# Photoresponsive Spiropyran and DEGMA-Based Copolymers with Photo-Switchable Glass Transition Temperatures

*Vaishali Pruthi, Yosuke Akae, and Patrick Théato**

**Herein, novel photoresponsive spiropyran (SP)-based P(DEGMA-*co*-SpMA) copolymers with variable percentages of SP fractions are synthesized. The SP group present in these polymers exhibited the abilities of reversible photoisomerism. Their photoresponsive, structural, and thermal properties have been investigated and compared using various characterization techniques. These light-responsive copolymers are found to exhibit photoswitchable glass transition temperature ($T_g$), high thermal stability ($T_d$ > 250°C), instant photochromism as well as fluorescence upon exposure to UV light. It is demonstrated that the $T_g$ of these synthesized polymers increased when irradiated with UV light ($\lambda = 365$ nm), as a consequence of the photoisomerization of incorporated SP groups into their merocyanine form. This increase in $T_g$ is attributed to an increase in polarity and a decrease in the overall entropy of the polymeric system when it switches from the ring-closed SP form (less-ordered state) to the ring-opened merocyanine form (more-ordered state). Therefore, such polymers with a unique feature of phototunable glass transition temperatures provide the possibility to be integrated into functional materials for various photoresponsive applications.**

## 1. Introduction

The advancements in reversibly photoswitchable materials have gained enormous recognition over the years because of their plenty of promising applications like biosensors,[1] soft robotics,[2] smart coatings,[3] and so on. Such materials have the capability to show a precise modification in their physical or chemical properties when exposed to light. These materials generally contain chromophoric groups such as spiropyran (SP),[4,5] azobenzene,[6,7] or stilbene[8,9] which undergo alteration in their molecular structure on light exposure. When such chromophoric groups are integrated into polymers, they can lead to changes in the conformations of the polymer chains, which can result in a change in the physical and chemical properties of the polymer as a consequence of photoisomerization as well as photo-induced expansion or contraction.[10]

SPs have an advantage over other photochromic compounds as they show pronounced differences in the properties of two isomers, including structural properties, color, dipole moment, absorption spectra, fluorescence, and stability. These significant changes in its properties can efficiently regulate molecular functionalities by external stimuli that can be useful in creating new photoswitching devices. Under UV irradiation, SP undergoes photoisomerization from its closed SP form, which is electrically neutral, to the open merocyanine (MR) form, which is zwitterionic. The reversible conversion from MR to SP occurs in the presence of visible light or heat. The SP form consists of a benzopyran ring along with an indoline moiety, which is linked orthogonally to the spiro carbon, while the MR form an extended configuration of the $\pi$ electrons between the two rings. The photoisomerization of SP results not only in a structural transformation but also a notable elevation in the polarity of the molecule. This is attributed to the creation of electric charges on MR as a result of the irradiation. Furthermore, the photogenerated zwitterionic MR molecules tend to associate with each other and form different forms of molecular aggregate.[11] SP provides immense versatility, encompassing various functionalities such as thermochromism, solvatochromism, mechanochromism, redox properties, acidochromism as well as pH-gated isomerization.[12,13] Multifunctional SP compounds have already proven to be a major asset

---

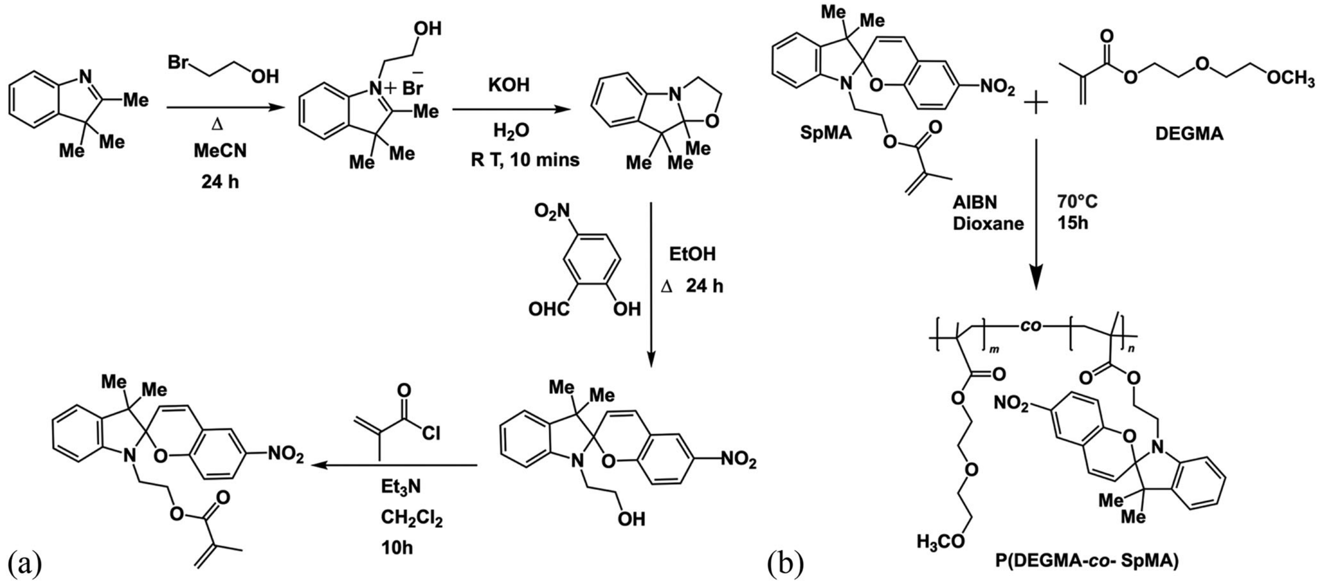
V. Pruthi, Y. Akae, P. Théato
Institute for Chemical Technology and Polymer Chemistry (ITCP)
Karlsruhe Institute of Technology
Engesserstraße 18, 76128 Karlsruhe, Germany
E-mail: patrick.theato@kit.edu

