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Polybenzimidazole-based thiol-ene photosensitive composition for DLP 3D printing

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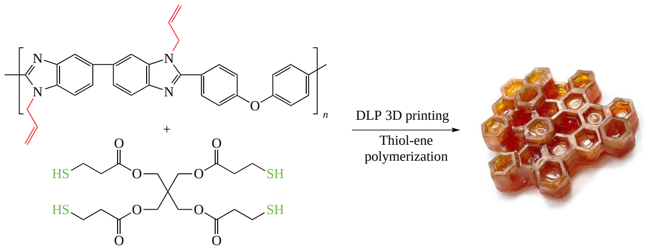
A photosensitive composition based on *N*-allylated poly[2,2′-(*p*-oxydiphenylene)-5,5′-dibenzimidazole] and pentaerythritol tetrakis(3-mercaptopropionate) has been developed. This photosensitive composition is capable of forming cross-linked 3D-structures due to UV-initiated thiol-ene polymerization. Using digital light processing 3D printing, 3D-objects with high resolution, mechanical strength and thermal resistance up to 397 °C are formed.



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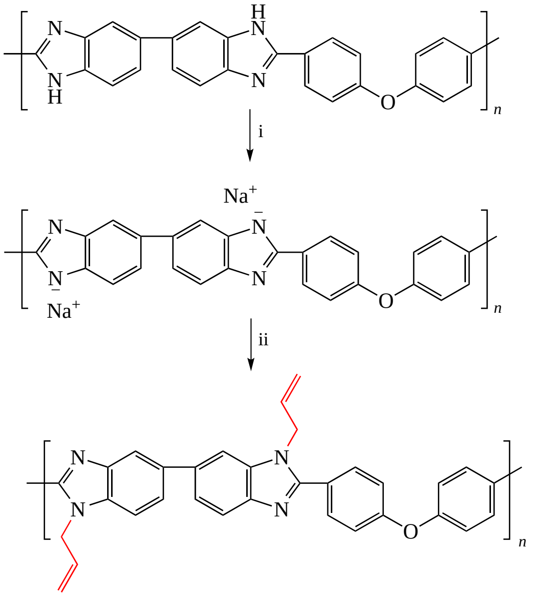
Polybenzimidazoles (PBIs) represent a class of high performance polymers that exhibit excellent thermal stability, mechanical strength and chemical resistance and therefore appear to be ideal materials for use under harsh conditions.[1–4] Meanwhile, PBIs also have extremely high glass transition temperatures (>350 °C), which makes traditional processing methods energy consuming.[1] Moreover, these methods are rarely used for formation products of complex geometric shape and/or small size. To overcome the existing problems of PBIs processing, new original synthetic and technological approaches are needed.

The solution to these problems may consist in the use of digital light processing (DLP) 3D printing technology, which makes it possible to simplify significantly the manufacture of objects of complex architecture, and low temperatures make the process of forming objects energy efficient.[5,6] Previously,[7–11] we obtained photosensitive compositions based on various aromatic heterochain polymers capable of forming 3D structures by DLP 3D printing. In particular, the possibility of obtaining crosslinked polymer networks as a result of thiol-ene polymerization of *N*-allylated aromatic polyamide and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) was shown.[11] Such thiol-ene compositions are insensitive to moisture and atmospheric oxygen, which inhibit the polymerization of (meth)acrylate derivatives traditionally used in DLP 3D printing.[5] Given the above, the aim of the work was to develop new thiol-ene photosensitive compositions based on PBI.

In this study, we used *N*-allylated poly[2,2′-(*p*-oxydiphenylene)-5,5′-dibenzimidazole] (AOPBI) as a polyfunctional ene component of photosensitive compositions. The synthesis of AOPBI was carried out in two stages (Scheme 1) by analogy with the previously described methods.[12,13] At the first stage, solution of poly[2,2′-(*p*-oxydiphenylene)-5,5′-dibenzimidazole] (OPBI) in *N*-methyl-2-pyrrolidone (NMP) was treated with an excess of NaH to deprotonate the NH groups of the benzimidazole moieties. The polyanion thus formed was further alkylated *in situ* with allyl bromide to afford the target AOPBI. The ^{1}H NMR spectrum of AOPBI (see Online Supplementary Materials, Figure S1) contains new signals at ~5.0 (–N–CH_2–), ~5.3 and ~6.1 ppm (–CH=CH_2), which confirms the occurrence of *N*-allylation while the signal at ~13.0 ppm for NH groups of OPBI completely disappears. Comparison between the integral intensities of aromatic and allyl protons shows that this ratio is 14.00 : 10.40, which is very close to the theoretical value of 14 : 10.

