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Light-triggered surface properties of a glycolized PolyEthylene Terephthalate film by Surface-initiated ATRP of azobenzene monomer

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Abstract

The surface modification of glycolized polyethylene terephthalate (PETg) was performed by surface-initiated ATRP with a statistical copolymer composed of poly(butyl acrylate) (PBuA) and poly(styrenic azobenzene) (PSA). First, a bromo end-capped PETg was previously synthesized and then used to obtain thick films by melting under pressure. The top surface Bromo moieties of the PETg were activated as ATRP macro-initiator to polymerize Butyl Acrylate (BuA) and styrenic azobenzene (SA) monomer. In the meantime, a serial of statistical copolymers was synthesized based on SA and BuA units to finely tune the glass transition temperature value of copolymer close to the room temperature. The introduction of the BuA unit decreased the initial T_g value of the PSA from 100 to -10°C. A statistical copolymer P(BuA-*stat*-SA) with 40 wt% of BuA units with a T_g value around 20°C was then initiated from the surface of the PETg film to be chemically anchored. Under illumination at 365 nm and 450 nm, a reversible Trans to Cis isomerization of the P(BuA-*stat*-SA) layer is observed which induces a strong shift of the transmittance of the PET film as a light-triggered UV-protection and wettability. Such materials can be used in the field of flexible substrates for electronic to create light-triggered surfaces properties to tune their adhesion and wettability.

1. Introduction

Even though the actual performance of flexible electronics remains lower than that of silicon technologies, they offer certain benefits such as flexibility, thinness, semi-transparency, and cost of production. For flexible electronics, it is well known that the performance of printed circuit (*i.e.* resistance to bending, electrical properties) crucially depends on the properties of the ink-polymer interface.[1,2] Ink substrate adhesion is governed by surface tension of both ink and substrate, substrate morphology and thermomechanical properties (T_g).[3] To illustrate this, Siniscalco *et al.* have demonstrated that the deposition of gold by Physical Vapor Deposition (PVD) technique when the substrate temperature is above its T_g leads to an interpenetration of the gold and polymeric material leading to a better adhesion and a control of the electrical properties of the metal coating.[4]

Poly(ethylene terephthalate) (PET) is widely developed for a large range of applications such as fibers, films, packaging, and engineering plastics for automobiles and electronics. The huge use of PET based polymers in the flexible industry is due to their flexibility, thermal properties and high recycling capacity. [5] However, because of its poor solubility in organic solvents modification of its surface properties becomes a challenge. To enhance this ability, reclaimed polyethylene terephthalate and chemicals derivable from renewable resources, *i.e.* ethanediol, are combined to create deconstructed glycolized PET, *i.e.* PETg, with properties exceeding those of standard petroleum-based materials and solubility.[6]

The final objective of this work is to create a new material which can tune its surface properties under illumination. Regarding its properties, PETg was used as flexible substrate to this study. Azobenzene derivatives which *Trans-Cis* isomerization upon irradiation with UV or visible light[7] are selected as light-triggered moiety. This choice was governed by studies which have shown their efficient and robust photo-chemistry.[8–10] More specifically polyazobenzene can photo-induced liquefaction and softening.[11] Indeed, when azobenzene derivatives are incorporated in a polymer matrix or grafted on polymer backbones (*i.e.* azopolymer), the change of dimension due to the reversible isomerization induces motion of the polymer chains[12] leading to a reversible change of the glass transition temperature T_g and of the elastic modulus.[11,13–15] The most important decrease of T_g from 48°C to -10°C was observed by Zhou *et al.* upon photo-isomerization for azopolymer with an acrylate backbone.[16]