Y. Akae
Research Fellow of Japan Society for the Promotion of Science
Tokyo 102-0083, Japan

P. Théato
Soft Matter Synthesis Laboratory
Institute for Biological Interfaces III
Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen,
76344 Karlsruhe, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.202300270

**DOI: 10.1002/marc.202300270**



**Scheme 1.** a) Synthesis of spiropyran methacrylate. b) Synthesis of P(DEGMA-*co*-SPMA).

in the fabrication of functional responsive materials, such as multi-responsive porous films[14] and self-assembled polymeric nanoparticles with controlled release of molecules.[15]

The introduction of SP-side groups in the synthesis of photochromic copolymers has been explored recently.[16–18] These materials have been widely investigated for developing applications in chemical sensing,[19] optically rewritable data storage,[20] photochromic smart coatings,[7] and optical switching.[21] Zhou et al. recently showed that azobenzene-containing polymers exhibit photoswitchable glass transition temperatures $T_g$, which provides a way for designing polymers with a healing ability. High spatiotemporal resolution to process and heal polymers is a major advantage of using light as a stimulus in such an approach.[22] Lately, Hu et al. also reported SP-based liquid crystalline cross-linkable materials with programmable photochromism and tunable $T_g$.[23] However, the extent of the effect of UV irradiation on the $T_g$ of various SP-containing polymers has not been explored in detail yet. Moreover, the photo-modifiable glass transition temperature of photochromic polymers could open a door for the incorporation of such polymeric materials in various applications, such as photoswitchable adhesives,[24] nanoimprint lithography,[25] and so on, due to changes in the polarity as well as rheological properties of the polymers.

In this work, different di(ethylene glycol)methyl ether methacrylate (DEGMA) and spiropyran methacrylate (SpMA) copolymers have been synthesized with varying SP content, and their structural and thermal properties have been investigated and compared using various characterization techniques. DEGMA as a monomer also attributes to the high flexibility and adsorbability of the synthesized polymers, which makes them a good candidate as a comonomer. Essentially, it is also demonstrated that these photoresponsive SP and DEGMA-containing copolymers exhibit photoswitchable glass transition temperature with distinct properties and appearance on exposure to UV.

## 2. Results and Discussion

### 2.1. Synthesis of SP-Based Copolymers P(DEGMA-co-SpMA)

Different copolymers of SpMA and DEGMA were synthesized using free-radical polymerization, varying the ratio of monomers (**Scheme 1**b and **Table 1**). Polymerization of SpMA, DEGMA, and 1 mol% initiator (AIBN) was conducted in 1,4-dioxane at 70°C overnight and the polymers were purified by precipitation in petrol ether to remove the unreacted small molecule compounds. After filtration and drying under vacuum at 40°C for 48 h, the purified polymers P(DEGMA-*co*-SPMA) with various ratios were obtained with a reddish-orange color.

$^1$H NMR spectra of the monomers (**Figure 1**a) and synthesized polymers (Figure 1b,c) measured in CDCl$_3$ confirmed the successful copolymerizations. The presence of aromatic peaks between 5.75 to 7.88 ppm verified the presence of SP in the copolymers, along with significant peaks originating from the incorporation of the DEGMA monomer. The composition of copolymers was calculated from the ratio of peak integral attributed to protons of the benzopyran phenyl group and the protons of the methylene group next to the ester group of DEGMA, as listed in Table 1.

Furthermore, to determine the average molecular mass ($M_n$) and the molecular mass distribution ($M_w/M_n$, $Đ$), GPC measurements were carried out for all synthesized P(DEGMA-*co*-SpMA) copolymers with varying composition of SpMA and DEGMA, as shown in Figure 1d. As shown in Table 1, the number average molecular mass ($M_n$) of the polymer increased with an increase in the percentage of DEGMA and a decrease in the percentage of SP. The elution time in the GPC traces was longer, that is, $M_n$ was smaller, and the molecular mass distribution was narrower for the copolymers with less amount of DEGMA in their composition. The properties of the polymer, including the color and viscosity, also changed with the increasing DEGMA content.