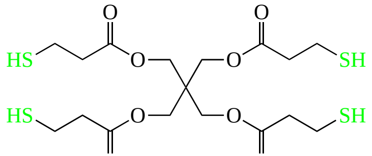
The AOPBI substance, in contrast to the non-modified OPBI, is soluble in chlorinated hydrocarbons (CH_2Cl_2, $CHCl_3$). In addition, the grafting of allyl groups significantly improves the solubility of AOPBI in amide solvents (NMP, *N*,*N*-dimethylacetamide and DMF). OPBI is limitedly soluble in



Scheme 1 *Reagents and conditions*: i, NaH (2 equiv.), NMP, 80 °C, 4 h; ii, CH_2=$CHCH_2Br$, NMP, 40 °C, 72 h.

these solvents forming highly viscous solutions at relatively low concentrations (up to 5 wt%), which is due to strong intermolecular hydrogen bonds involving the benzimidazole NH groups. In contrast, AOPBI is able to form much more concentrated solutions (up to 15 wt%), which is associated with a weakening of intermolecular interactions due to the presence of allyl groups.

At the next stage, a thiol-ene photosensitive composition was obtained based on the synthesized AOPBI. As a thiol component, analogously to our previous work,[11] we used PETMP, which makes it possible to obtain networks with a high crosslinking density.[5,14] Irgacure 819 was used as a photoinitiator, which provided initiation of thiol-ene polymerization at the wavelength of a DLP 3D printer (405 nm). A photosensitive composition was prepared by dissolving AOPBI, PETMP and Irgacure 819 in NMP or *N*,*N*-dimethylacetamide at an equimolar ratio of allyl and thiol groups. Hydroquinone was additionally added to the composition, which increases the stability of the composition over time and improves printing accuracy.[11] The resulting composition remained stable for at least three months without gelation or phase separation.


PETMP

To study the patterns of photocuring, the resulting composition was irradiated with an UV LED (395–400 nm, 10 W) for 30 s. It was found that this thiol-ene system demonstrated a high UV curing rate. The result of photocuring is the formation of an organogel 3D matrix containing the absorbed solvent. Subsequent drying at a stepwise raising the temperature from 20 to 200 °C leads to complete removal of the solvent and obtaining a homogeneous transparent film based on AOPBI-PETMP.

The degree of conversion of thiol and allyl groups was estimated by IR spectroscopy (Figure 1). The absorption band for the S–H groups of PETMP is observed at 2568 cm^{-1}, while it is absent in the IR spectrum of the UV-cured AOPBI-PETMP. Moreover, after photocuring, the absorption band at 3071 cm^{-1} related to the =C–H bonds of the AOPBI allyl groups completely disappears. These data allow us to conclude that the conversion of both double bonds and thiol groups is close to 100%. In addition, by extracting with NMP, it was found that the content of the gel fraction in the AOPBI-PETMP is more than 95%. Thus, the resulting thiol-ene composition based on AOPBI and PETMP is capable of forming crosslinked 3D-networks under the action of UV radiation (see Online Supplementary Materials, Figure S2), with the high degree of conversion of UV reactive groups. It should also be noted that in the absence of PETMP, photocuring of the composition occurs only at a higher UV radiation power.[15]

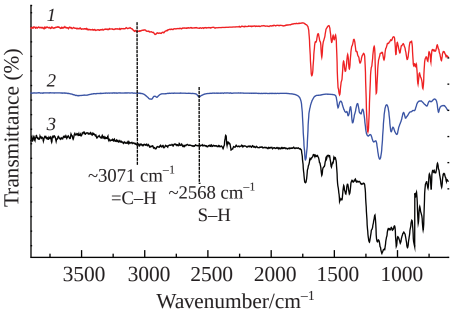


Figure 1 IR spectra of (*1*) AOPBI, (*2*) PETMP and (*3*) AOPBI-PETMP.

