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A novel photodegradable hyperbranched polymeric photoresist[†]

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We report the first synthesis of a photodegradable hyperbranched polyacetal, wherein every repeat unit carries a photo-labile 2-nitrobenzyloxy moiety. The pristine HBP serves as a positive photoresist to create micron-size patterns; furthermore, by changing the terminal groups to dipropargyl acetal, clickable photo-patterned substrates can be generated.

Photodegradable polymers have been exploited for a wide range of applications, such as for photo-resist formulations in the electronics industry,¹ for biomedical and drug delivery applications,² etc. Several photo-labile moieties³ have been explored over the years; among them the o-nitrobenzyloxy unit has recently gained special attention, even though the first observation of its photosensitive nature was reported over 40 years ago.⁴ Much of the early efforts were mainly confined to exploiting its use as a protecting group.³ In the recent past, however, this photo-cleavage reaction has been ingeniously utilized to photomodify the solubility of block copolymers and consequently modulate their aggregation behaviour;⁵ this change in aggregation behaviour has, in turn, been exploited to trigger the delivery of drugs and other occluded molecules from micelles⁶ and vesicles,⁷ and it has also been used to alter their LCST.8 Suitably designed linkers based on the 2-nitrobenzyloxy unit have also been used as the junction in diblock copolymers; by fine-tuning the morphology followed by photocleavage and selective dissolution of one of the blocks, nanoporous membranes have been generated.9 Besides these studies, there have been a few reports that have used this photo-cleavage to generate photopatterns.¹⁰ For example, Ober and co-workers designed a block copolymer wherein one block carries a fluorinated hydrocarbon unit and the other block an o-nitrobenzyl protected methacrylate; selective dissolution of the unexposed regions using a fluorinated solvent was used to generate micropatterns.¹¹ Similarly, block copolymers have also been used to generate micro-patterns, which have subsequently been used as templates to pattern protein and cells.¹² Most of these earlier studies, based on o-nitrobenzyloxy units, have exploited the

photo-deprotection of pendant groups to modify the solubility of the polymer. However, very few reports describe polymers that contain this moiety in every repeat unit of the polymer backbone; a very recent report by Nazemi *et al.* describes the use of the nitrobenzyloxy unit for the preparation of photo-labile dendrimers, but only up to the third generation was prepared and no photopatterning was studied.¹³

In the present study, we have designed a straightforward approach to prepare a photo-degradable hyperbranched polymer that breaks down into low molecular weight organic molecules upon irradiation; this creates a dramatic difference in the solubility between the exposed and unexposed regions, and, therefore, makes it a potentially useful candidate for photo-patterning. Hyperbranched polymers (HBP), just like their structurally well-defined dendrimeric analogues, are highly branched structures that adopt a very compact conformation and consequently exhibit very low solution and melt viscosities; in addition, they provide ample scope for modification of numerous peripheral terminal groups. Therefore, the development of a HBP that can be used for photo-patterning would be of immense value; the low viscosity would enable the preparation of very thin uniform films and numerous peripheral functional groups would provide an excellent opportunity for easy variation of the surface chemistry by post-patterning functionalization. Importantly, HBPs can be prepared in a single step unlike the photo-labile dendrimers previously reported.13

Recently, we showed that a simple AB_2 monomer carrying a hydroxyl group and a dimethyl acetal unit (A) (Scheme 1) undergoes melt polymerization in the presence of an acid catalyst *via* a *trans*acetalization process to yield a hyperbranched polyacetal; this polymer degrades under mild acidic conditions, the rate of which could be tuned by varying the hydrophobicity of the peripheral alkyl groups.¹⁴ In an effort to develop a derivative that would be photodegradable, we designed new monomer **B** (Scheme 1) that carries an additional nitro-group *ortho* to the hydroxymethyl substituent; this monomer upon polymerization under similar *trans*-acetalization conditions yielded a HBP that carries a photo-labile *ortho*-nitrobenzyloxy moiety in every repeat unit. The monomer **B** was readily prepared starting from terephthalaldehyde (see ESI[†]). Melt polymerization of the monomer was carried out in two stages in the presence of 2 mol% *p*-toluenesulphonic acid; first the melt was maintained at

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Scheme 1 Synthesis of the parent HB polyacetal (HBPA) and its photodegradable nitro-derivatives.