**Table 1.** Synthesis of different copolymers P(DEGMA-*co*-SpMA).

| Copolymer | DEGMA [mmoles] | SpMA [mmoles] | Feed SpMA% | Incorporated SpMA%[a] | $M_n$[b] | $M_w$[b] | Đ[b] | $T_g$[c] [°C] (before irradiation) | $T_g$[c] [°C] (after irradiation) | $T_d$ (5%)[d] [°C] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.25 | 0.6 | 70 | 69.9 | 17 600 | 31 000 | 1.7 | 111.8 | 127.5 | 257 |
| 2 | 0.75 | 0.5 | 40 | 37.5 | 25 300 | 71 500 | 2.8 | 45.7 | 63 | 254 |
| 3 | 1.17 | 0.5 | 30 | 25.6 | 41 300 | 102 400 | 2.4 | 34.8 | 51.3 | 272 |
| 4 | 2.0 | 0.5 | 20 | 20.0 | 49 000 | 226 000 | 4.6 | 24.6 | 39.3 | 273 |
| 5 | 3.0 | 0.33 | 10 | 7.2 | 52 300 | 100 300 | 1.9 | −4.4 | 1 | 272 |
| 6 | 3.0 | 0.16 | 5 | 4.8 | 65 700 | 267 900 | 4.1 | −20.8 | −9.4 | 277 |
| 7 | 5.5 | 0.055 | 1 | 1.4 | 80 000 | 194 200 | 2.4 | −28.2 | −7.2 | 266 |
| Homopolymer | 5.5 | 0 | 0 | 0 | 82 000 | 223 100 | 2.7 | −37.8 | | 218 |

[a] % SpMA in the synthesized copolymers determined by NMR (calculation details mentioned in the Supporting Information); [b] Number average molecular mass $M_n$, weight average molecular mass $M_w$ and dispersity $Đ$ determined by GPC analysis; [c] glass transition temperature $T_g$ determined by DSC analysis; [d] decomposition temperature $T_d$ (5%) determined by TGA analysis.

P(DEGMA-*co*-SpMA) with 1 to 20% SpMA were extremely viscous polymers, while copolymers with 30% or more SpMA content were completely solid.

### 2.2. Photochromism and Photo-Induced Isomerism of SP in P(DEGMA-*co*-SpMA)

UV–vis absorption spectroscopy was conducted in order to investigate the photoisomerization of P(DEGMA-*co*-SpMA). When dissolved in $CHCl_3$, the SP polymer solution appeared to be pale yellow in color. Upon irradiation of UV light ($\lambda$ = 365 nm) on the copolymer solution with a concentration of 0.03 mg mL$^{-1}$ in $CHCl_3$, SP present in the copolymer underwent photoisomerization into its open-ring form merocyanine (MR) as shown in **Figure 2**a. Also, the solution turned bright purple in color. Two localized transitions can be noted in the absorbance spectrum of the closed SP form, one corresponding to the $\pi$–$\pi^*$ transition in the indoline molecule (275 nm) and the other (360 nm) attributed to the chromene group.[4,26,27] Whereas, the photo-induced open ring MR isomer showed one transition (560 nm) in the visible region, responsible for the coloration of the solution. The UV spectra of the MR isomer of P(DEGMA-*co*-SpMA) copolymers with variable SP composition after UV irradiation for 2 min are shown in Figure 2b. Noticeably, the absorbance at 560 nm increased with an increase in the percentage incorporation of SP.

Furthermore, photochromism was observed in P(DEGMA-*co*-SpMA) in solution as well as solid state within a minute of UV irradiation at 365 nm (Figure 2c,d). The reversibility of photoisomerization and accompanying photochromism of the polymers was investigated in both solid and solution. While the MR form in solution transformed back to its SP form at room temperature within a couple of mins, the MR form in solid reversed back to its SP form over a time period of 2–3 h. The probable reason for this would be the closed packing of molecules in solid state that hinders structural transformation and photoswitching.[28]

Moreover, in order to investigate the reversibility with time evolution, the UV-irradiated polymer solution was kept under visible light at room temperature and the absorbance was measured at different time intervals. Clearly, the reversible conversion of MC back to SP at room temperature was detected as shown in Figure 2e. The absorbance of P(DEGMA-*co*-SpMA) at 275 and 365 nm increased and at 560 nm decreased with increasing time of exposure to visible light, as per the fact that the ring-closing photoisomerization gradually transforms MR form to SP form. Therefore, on account of the instability of the MR form at room temperature, P(DEGMA-*co*-SpMA) exhibits good reversibility. Additionally, the reversibility with temperature evolution was also studied using UV–vis absorption spectroscopy (Figure 2f). With an increase in temperature, the transformation occurred very rapidly. When the UV-irradiated polymer solution was kept at 50 °C for 1 min, the absorbance of the SP group at 560 nm completely recovered back to its original state.