In order to combine the photochemical properties of polyazobenzene and the flexibility of the PETg, the challenge is to chemically anchor the light-triggered polymer onto the polymeric substrate. As described above, PET has an excellent chemical resistance,[17] but it is not soluble in usual solvent for chemical modification. Due to this property, the major part of copolymer containing PET are statistical and obtained by step growth polymerization also called polycondensation.[18,19] However, block copolymer can be obtained by surface modification by either grafting from[20–26] or grafting to[27] method. For example, the use of the PET for block copolymer can be achieved by *grafting from* process, which can be realized by Atom transfer radical polymerization (ATRP).[28,29] However, a previous modification should be realized to use PET as ATRP macro-initiator. For example, Pan *et al.* modified a PET surface in three steps in order to create a Bromo end group at the surface and used it as macro-initiator for the Hydroxyethyl-Methacrylate polymerization.[20] Maaz *et al.* also modified PET, by a three steps reaction to initiate the 4-vinylpyridine polymerization from a benzyl chloride-modified surface.[25]

SA) copolymers were determined by ^1H NMR. An example of ^1H NMR characterization is represented in **Figure S1**. The different statistical copolymer obtained are then described in **Table 1**. As expected, the T_g values followed the Fox equation[30]: $1/T_g = F_{PBuA}/T_{gPBuA} + F_{PSA}/T_{gPSA}$ where F_{PBuA} and F_{PSA} are weight fractions of polymer and T_{gPBuA} (221.35 °K[31]) and T_{gPSA} (373 °K) are their T_g values in Kelvin (**Figure 1**). The statistical copolymer leading to a T_g value around 20°C has to be composed by 40 and 60 wt% of BuA and SA, respectively.

Table 1. Initial condition and final properties of all statistical copolymer based on styrenic azobenzene and butyl acrylate.

Initial condition				Final properties							
n_{BuA} mmol	n_{azo} mmol	$n_{\text{ini}}^{\text{a}}$ and n_{CuBr} mmol	n_{PMDETA} mmol	Mol% PBuA	Wt% PBuA	Conv BuA ^{b)} %	Conv Azo ^{b)} %	$M_n^{\text{c)}$ g.mol ⁻¹	$M_n^{\text{d)}$ g.mol ⁻¹	\bar{D}	T_g (°C)
-	1.59	1.67×10^{-2}	3.33×10^{-2}	-	-	-	30	9 000	10 600	1.6	100
3.90	1.59	4.58×10^{-2}	9.16×10^{-2}	38	20	43	70	12 500	16 600	1.5	45
2.60	1.59	3.49×10^{-2}	6.99×10^{-2}	48	28	27	50	10 000	11 100	1.6	39
7.24	1.59	7.36×10^{-2}	10.47×10^{-2}	64	42	37	84	10 600	15 400	2.3	22
7.24	1.59	7.36×10^{-2}	10.47×10^{-2}	69	49	41	86	11 200	14 300	2.1	11
5.85	1.59	6.20×10^{-2}	10.41×10^{-2}	72	52	42	75	11 300	15 200	2.1	-12

^{a)}ini = 2-Azidoethyl 2-bromoisobutyrate; ^{b)}Conv = Conversion ^{c)}Theoretical molecular weight; ^{d)} Molecular weight in number obtained by SEC in THF.

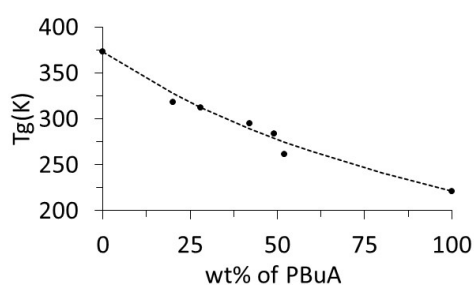


Figure 1. (Dot) T_g of P(BuA-*stat*-SA) in Kelvin against the wt% of PBuA, (Dashed line) simulation from the Fox equation.[30]

2.2. PETg analysis:

To facilitate the taking in hand and its chemical modification, a commercial glycolized PETg [32] from Polycasa was used for its solubility in usual organic solvents as dichloromethane (chemical modification) or chloroform (NMR analysis) (**Figure S2**)., By ^1H NMR,[33] an estimated molecular weight of 23 100 g.mol⁻¹ with 70 % of ethylene glycol terephthalate ($M_{\text{repetitive unit}} = 192$ g.mol⁻¹) and 30 % of 1,4-cyclohexanedimethanol terephthalate units ($M_{\text{repetitive unit}} = 274$ g.mol⁻¹) with hydroxy end groups. The average molecular weight of $M_n = 33\,600$ g.mol⁻¹ with a dispersity value D of 1.7 was also calculated by SEC in DMF with a PMMA calibration. Wettability determined by contact angle with water of PETg is $65.7 \pm 0.7^\circ$. The thermal properties and the semi-crystallinity of the PETg were determined by DSC with a T_g of 79°C and a melting point temperature T_m of 189°C.