100 °C under dry N₂ purge for 45 min, which was followed by application of reduced pressure (10 Torr) at the same temperature for additional 30 min (see ESI†). The polymer was obtained as a light yellow solid after purification. The molecular weight (M_w) of the polymer was estimated to be about 11 800 (PDI of 2.9) by GPC and its T_g was ~ 22 °C (Fig. S9, ESI†).

The proton NMR spectra of monomer **B** and **Nitro-HBPA**, along with their peak assignments, are shown in Fig. 1. Several interesting changes were noticeable when the monomer was transformed into the polymer, the most interesting is the transformation of the single methine proton (peak a) into three well-resolved peaks with an approximate intensity ratio of 1:2:1 in the polymer spectrum; this is due to the presence of Dendritic (D), Linear (L) and Terminal (T) repeat units.¹⁴ From the relative intensities of these three peaks, the degree of branching (DB) of the HBP was estimated to be around 51% (see ESI[†]), which is in accordance with the value expected for a



Fig. 1 ¹H-NMR spectra of the monomer, Nitro-HBPA and Nitro-HPBA-P; the peak at \sim 10.1 ppm (marked by an arrow) is due to inadvertent hydrolysis of the terminal acetal groups. Expansion of the monomer spectrum reveals two closely spaced peaks at \sim 7.75 ppm.

statistically random growth.¹⁵ In addition, the aromatic region also exhibits several sets of peaks, which again is reflective of the different types of repeat units that are present in the HBP. Furthermore, inadvertent hydrolysis of a small fraction of the terminal acetal groups also generates an aldehyde moiety (\sim 12%), which was confirmed by the peak at \sim 10.1 ppm and associated weak peaks in the aromatic region (marked with arrows). One other interesting feature is that the methoxy protons (peak d) appear as two singlets; one due to the T units and the other due to L units.

The photo-degradation studies were first carried out by irradiating the polymer solution with a Hg-vapor lamp (150 watt); aliquots of the solution after different exposure times were taken and analyzed by GPC. From the GPC curves (Fig. S10, ESI⁺), it was clear that the molecular weight, as expected, continuously decreased with irradiation time. Although the postulated major final product of photodegradation of Nitro-HBPA would be 2-nitroso terephthalaldehyde based on the currently accepted mechanism,¹⁶ (Scheme S4, ESI[†]); experiments reveal the formation of several low molecular weight products (Scheme S5, ESI⁺). FT-IR spectra of the photo-degraded product at different stages of the degradation were also recorded; it was evident that the intensity of peaks due to the nitro-groups at 1350 and 1530 cm⁻¹ decreased with irradiation time and a new band corresponding to the aldehyde carbonyl at around 1700 cm⁻¹ increased with time (Fig. S11, ESI⁺). Similarly, the variation of ¹H-NMR spectra of a polymer solution with irradiation-time revealed the formation of several aldehydic products, while prolonged irradiation of a thin polymer film yielded a slightly different set of products; this is possibly due to inadvertent hydrolysis of a photodegraded intermediate in the solution studies (Fig. S6-S8, ESI⁺).

In an effort to examine the utility of the nitro-HB polyacetal, as a potential photoresist material, the polymer was spin-coated on the piranha-cleaned glass slide or silicon wafer; the film thickness was typically of the order of ~100 nm, as measured by optical profilometry. The photo-patterning was achieved by exposure to a 365 nm light source (600 mJ cm⁻²) using an EVG double-sided mask aligner; typical exposure time was ~5 min. The substrate was then developed in isopropanol for 30 s to reveal the pattern. Fig. 2 shows the scanning electron micrographs of the micropatterns generated using **Nitro-HBPA**; it is evident that excellent pattern reproduction with micron-level resolution is readily obtainable (see Fig. S12, ESI⁺ for additional SEM images).