The thermal resistant characteristics of AOPBI-PETMP in comparison with those of OPBI and AOPBI were studied by the TGA method [Table 1, Figure 2(*a*)]. OPBI and AOPBI are characterized by extremely high thermal stability (>550 °C), which is in a good agreement with the previous results.[12,16] In addition, polymers retain more than 70% of their original weight at 750 °C. At the same time, AOPBI has the lower temperature of 10% weight loss ($T_{10\%}$) and the lower char yield compared to OPBI due to the presence of allyl groups that are less resistant to thermal action. AOPBI-PETMP has a significantly lower thermal stability: 10% weight loss is observed at 397 °C, and the char yield is 62.7%, which is due to the presence of aliphatic fragments of PETMP. However, the material is completely stable up to 300 °C, which predetermines the possibility of its use in high-tech industries.

The results of mechanical testing of film materials based on OPBI, AOPBI and AOPBI-PETMP are presented in Table 1 and Figure 2(*b*). OPBI possesses typical mechanical properties for this class of polymers, and has the highest elongation among the studied materials, which is due to the presence of flexible *p*-oxydiphenylene fragments. Grafting of allyl groups to the main chain leads to a decrease in both tensile strength σ and elongation at break ε, which is due to the absence of strong intermolecular interactions. In addition, AOPBI-PETMP possessing cross-linked 3D-structure has excellent mechanical strength and is significantly superior to both AOPBI and OPBI. In terms of mechanical characteristics, the material herein obtained is at the level of the best representatives of high-tech engineering polymers.

Due to high UV curing rate and the high gel fraction yield, the resulting photosensitive composition is promising for the formation of thermally-resistant and mechanically strong 3D-objects using DLP 3D printing. It was found that the use of a commercial 3D printer 'Anycubic Photon Mono' makes it possible to form structures with complex geometric shapes with high accuracy. As a result of DLP 3D printing, as in the case of the test film samples, the solvent-containing gel is formed. Post-processing with a gradual increase in temperature from 20 to 200 °C allows for complete removing the solvent from this organogel and preserving the shape of the 3D-object (Figure 3). The isotropic shrinkage is ~22% and practically does not depend on the geometry of the formed object.

Table 1 Thermal and mechanical characteristics of OPBI, AOPBI and AOPBI-PETMP.

Sample	$T_{10\%}$/°C	Char yield (%)[a]	Σ/MPa	ε (%)
OPBI	647	76.5	97.3 ± 3.5	32.0 ± 4.0
AOPBI	594	72.8	72.5 ± 3.1	7.7 ± 1.1
AOPBI-PETMP	397	62.7	164.7 ± 7.9	8.1 ± 1.5

[a] Weight of residue at 750 °C.

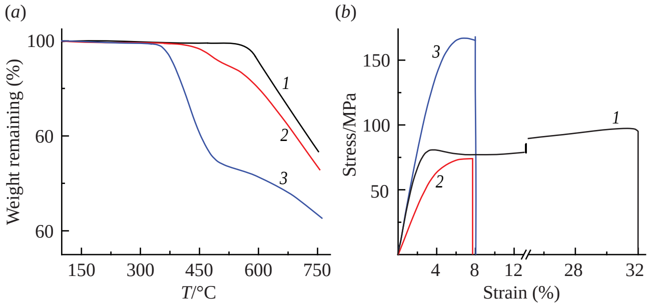


Figure 2 (*a*) TGA and (*b*) stress–strain curves of (*1*) OPBI, (*2*) AOPBI and (*3*) AOPBI-PETMP.

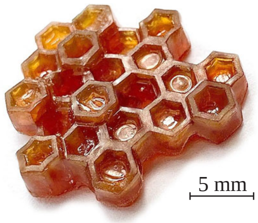


Figure 3 Image of an object formed by DLP 3D printing based on AOPBI-PETMP.

In summary, the novel photosensitive composition based on polybenzimidazole modified with allyl groups and tetrathiol can be used to form mechanically strong thermally stable 3D-structures by DLP 3D printing.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.035.

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