2.3. PETg-Br synthesis:

The PETg was modified as a macro-initiator to polymerize the SA/BuA mixture by ATRP from the Bromo end chain modification. This chemical modification was realized from a PETg solution in dichloromethane by esterification of the terminal hydroxy function with the 2-bromopropionyl bromide to form the bromopropionate-terminated PETg (PETg-Br, **Figure S3**). The efficiency of the reaction was verified by ^1H NMR with the disappearance of the peak at 4.05 ppm ($-\text{CH}_2\text{-OH}$) and the appearance of peak at 4.6 ppm ($-\text{CH}_2\text{-O-CO-C}(\text{CH}_3)_2\text{-Br}$). By ^1H NMR DOSY, the peak with a 4.6 ppm shift has the same coefficient diffusion than PETg demonstrating the successful chemical modification by the 2-bromopropionyl bromide. Indeed, this 2D method allows to separate the different species of a blend according to their different translation diffusion coefficients meaning their difference of size, shape and their surrounding environment (**Figure S4**).^[34] Thick films with PETg-Br were prepared by cooling in a mold and then press at 150°C. The final thick films obtained have a diameter of 2 cm for a thickness of 0.5 mm (**Scheme 1**).

2.4. Chain extension of PETg-Br thick film by surface-initiated copolymerization of P(BuA-stat-SA):

Thick films of PETg-Br were used for surface ATRP initiation for statistical copolymerization of 65 mol% BuA with 35 mol% SA using CuBr(I) as catalyst and PMDETA as ligand in toluene as non-solvent of the PETg (**Scheme 1**). After several washing in acetone, some samples were solubilized in chloroform and characterized by ^1H NMR and ^1H NMR DOSY to validate the composition of the block copolymer PETg-*b*-P(BuA-*stat*-SA) (**Figure 2**). The final composition of the block copolymer PETg-*b*-P(BuA-*stat*-SA) is 68 mol% of PBuA (47 wt%) and 32 mol% of PSA (53 wt%). This composition corresponds to a T_g equal to 14°C using the linear variation determined previously (**Figure 1**). In the ^1H NMR DOSY spectra, the peak corresponding to the PSA at $\delta = 7.93$ ppm has the same coefficient diffusion than the peaks assimilated to the PETg ($\delta = 8.12$ ppm) and PBuA ($\delta = 4.01$ and 0.97 ppm). These NMR results confirm the successful of 1) the surface chemical modification and 2) the surface initiation of the potential light sensitive P(BuA-*stat*-SA) block. By SEC analysis, no significant modification was observed because of the very low amount of the PETg-*b*-P(BuA-*stat*-SA) over PETg-Br of $\approx 1\%$.