Owing to their great potential applications in imaging and detection, the fluorescence properties of SP have been extensively studied in the past years.[4] Thus, the fluorescence spectra were recorded for polymers with varying SP content in chloroform. As shown in Figure 2g, the excitation spectra of the polymers showed two absorption bands at around 390 nm (minor) and 550 nm (major). A gradual decrease in the intensity of these bands with respect to the decrease in the SP content in the polymers was observed. Figure 2h represents the emission spectra of polymers at an excitation wavelength of 550 nm. A similar trend was observed in the emission spectra as well. The emission maximum was observed at around 570 nm for all polymers.

Besides, smart photoresponsive polymer-coated polypropylene fabrics were prepared by simply coating the surface of the fabric with P(DEGMA-*co*-SpMA) by spin-coating a solution of the copolymer in $CHCl_3$. After drying, the photoisomerization on the fabric was also investigated. Upon exposure to UV light at 365 nm, the fabric's surface underwent photoisomerization, as evidenced by the change in color. Moreover, localized irradiation within the irradiated spot and a visible bright fluorescence was observed on the P(DEGMA-*co*-SpMA) coated PP fabric when irradiated with a UV laser (365 nm) as shown in Figure 2i.

### 2.3. Thermal Analysis

To evaluate the thermal stability of the synthesized polymers, thermogravimetric analysis (TGA) was performed. The thermal stability of the polymer corresponds to its chemical and microscopic structure and, therefore, is of great information to evaluate its use for various applications.[29] As shown in **Figure 3**a, the

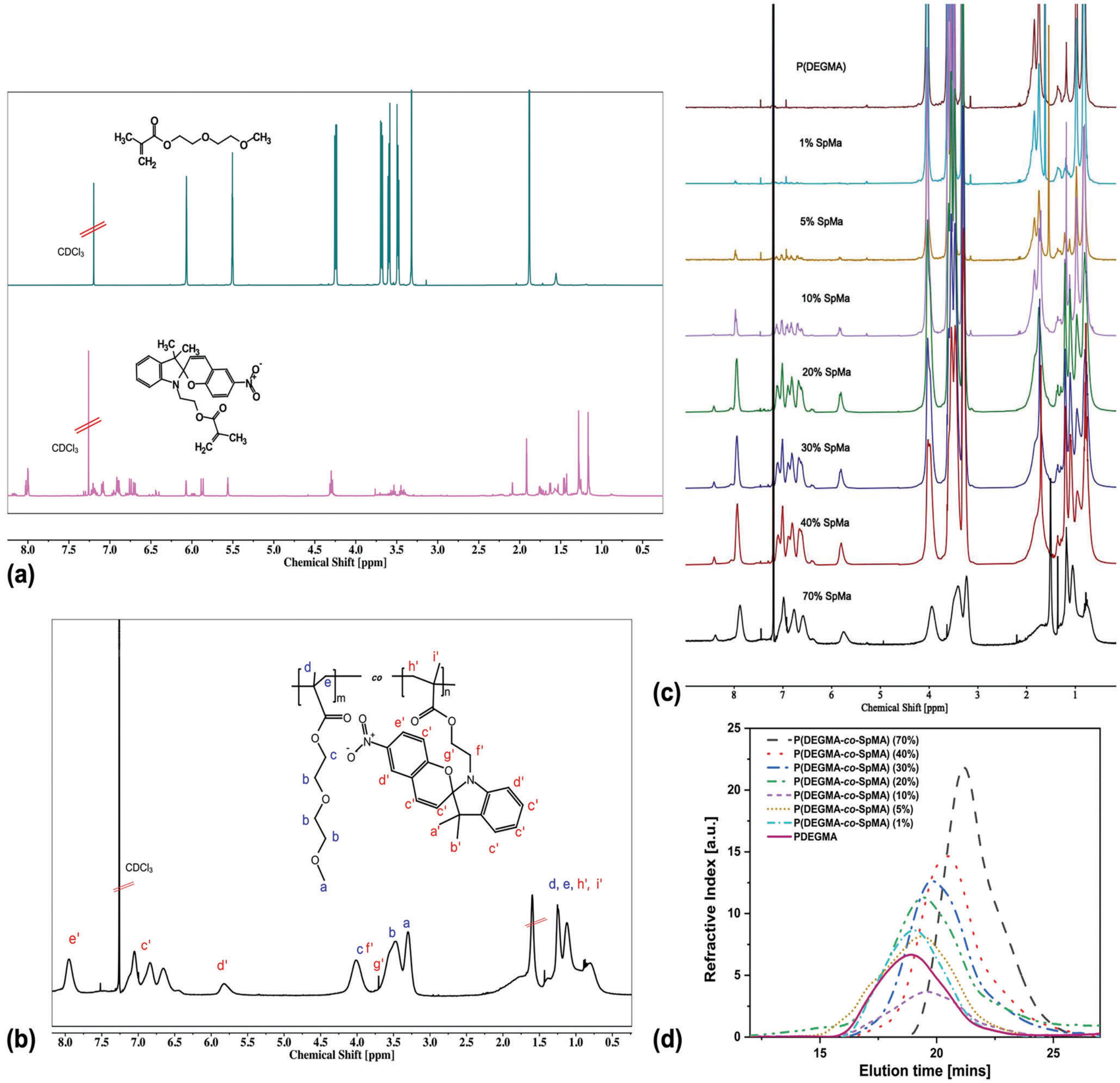


**Figure 1.** $^1$H NMR spectra of a) monomers DEGMA and SpMA, b) P(DEGMA-*co*-SpMA) copolymer with 70% SpMA, c) P(DEGMA-*co*-SpMA) copolymers containing different percentages of spiropyran methacrylate (SpMA) and DEGMA in CDCl$_3$ (400 MHz, 298 K); and d) comparison of GPC chromatography (eluent: THF) of the synthesized P(DEGMA-*co*-SpMA) copolymers.

