Photo-embossed Surface Relief Structures with an Increased Aspect Ratio by Addition of Kinetic Interfering Compounds

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The aspect ratio of photo-embossed relief structures has been improved significantly by addition of a reversible addition-fragmentation chain transfer (RAFT) agent, typically used for controlled radical polymerization in particular of acrylate monomers. The increase is independent of the atmospheric conditions since oxygen inhibition hardly occurs, which represents a major advantage for industrial applications of photo-embossing. The aspect ratio could be improved due to the controlled acrylate polymerization upon addition of a RAFT agent and increased by a factor of almost 10. The insensitivity to oxygen inhibition is related to the ability of the RAFT agents to form stable radicals.

Keywords: photo-embossing, relief structure, RAFT agent, aspect ratio.

1. Introduction
Photo-embossing is a relatively new and easy technique for the generation of polymeric relief structures by photolithography.[1] Standard lithography techniques to create relief structures use light-induced solubility changes of a polymeric photoresist.[2] After a wet-etching step the final structure is developed. The etching step is a time and cost consuming factor in the production of relief structures and not favourable in terms of sustainability and environmental effects.

In contrast, photo-embossing does not involve any etching steps, which reduces the number of processing steps and thereby the production costs. Furthermore, unlike conventional patterning techniques, like hot-embossing[3-4] or micro-contact printing[5-6] techniques, photo-embossing does not require expensive moulds and, as a consequence, photo-embossing is a simple and inexpensive technique to create a surface relief.

The relief structures are created by a deformation of the surface of the film which is caused by a material flux induced by a local polymerization,[1,7-8] as depicted in Figure 1. This technique offers a simple and versatile alternative for the production of large-scale/large-area relief structures in thin polymer films, that find applications in biosensors, cell growth arrays and microelectronic elements.[9]
One of the main problems to overcome in the photo-embossing process is the low aspect ratio of the formed features, which is typically 0.05 in an inert atmosphere or 0.2 in an ambient atmosphere. It has been found that the material flux, and thus the aspect ratio, is highly affected by the polymerization kinetics and can be optimized by modifying the rate of initiation by changing initiator content or light intensity.[1]

2. Method
Recently, we described a new development in creating high aspect ratio photo-embossed structures using the addition of t-butyl hydroquinone (TBHQ), which improves the aspect ratios by a factor of 5 to 7.[10] However, the presence of atmospheric oxygen has a significant negative influence on the obtained aspect ratio, since it inhibits further polymerization due to the formation of a stable radical with the TBHQ radicals. As a consequence, no structure will be developed. Although this problem can be solved by nitrogen blanketing during processing, it is highly interesting from an applied point of view to discover additives or alternative processes that yield high aspect ratios in all atmospheric conditions including air.

More recently, we found that the addition of a reversible addition-fragmentation chain transfer (RAFT) agent to the photopolymer system also improves the aspect ratio significantly.[11] The increase, however, is independent of atmospheric conditions. Since oxygen inhibition hardly occurs, this approach has a major advantage for industrial applications of photo-embossing. The aspect ratio could be improved due to the controlled acrylate polymerization upon addition of a RAFT agent and increased by a factor of almost 10.

3. Results & discussion
The addition of different RAFT agents during the photo-embossing process was investigated in order to gain control over the acrylate polymerization, which could lead into an improvement of the aspect ratio of the formed structures. Hereto, the activating group (Z) and leaving group (R) of the RAFT agents were altered and the aspect ratios were investigated and are schematically depicted in Table 1.

To minimize the amount of samples and to increase the accuracy of the experiments, a two-dimensional library has been generated in which the period of the grating structure and the energy dose were systematically varied over its two axes.[7-8] Hereby libraries of 49 different samples, as shown in Figure 2, could be created that were

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**Table 1. Schematic representation of a reversible addition-fragmentation chain transfer (RAFT) agent, where Z is the activating group and R the leaving group (left). Details of the Z- and R-group for the tested RAFT agents (right).**

<table>
<thead>
<tr>
<th>S-S (\text{R})</th>
<th>Activating group (Z)</th>
<th>Leaving group (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Z})</td>
<td>(\text{SC}<em>{2}H</em>{5})</td>
<td>(\text{COOH})</td>
</tr>
<tr>
<td>(\text{R})</td>
<td>(\text{SC}<em>{2}H</em>{5})</td>
<td>(\text{COOH})</td>
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characterized by confocal microscopy in a fast and efficient way.

Figure 3 shows the aspect ratio as function of dose for various RAFT agents, obtained under ambient atmosphere. In general a higher dose results in higher aspect ratios, but not for all grating sizes that are used. Figure 3a shows the relation for 2-cyanobut-2-yl dithiobenzoate (CBDB) as added RAFT agent. It can be seen that there is an optimum in aspect ratio of 0.32 for a grating size of 20 µm: when smaller or larger grating sizes are used the effect of the added RAFT agent diminishes. A similar trend can be observed when using 2-(methoxycarbonyl)prop-2-yl dithiobenzoate as RAFT agent (Figure 3b). This can be explained in by the similarity in activating group of the RAFT agent.

Furthermore, Figures 3c and 3d both show overlapping grating sizes of 30 and 40 µm, which suggests that there must be an optimum grating size between these two values and higher than the 20 or 30 µm for RAFT agents with an aromatic Z-group as activating group. It is believed that the optimum grating size correlates with diffusion properties, which is dependent on the transfer constant of the activating group of the RAFT agent.

In contrast, the RAFT agents 2-n-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (Fig. 3c) and 2-phenylprop-2-yl phenyl dithiocetate (Fig. 3d) do not have an optimum, but show a linear trend between the aspect ratio and exposure dose. The obtained aspect ratios are all below 0.10 and much smaller than for the previously mentioned RAFT agents. This can be explained by the fact that both a benzyl and an alkyl activating Z-group have a low transfer constant.[12]

Figures 3c and 3d both show overlapping grating sizes of 30 and 40 µm, which suggests that there

![Aspect Ratio as function of exposure dose for different grating sizes with 2-cyanobut-2-yl dithiobenzoate (a), 2-(methoxycarbonyl)prop-2-yl dithiobenzoate (b), 2-n-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (c), 2-phenylprop-2-yl phenyl dithiocetate (d) as used RAFT agents, under ambient conditions. The RAFT to initiator ratio was 2. Lines are drawn with a spline fit in (a) and (b) in order to guide the eye, whereas the dashed lines in (c) and (d) represent linear fits to the data.](image-url)
radical scavenger and retards the polymerization, which reduces the aspect ratio of the final features.

4. Conclusion

By adding a reversible addition-fragmentation chain transfer (RAFT) agent the aspect ratio of photo-embossed surface relief structures can be improved significantly. The increase of the aspect ratio depends on the activating group (Z) and leaving group (R) of the RAFT agent. When the Z-group consists of a phenyl-group the highest aspect ratios where found. The aspect ratio could be enhanced due to the controlled acrylate polymerization upon addition of a RAFT agent and increased by a factor of almost 10.

Moreover, the increase is independent of atmospheric conditions since oxygen inhibition hardly occurs, which is a major advantage for industrial applications of photo-embossing. The improved photo-embossed structures offer a simple and versatile alternative for the production of large-scale/large-area relief structures in thin polymer films and finds applications in microelectronic elements, biosensors and cell growth arrays.

Acknowledgements

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References