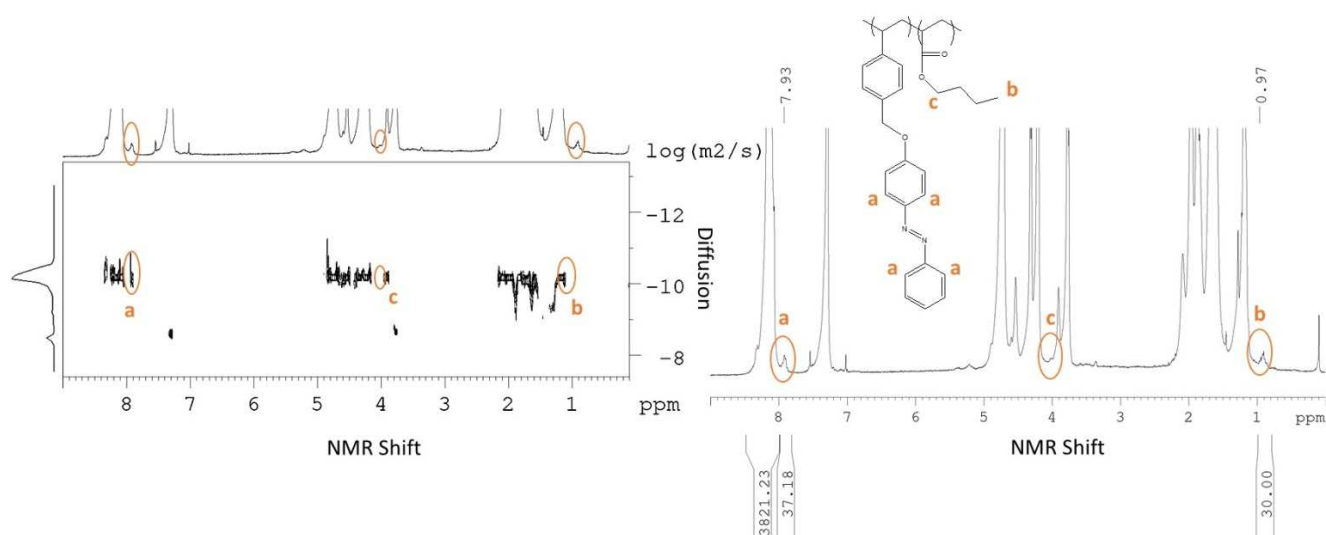


Figure 2. (Left) ^1H NMR DOSY and (Right) ^1H NMR of thick film dissolved in deuterated chloroform; “a” corresponds to 4 protons of PSA and a satellite of PETg, “b” corresponds to 3 protons of PBuA and “c” corresponds to 2 protons of PBuA.

2.5. *Trans to Cis* isomerization characterization of PETg functionalized by P(BuA-*stat*-SA):

After the successful chemical surface modification of PETg film, a color change is observed from transparent PETg to light brownish P(BuA-*stat*-SA)-grafted PETg film. Under UV irradiation, an evolution is observed with a dark brown color (**Figure 3D**). To evaluate this behavior, UV-visible characterizations were realized. Thus, a part of the thick film was solubilized in chloroform and dried on a face of UV-visible cuvette under thin film state which was irradiated under UV and visible light, alternatively (**Figure 3A**). Under UV light at 365 nm for 30 s, the adsorption band at 350 nm decreases and the one at 450 nm increases due to the apparition of the *Cis* isomer. Then, the *Trans to Cis* isomerization provokes a shift of the transmittance to the visible wavelength range as a UV-protection of the PETg, with a jump of the onset transmittance from 300 to 375 nm. Reversible isomerization was observed after irradiation under visible light at 450 nm for 10 min with the apparition of the *Trans* form (**Figure 3A & B**). Although the light-triggered isomerization in solution, on thin film or from thick film surface was successful observed. If the T_g evolution are delicate to evaluate by DSC due to thermal instability of the *Cis* form (**Figure S5**), the light-triggered surface properties of wettability evolve reversibly from 80.0 ± 2.4 to $68.6 \pm 2.4^\circ$ with the *Trans-Cis* isomerization due to the more hydrophilic *Cis* form (**Figure 3C**). Herein, the light-triggered isomerization *Trans to Cis* of the P(BuA-*stat*-SA) layer induces for the first time a dual property with UV protection and sensitive wettability of the PETg surface.