thermal degradation of all synthesized SP-containing polymers started above 250 °C and the main mass loss was observed in the temperature range between 300 to 400 °C, indicative of their high thermal stability up to 300 °C. Noteworthy, the comparative PDEGMA homopolymer showed a lower degradation temperature of just above 200 °C. Further, while PDEGMA decomposed completely with no residue char left behind, the char residue of the copolymers in the TGA curve also increased with increasing SP content due to more aromatic structures.

Next, differential scanning calorimetry (DSC) measurements were performed for all synthesized polymers in order to assess their glass transition temperatures (Figure 3b). In accordance with Figure 3c, it was observed that the $T_g$ of the P(DEGMA-*co*-SpMA) copolymers increased with an increase in the spiropyran content in the polymers. The glass transition temperature was found to increase linearly from −28.2 °C for copolymers with 1% SpMA to 111.8 °C for copolymers with 70% SpMA content. On the other hand, the homopolymer P(DEGMA), with no SP in it,

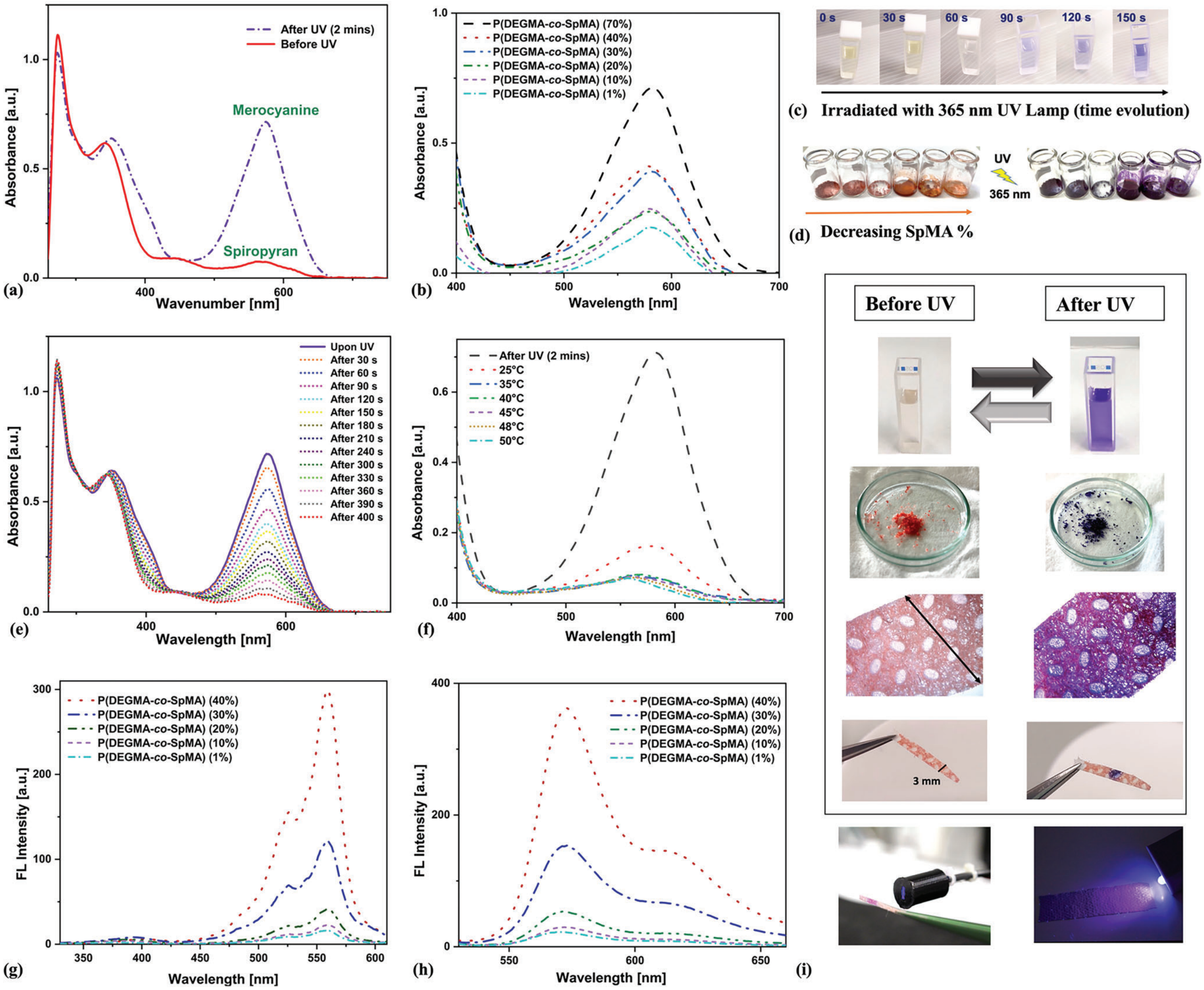


**Figure 2.** a,b) UV–vis absorption spectra of P(DEGMA-*co*-SpMA) copolymers upon UV irradiation for 2 min, c) reversible photochromism in P(DEGMA-*co*-SpMA) (1%) copolymer solution with time evolution, d) solid-state photochromism from SP form to MR form, e) when kept under visible light