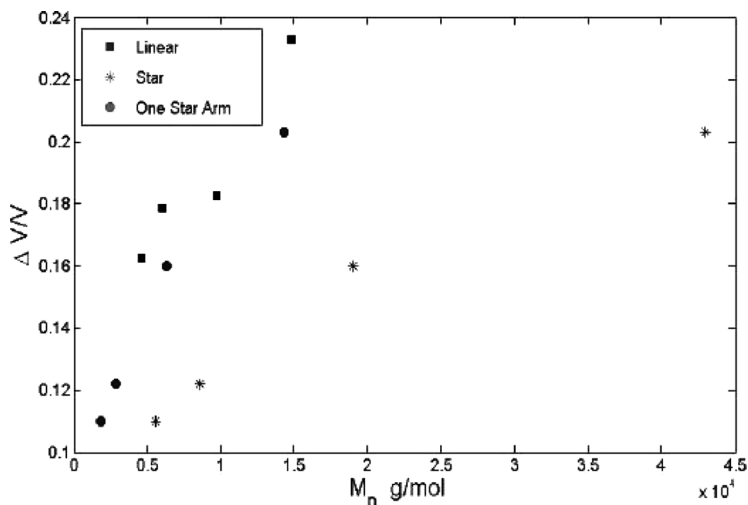
FIGURE 3 Percentage volume variation as a function of the molecular weight of the linear polymers (squares), Star Polymers (Stars) and of each branch ($N_f = 3$) of the Star polymers (Circles).

the molecular weight in both cases, either for linear and star polymers, due to the ability of longer chain to store more free volume. However the effect of central core coupling present in the star polymers, could suggest that for an efficient photoexpansion also independent chains are required. As a matter of fact, also plotting the expansion as a function of the single arm length of the star polymers, obtained by molecular weight (Table 1) divided by the number of arms (functional number $N_f = 3$), the trend of expansivity remains still lower than that of the related linear polymers (Fig. 3). Such phenomenon can be ascribed to the reduction of possible chain conformations introduced by the constrain represented by the aromatic central core.

Moreover an other possible cause of this effect may lay in the initial structure of the star polymers which is generally characterised by an higher density at given molecular weight, as it can be measured by the refractive index values. In Figure 4 we report the photoinduced expansivity for films of different composition (star and linear geometry, with different chain lengths) as a function of the refractive index, which in turn, at a given molar refractivity, is related to the sample density via the Lorentz–Lorenz equation. Data were taken at RT and at 55°C. The major finding observing Figure 4 is that there is an overall correlation between the density and the photoinduced expansivity: the samples with higher refractive index and hence higher density exhibit a
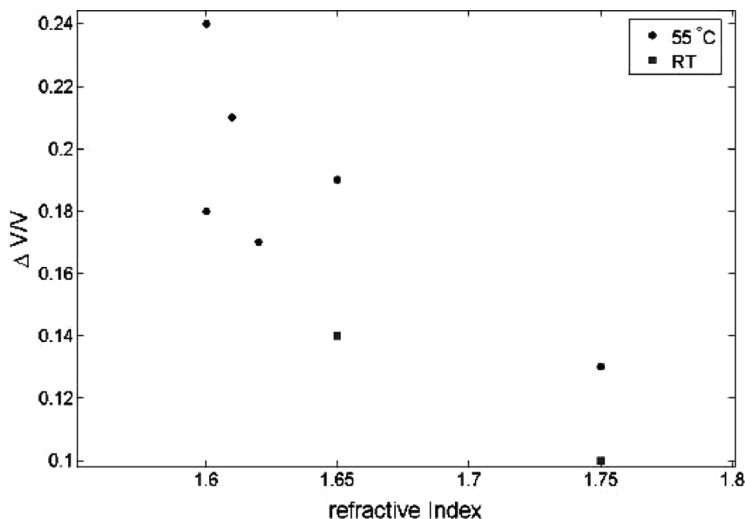
FIGURE 4 Correlation between expansion and refractive index (density), data acquired at 55°C (circles) and at room temperature (squares).

smaller expansivity, which is a clear indication of the importance of the free volume in determining not only the time scale on which the expansion occurs, but also its overall extension. Interestingly enough, focusing on the linear polymers only, as the polymeric length is increased, a larger photoinduced expansion is found, while the refractive index stays roughly constant. This suggests that the amount of the photoinduced expansion can be reduced by the rearrangement that can occur with a high density of free polymer ends, as it happens for the shorter polymers. Comparing star and linear geometry, it seems that, at a given chain length, the presence of the three arms originating at the same central rigid core induces a larger refractive index, which is reasonable, being the star polymer a more dense material, while at the same time the star geometry reduces the expansion.

4. CONCLUSIONS

We characterised the effect of the inter-chain coupling on the photomechanical properties in azo-PLC by a comparative study of star-polymers with the related linear ones. The synthesized highly monodispersed compounds with a fixed number of arms allowed us to investigate a well defined coupling element. Such a coupling is required and generally introduced statistically in other azo systems

[7] in order to transfer the transduction from a molecular to a macro-scopic level. We observed however that such desirable inter-chain interactions, in the case of star polymer correspond to a slowdown of dynamics and a reduction in photoexpansion. Our results indicate that trade off between an efficient macroscopic transduction and overall extension should be sought.

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