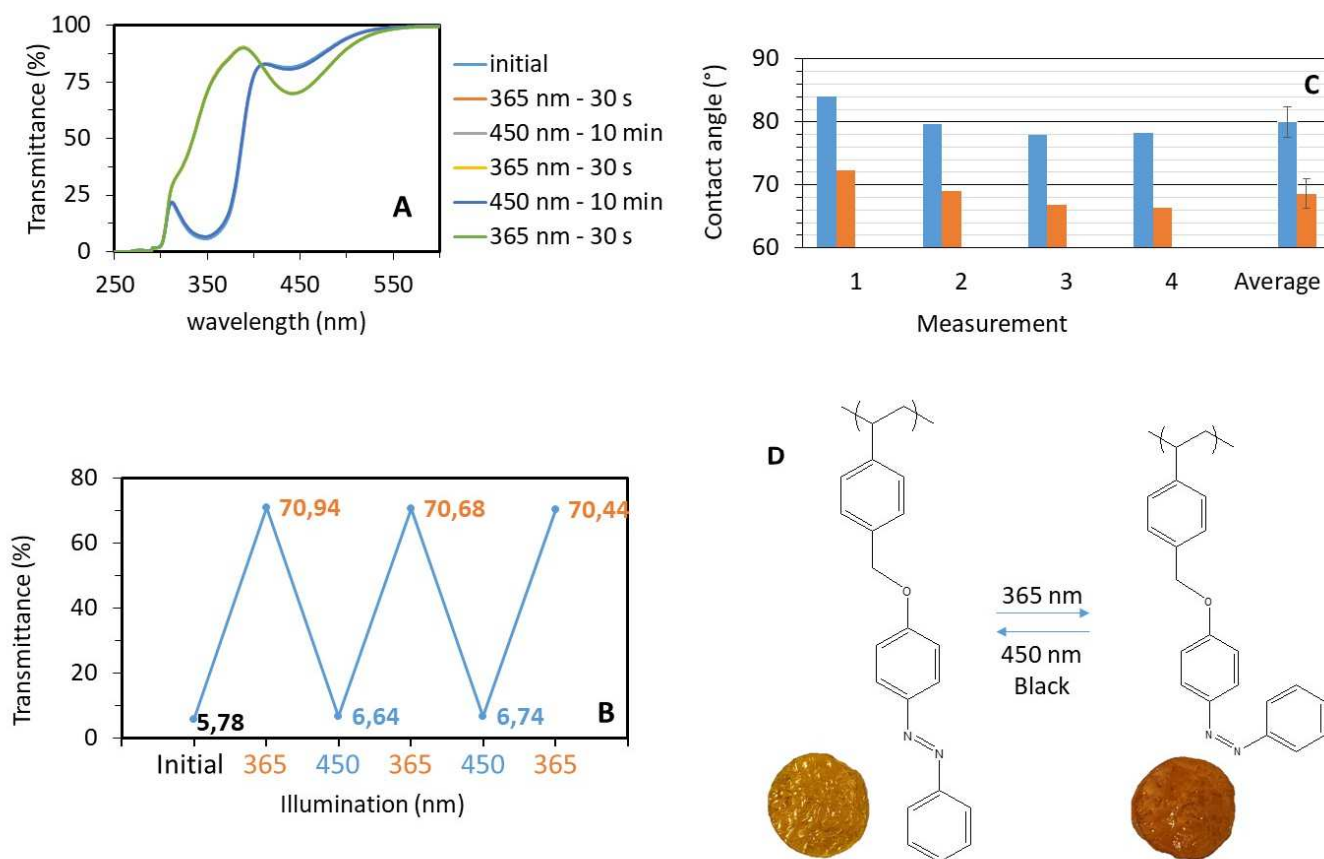


Figure 3. A) UV-visible features of a casted film on the UV cuvette alternatively illuminate under 450 and 365 nm; B) Transmittance at 350 nm of the film at the initial state (black), illuminate at 365 nm (orange) and at 450 nm (blue); C) Contact angle of PETg-*b*-P(BuA-*stat*-SA) thick film before illumination at 365 nm (blue, *Trans*) and after illumination (orange, *Cis*); D) structure of SA unit and color of the thick film under 450 nm (left, *Trans*) and under 365 nm (right, *Cis*).