after UV irradiation showing photo-reversibility back to MR form with time evolution at room temperature, f) UV–vis spectra showing reversibility with temperature evolution, g) fluorescence excitation spectra, and h) emission spectra of P(DEGMA-*co*-SpMA) with different % SP. i) Photochromism in different forms of P(DEGMA-*co*-SpMA) and coatings. (All of the copolymers were measured in $CHCl_3$ with a concentration of 0.03 mg mL$^{-1}$ at 20 °C).

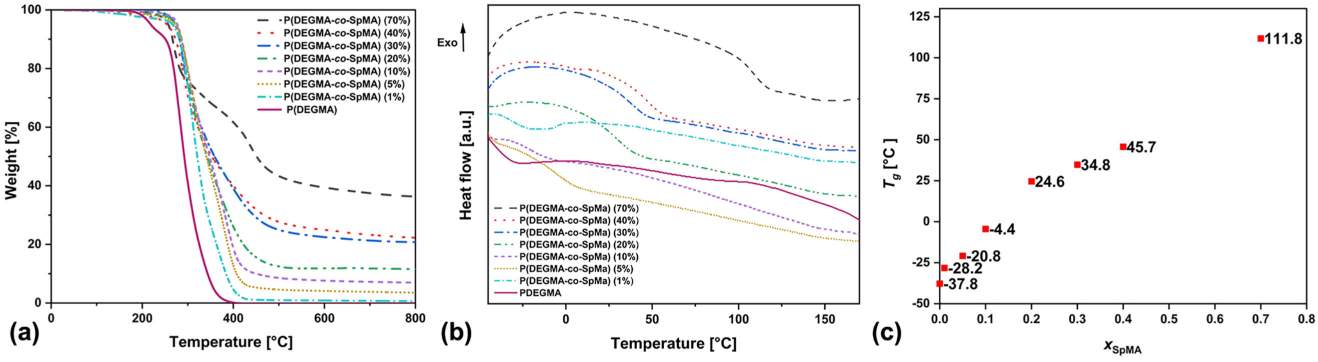


**Figure 3.** a) TGA profiles, b) DSC plots, and c) glass transition temperature ($T_g$) of synthesized P(DEGMA-*co*-SpMA) copolymers with different ratios of SpMA (determined using DSC).

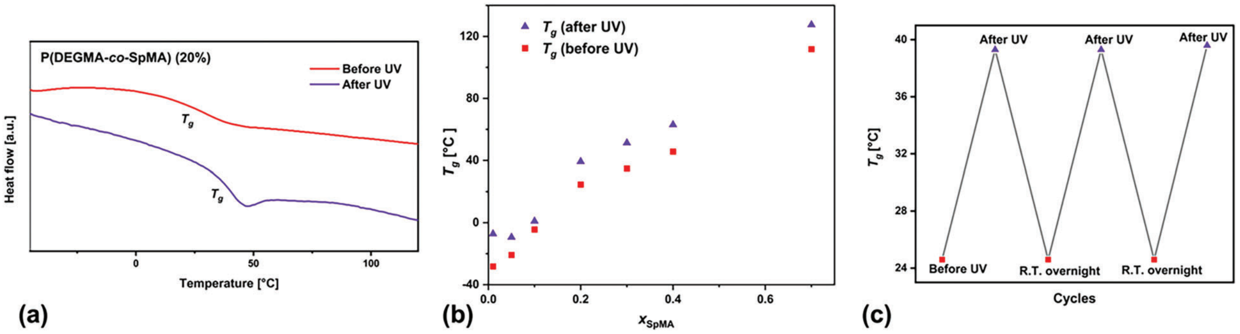


**Figure 4.** a) Exemplary DSC trace for a photoswitchable $T_g$ before and after UV of P(DEGMA-*co*-SpMA) with 20% SpMA, b) Comparative trends of glass transition temperature ($T_g$) as a function of spiropyran content in the polymers, showing distinct behaviors before and after UV irradiation, c) Graph representing reversibility in $T_g$ with on/off cycles of UV irradiation on P(DEGMA-*co*-SpMA) with 20% SpMA.

was found to have a $T_g$ of −37.81 °C. The trend of the glass transition temperatures showed a slight deviation from a linear relation, which appeared indicative of specific interactions or breaking of the local, flexible structure, as discussed in a recent study by the group of Liu.[30]