Recently, we reported several single-step methodologies for the preparation of peripherally clickable HB polyethers and polyesters,¹⁷ using suitably designed AB₂ monomers containing either propargylor allyl-bearing B groups; these polymers could be quantitatively



Fig. 2 Scanning electron micrograph of the positive pattern obtained using Nitro-HBPA. Exposure to 600 mJ cm⁻² (365 nm) UV radiation and isopropanol was used as the developer.



Fig. 3 Schematic representation of the process for generating a reactive photopatterned film using **Nitro-HBPA-P** and thereafter clicking with a fluorescent azide. The fluorescence microscopic image confirms the occurrence of the click reaction.

derivatized using either an organic azide or an organic thiol. Based on a similar concept, instead of the dimethylacetal in the AB₂ monomer B, we designed another AB₂ monomer containing a dipropargyl acetal group as the B2 functionality (see Scheme 1 and Scheme S2, ESI⁺). Polymerization of this monomer under similar conditions yielded a hyperbranched polymer (Nitro-HBPA-P) with peripherally clickable propargyl units. ¹H-NMR spectra of the resulting polymer are also shown in Fig. 1; one unexpected observation was that, unlike the case of dimethyl acetal polymer, the terminal, linear and dendritic methine protons do not appear as three well-resolved peaks but as a single broad peak, while all other aspects were in accordance with the structure. Since the primary backbone of both the polymers is identical, subjecting the polymer Nitro-HBPA-P to UV (365 nm) irradiation using a mask generated similar micro-patterns as before (Fig. S14, ESI⁺); the patterned substrate could then be subjected to surface click reaction.¹⁸ To achieve this, the photo-patterned glass substrates were dipped into an ethanol solution containing a catalytic amount of CuSO₄, Na-ascorbate and 4-N,N-dimethylamino-N-(2-azido-ethyl)-1,8naphthalimide, which is a fluorescent dye. After 12 h, the glass slide was rinsed with ethanol and dried under a slow stream of dry nitrogen. The fluorescence microscopic image (Fig. 3) clearly reveals the expected photopattern confirming the occurrence of the click reaction with the residual polymer. Additionally, the IR spectrum of the polymer after clicking showed a significant reduction of the alkyne C-H stretching peak at ~ 3350 cm⁻¹ (Fig. S13, ESI⁺), which confirms that interfacial click reaction had indeed occurred; this clearly demonstrates the accessibility of the peripheral propargyl groups towards other potentially useful surface modifications.

In summary, we have developed a novel photodegradable hyperbranched polyacetal by suitably designing the AB_2 monomer that carries an *ortho*-nitrobenzyloxy unit; importantly, the polymer was readily prepared by a solvent-free melt *trans*-acetalization process. The intrinsic photo-lability of this polymer permitted its use directly as a photoresist in the absence of any photo-catalyst that is often required for most photoresists. One very interesting and useful feature of this hyperbranched polymer-based photoresist is the presence of numerous readily accessible terminal groups, which can be varied by suitably modifying the B-group in the AB_2 monomer; thus by using a

monomer bearing a dipropargyl acetal, a HB photoresist carrying numerous clickable peripheral groups was synthesized. This clickable HB photoresist was used to create reactive micro-patterns that could be subsequently modified interfacially by clicking an organic azide under standard Cu-catalysed conditions, as was demonstrated using a fluorescent azide. The concept of introducing multiple functionality into a single hyperbranched polymer, such as photo-lability and clickability, opens up several interesting possibilities for the creation of micro-patterned substrates for specific applications, such as patterning of quantum dots, metalnanoparticles, proteins, cells, *etc.*

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