3. Conclusion

In this work, the synthesis of a Bromo end-capped PETg by esterification of the hydroxy end group with the 2-bromopropionyl bromide to lead the bromopropionate-terminated PETg-Br macro-initiator was succeeded and thick films was obtained by melting under pressure. Then, from a series of statistical P(BuA-*stat*-SA) copolymers, a composition with 65/35 mol% of BuA/SA, demonstrated a T_g around 20°C. Its grafted homologue PETg-*b*-P(BuA-*stat*-SA) initiated from the surface of the PETg-Br film is light sensitive with a *Trans-Cis* isomerization associated to a change in the color, in relation with a strong shift of 75 nm of the transmittance to higher wavelength as a UV protection layer and more hydrophilic surface with wettability from 80 to 68°. The synthesis of new monomeric designs are under way to impact the surface dual property of the grafted PETg, more significantly or to induce a multi-functional PET surface.

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Credit authorship contribution statement

Laurence Pessoni: investigation, writing - original draft, editing, **Nicolas Delorme:** supervision, writing - review, funding acquisition, **Laurent Billon:** supervision, writing - review.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

References

- [1] R. Van Tijum, J.Th. De Hosson, Effects of self-affine surface roughness on the adhesion of metal-polymer interfaces, *J. Mat. Sci.* 40 (2005) 3503.
- [2] V. Zaporojtchenko, K. Strunskus, K. Behnke, C. v. Bechtolsheim, A. Thran, F. Faupel, Formation of metal-polymer interfaces by metal evaporation: influence of deposition parameters and defects, *Microelec. Eng.* 50 (2000) 465.
- [3] S.M.F. Cruz, L.A. Rocha, J.C. Viana, Printing Technologies on Flexible Substrates for Printed Electronics, in: S. Rackauskas (Ed.), *Flexible Electronics*, IntechOpen, 2018: p. 47. <https://doi.org/10.5772/intechopen.76161>.
- [4] D. Siniscalco, J.F. Bardeau, M. Edely, A. Gourbil, N. Delorme, Temperature-Induced Structural Transitions on Hybrid Nanothick Metal/Polymer Assemblies, *The Journal of Physical Chemistry C*. 117 (2013) 7391–7397. <https://doi.org/10.1021/jp401107s>.
- [5] W.S. Wong, A. Salleo, *Flexible Electronics, Electronic Materials: Science & Technology*. (2009).
- [6] N.A. Rorrer, S. Nicholson, A. Carpenter, M.J. Bidy, N.J. Grundl, G.T. Beckham, Combining Reclaimed PET with Bio-based Monomers Enables Plastics Upcycling, *Joule*. 3 (2019) 1006–1027. <https://doi.org/10.1016/j.joule.2019.01.018>.
- [7] H. Jiang, S. Kelch, A. Lendlein, Polymers move in response to light, *Adv. Mater.* 18 (2006) 1471–1475.
- [8] C. Dugave, L. Demange, Cis-Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications, *Chem. Rev.* 103 (2003) 2475–2532.
- [9] N. Delorme, J.-F. Bardeau, A. Bulou, F. Poncin-Epaillard, Azobenzene-Containing Monolayer with Photoswitchable Wettability, *Langmuir*. 21 (2005) 12278–12282.
- [10] L. Oscurato Stefano, M. Salvatore, P. Maddalena, A. Ambrosio, From nanoscopic to macroscopic photo-driven motion in azobenzene-containing materials, *Nanophotonics*. 7 (2018) 1387. <https://doi.org/10.1515/nanoph-2018-0040>.
- [11] T. Yamamoto, Y. Norikane, H. Akiyama, Photochemical liquefaction and softening in molecular materials, polymers, and related compounds, *Polymer Journal*. 50 (2018) 551–562. <https://doi.org/10.1038/s41428-018-0064-4>.
- [12] J. Kumar, X.L. Jiang, D.-Y. Kim, T. Seung Lee, S. Tripathy, Gradient Force: the Mechanism for Surface Relief Grating Formation in Azobenzene Functionalized Polymers, *Applied Physics Letters*. (1998) 2096–2098.