### 2.4. Photoswitchable Glass Transition Temperatures

The glass transition temperature of a polymer can be impacted by different configurations (ring-opened or closed) in the polymer due to changes in the volume, the stiffness of the polymer chain, and also interchain cohesion of the polymer chain.[22] Thus, it was expected that the photoisomerization of SP would have an impact on the glass transition temperature. Therefore, differential scanning calorimetry (DSC) measurements were employed to measure the $T_g$ before and after the UV irradiation with 365 nm for 2 min, directly on the dried finely powdered polymer samples. The photochromism in the solid polymer samples was visually observed as the orange-colored SP-containing polymer changed its color to bright purple. It was found that the glass transition temperature ($T_g$) increased for all P(DEGMA-*co*-SpMA) copolymers after irradiation, as shown in **Figure 4**a,b and Table 1.

Noteworthy, this trend of increasing $T_g$ is exactly opposite to that of the azobenzene-containing polymer as reported previously.[22] Further, we observed that the $\Delta T$ change in $T_g$ (i.e., the difference in $T_g$ before and after irradiation) depended very much on the SpMA content in the polymer and did not follow a linear trend (Figure 4b). While a rather dramatic change of $\Delta T \approx 20$ °C was observed for the copolymer with 1% SpMA, a minimum of $\Delta T \approx 5$ °C was detected for the copolymer with 10% SpMA.

One possible explanation for the rise in the $T_g$ of the polymers under UV exposure is the increase in polarity of the polymer when SP photoisomerizes to merocyanine. This increase in polarity can lead to an increase in the intermolecular forces between the polymer chains, making them more closely packed and ordered. This transition from a less-ordered state towards a more ordered state leads to a decrease in the entropy of the polymeric system.

Moreover, due to the viscoelastic nature of the polymers, the glass transition temperature ($T_g$) of the polymers directly influences their mechanical properties. Additionally, it was also visibly observed that as SP isomerized into merocyanine, the polymers in viscous gel form (with high DEGMA content) become slightly harder, which is likely attributed to a rise in $T_g$.[31] This photo-induced visible shift in the texture of the polymers could also result from the increasing interactions of highly polar merocyanine isomers with the polymeric chains. In other words, the chain mobility is restricted due to the dipole-dipole interaction between the merocyanine and the polymeric chain.[32]

It is worth noting that the exact mechanism behind the elevation in $T_g$ on UV exposure could be complex and depends on several factors, such as specific polymer composition and the degree of SP incorporation.

Furthermore, to confirm the reversibility of the glass transition temperature, DSC measurements were conducted in a cyclic manner: initially before UV exposure, subsequently after UV exposure, and finally after the removal of light, allowing the polymer to rest at room temperature overnight between each cycle. As depicted in Figure 4c, $T_g$ demonstrated consistent readings throughout these cycles, thus substantiating the reversibility of the glass transition.

## 3. Conclusion

In this work, we successfully synthesized different P(DEGMA-*co*-SpMA) copolymers with variable percentages of incorporated spiropyran. All synthesized copolymers were found to undergo instant photoisomerization in the solid as well as solution phase upon irradiation of UV light at 365 nm. The polymers featured high thermal stability, with a decomposition temperature of over 250 °C. In addition, they also exhibit instant photochromism and fluorescence when exposed to UV light. Such properties of SP could be useful for environmental detection or biosensing.[33,34] Moreover, a positive correlation was observed between the $T_g$ and the spiropyran content within the polymers, with $T_g$ rising from −28.2 °C in copolymers containing 1% SpMA to 111.8 °C in those comprising 70% SpMA. Most importantly, as a consequence of an increase in polarity and a decrease in the overall entropy of the polymeric system when it switches from the ring-closed SP form to the ring-opened MC form, these copolymers showed an increase in $T_g$ after exposure to UV. Interestingly, this pattern contrasts with the previously reported behavior of azobenzene-containing polymers, where the $T_g$ demonstrated a reverse trend.[22] Additionally, our investigation highlighted that the change in $T_g$ ($\Delta T$), the difference between pre- and post-irradiation, was dependent on the SpMA content. However, this relationship did not exhibit a linear progression. For instance, the copolymer with 1% SpMA experienced a considerable $\Delta T$ change of ≈20 °C, while the copolymer with 10% SpMA revealed a relatively minimal change of $\Delta$T around 5 °C.

The research we conducted provides a pathway for the manipulation of the $T_g$, thereby advancing our knowledge of $T_g$ as well as broadening the range of applications of these polymeric materials. This unique property of polymers with a phototunable glass transition temperature ($T_g$) and tailored, responsive behavior can be exploited for various potential applications like – smart windows,[35] optical lenses,[36] smart coatings and adhesives,[22] and so on. This could provide more dynamic control over optical properties. The development of polymers that can switch reversibly between higher and lower $T_g$ forms is a very promising yet novel approach for functional materials.