- [13] P. Weis, W. Tian, S. Wu, Photoinduced Liquefaction of Azobenzene-Containing Polymers, *Chemistry – A European Journal*. 24 (2018) 6494–6505. <https://doi.org/doi:10.1002/chem.201704162>.
- [14] N. Hurduc, B.C. Donose, A. Macovei, C. Paius, C. Ibanescu, D. Scutaru, M. Hamel, N. Branza-Nichita, L. Rocha, Direct observation of athermal photofluidisation in azo-polymer films, *Soft Matter*. 10 (2014) 4640–4647. <https://doi.org/10.1039/c4sm00397g>.
- [15] Y. Yue, Y. Norikane, R. Azumi, E. Koyama, Light-induced mechanical response in crosslinked liquid-crystalline polymers with photoswitchable glass transition temperatures, *Nature Communications*. 9 (2018) 3234. <https://doi.org/10.1038/s41467-018-05744-x>.
- [16] H. Zhou, C. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G.K. Auernhammer, R. Berger, H.-J. Butt, S. Wu, Photoswitching of glass transition temperatures of azobenzene-containing polymers induces reversible solid-to-liquid transitions, *Nat Chem*. 9 (2017) 145–151. <https://doi.org/10.1038/nchem.2625> <http://www.nature.com/nchem/journal/v9/n2/abs/nchem.2625.html#supplementary-information>.
- [17] R. Rostami, M. Zarrebini, M. Mandegari, D. Mostofinejad, S.M. Abtahi, A review on performance of polyester fibers in alkaline and cementitious composites environments, *Construction and Building Materials*. 241 (2020). <https://doi.org/10.1016/j.conbuildmat.2020.117998>.
- [18] L. Chen, H.-B. Zhao, Y.-P. Ni, T. Fu, W.-S. Wu, X.-L. Wang, Y.-Z. Wang, 3D printable robust shape memory PET copolyesters with fire safety: Via π -stacking and synergistic crosslinking, *Journal of Materials Chemistry A*. 7 (2019) 17037–17045. <https://doi.org/10.1039/c9ta04187g>.
- [19] X.-K. Jing, X.-S. Wang, D.-M. Guo, Y. Zhang, F.-Y. Zhai, X.-L. Wang, L. Chen, Y.-Z. Wang, The high-temperature self-crosslinking contribution of azobenzene groups to the flame retardance and anti-dripping of copolyesters, *Journal of Materials Chemistry A*. 1 (2013) 9264–9272. <https://doi.org/10.1039/c3ta11267e>.
- [20] K. Pan, R. Ren, B. Liang, L. Li, H. Li, B. Cao, Synthesis of pH-responsive polyethylene terephthalate track-etched membranes by grafting hydroxyethyl-methacrylate using atom-transfer radical polymerization method, *Journal of Applied Polymer Science*. 131 (2014). <https://doi.org/10.1002/app.40912>.
- [21] G. Burillo, E. Bucio, M.D.P. Carreón-Castro, S. Castillo-Rojas, Photochemical effect of azocompounds acrylates grafted in different polymeric matrices, *Polymer Bulletin*. 55 (2005) 191–199. <https://doi.org/10.1007/s00289-005-0427-9>.
- [22] E. Bucio, P. Skewes, G. Burillo, Synthesis and characterization of azo acrylates grafted onto polyethylene terephthalate by gamma irradiation, *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*. 236 (2005) 301–306. <https://doi.org/10.1016/j.nimb.2005.03.262>.
- [23] J.A. Pitt, R. Trevisan, A. Massarsky, J.S. Kozal, E.D. Levin, R.T. Di Giulio, Maternal transfer of nanoplastics to offspring in zebrafish (*Danio rerio*): A case study with nanopolystyrene, *Science of The Total Environment*. 643 (2018) 324–334. <https://doi.org/10.1016/j.scitotenv.2018.06.186>.
- [24] K. Pan, H. Li, B. Liang, G. Qi, B. Cao, Synthesis of well-defined responsive membranes with fixable solvent responsiveness, *Polymer International*. 64 (2015) 138–145. <https://doi.org/10.1002/pi.4772>.
- [25] M. Maaz, T. Elzein, A. Bejjani, N. Barroca-Aubry, B. Lepoittevin, D. Dragoe, S. Mazerat, B. Nsouli, P. Roger, Surface initiated supplemental activator and reducing agent atom transfer radical polymerization (SI-SARA-ATRP) of 4-vinylpyridine on poly(ethylene terephthalate), *Journal of Colloid and Interface Science*. 500 (2017) 69–78. <https://doi.org/10.1016/j.jcis.2017.03.115>.
- [26] S. Nazari Pour, S. V Ghugare, R. Wiens, K. Gough, S. Liu, Controlled in situ formation of polyacrylamide hydrogel on PET surface via SI-ARGET-ATRP for wound dressings, *Applied Surface Science*. 349 (2015) 695–704. <https://doi.org/10.1016/j.apsusc.2015.04.181>.
- [27] M.K. Erdoğan, Ö. Akdemir, A. Hamitbeyli, M. Karakışla, Preparation of hydrophilic woven fabrics: Surface modification of poly(ethylene terephthalate) by grafting of poly(vinyl alcohol) and poly(vinyl alcohol)-g-(N-vinyl-2-pyrrolidone), *Journal of Applied Polymer Science*. 137 (2020). <https://doi.org/10.1002/app.48584>.
- [28] J.O. Zoppe, N.C. Ataman, P. Mocny, J. Wang, J. Moraes, H.-A. Klok, Surface-Initiated Controlled Radical Polymerization: State-of-the-Art, Opportunities, and Challenges in Surface and Interface Engineering with Polymer Brushes, *Chemical Reviews*. 117 (2017) 1105–1318. <https://doi.org/10.1021/acs.chemrev.6b00314>.
- [29] N. Corrigan, K. Jung, G. Moad, C.J. Hawker, K. Matyjaszewski, C. Boyer, Reversible-deactivation radical polymerization (Controlled/living radical polymerization): From discovery to materials design and applications, *Progress in Polymer Science*. 111 (2020) 101311. <https://doi.org/https://doi.org/10.1016/j.progpolymsci.2020.101311>.
- [30] T. Fox, Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Poly-mer System, *Bulletin of the American Physical Society . Series II.*, 1 (1956) 123.
- [31] M. Fernández-García, R. Cuervo-Rodríguez, E.L. Madruga, Glass transition temperatures of butyl acrylate-methyl methacrylate copolymers, *Journal of Polymer Science, Part B: Polymer Physics*. 37 (1999) 2512–2520. [https://doi.org/10.1002/\(SICI\)1099-0488\(19990901\)37:17<2512::AID-POLB22>3.0.CO;2-2](https://doi.org/10.1002/(SICI)1099-0488(19990901)37:17<2512::AID-POLB22>3.0.CO;2-2).
- [32] T. Chen, J. Zhang, Non-isothermal cold crystallization kinetics of poly(ethylene glycol-co-1,4-cyclohexanedimethanol terephthalate) (PETG) copolyesters with different compositions, *Polymer Testing*. 48 (2015) 23–30. <https://doi.org/10.1016/j.polymertesting.2015.09.008>.
- [33] T. Chen, G. Jiang, G. Li, Z. Wu, J. Zhang, Poly(ethylene glycol-co-1,4-cyclohexanedimethanol terephthalate) random copolymers: Effect of copolymer composition and microstructure on the thermal properties and crystallization behavior, *RSC Advances*. 5 (2015) 60570–60580. <https://doi.org/10.1039/c5ra09252c>.

- [34] N. Cherifi, A. Khoukh, A. Benaboura, L. Billon, Diffusion-ordered spectroscopy NMR DOSY: An all-in-one tool to simultaneously follow side reactions, livingness and molar masses of polymethylmethacrylate by nitroxide mediated polymerization, *Polymer Chemistry*. 7 (2016) 5249–5257. <https://doi.org/10.1039/c6py00927a>.