## 4. Experimental Section

*Materials*: Di(ethylene glycol)methyl ether methacrylate (DEGMA, Sigma Aldrich, 95%) was purified by passing through basic alumina before use. 2,3,3-Trimethyl-3H-indole, 2-bromoethanol, 2-hydroxy-5-nitrobenzaldehyde, methacryloyl chloride, AIBN (azobisisobutyronitrile), potassium hydroxide, and other dried solvents were used as received without further purification.

*Characterization*: $^1$H NMR (400 MHz) spectra were recorded on a Bruker Ascend 400 NMR spectrometer at ambient temperature using chloroform-d1 as a deuterated solvent. Gel permeation chromatography (GPC) was carried out in THF and at room temperature on a Tosoh Bioscience HLC-8320GPC EcoSEC system equipped with three PSS SDV columns, 5 µm (100, 1000, and 100 000 Å) (≈8 Å to 300 mm2), and a UV and a differential refractive index (RI) detector. For thermal studies, thermal gravimetric analysis (TGA) was carried out using a TGA 5500 (TA Instruments) at a heating rate of 10 K min$^{-1}$ under a nitrogen atmosphere up to 1000 °C, and differential scanning calorimetry was conducted using a DSC Q200 (TA Instruments) ranging from −50 to 200°C with a scan rate of 10 K min$^{-1}$ for all spiropyran polymers and from −70 to 180°C after UV irradiation. IR spectroscopy was performed using Bruker FT-IR spectrometer. Moreover, UV–vis absorption spectra were recorded using an Ocean optics spectrometer, whereas a Cary Eclipse fluorescence spectrophotometer was employed for recording fluorescence spectra.

*Synthesis of Photoresponsive Monomer- SpMA*: Using the commercially available compound 2,3,3-trimethyl-3H-indole, the SP derivative (SpOH) 2-(3’,3’-dimethyl-6-nitro-3’H-spiro[chromene-2,2’-indol]−1’-yl)-ethanol was synthesized with reference to the previously reported procedure.[37] Then, the polymerizable methacrylate group was introduced onto the spiropyran molecule following the procedure as represented in Scheme 1a.[5,38] The details of the synthesis steps and NMR data of all products in Scheme 1a can be found in the Supporting Information (Figures S1–S4, Supporting Information).

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors would like to acknowledge Ministry of Science, Research and Arts of Baden-Württemberg (MWK) for the financial support during the research.

Open access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information.

## Keywords

glass transition temperature, photoisomerization, photoresponsiveness, spiropyran

Received: May 9, 2023
Revised: June 11, 2023

---

[1] K. Mishra, J. P. Fuenzalida-Werner, F. Pennacchietti, R. Janowski, A. Chmyrov, Y. Huang, C. Zakian, U. Klemm, I. Testa, D. Niessing, V. Ntziachristos, A. C. Stiel, *Nat. Biotechnol.* **2022**, *40*, 598.
[2] M. Pilz Da Cunha, M. G. Debije, A. P. H. J. Schenning, *Chem. Soc. Rev.* **2020**, *49*, 6568.
[3] C. Zong, M. Hu, U. Azhar, X.u Chen, Y. Zhang, S. Zhang, C. Lu, *ACS Appl. Mater. Interfaces* **2019**, *11*, 25436.
[4] R. Klajn, *Chem. Soc. Rev.* **2014**, *43*, 148.
[5] S. Chen, F. Jiang, Z. Cao, G. Wang, Z. M. Dang, *Chem. Commun.* **2015**, *51*, 12633.
[6] S. L. Oscurato, M. Salvatore, P. Maddalena, A. Ambrosio, *Nanophotonics* **2018**, *7*, 1387.
[7] J. Shang, S. Lin, P. Theato, *Polym. Chem.* **2018**, *9*, 3232.
[8] Y. Wang, C. L. Sun, L. Y. Niu, L. Z. Wu, C. H. Tung, Y. Z. Chen, Q. Z. Yang, *Polym. Chem.* **2017**, *8*, 3596.
[9] S. Menon, R. Thekkayil, S. Varghese, S. Das, *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 5063.
[10] Y. Yu, T. Maeda, J. I. Mamiya, T. Ikeda, *Angew. Chem., Int. Ed.* **2007**, *46*, 881.
[11] S. Kado, K. Yamada, T. Murakami, K. Kimura, *J. Am. Chem. Soc.* **2005**, *127*, 3026.
[12] L. Kortekaas, W. R. Browne, *Chem. Soc. Rev.* **2019**, *48*, 3406.
[13] J. Keyvan Rad, Z. Balzade, A. R. Mahdavian, *J. Photochem. Photobiol. C* **2022**, *51*, 100487.
[14] J. Xie, J. Zhang, Y. Ma, Y. Han, J. Li, M. Zhu, *J. Mater. Chem.* **2022**, *10*, 7154.
[15] F. Jiang, S. Chen, Z. Cao, G. Wang, *Polymer* **2016**, *83*, 85.
[16] N. Murase, T. Ando, H. Ajiro, *J. Mater. Chem. B* **2020**, *8*, 1489.
[17] F. D. Jochum, P. Theato, *Chem. Soc. Rev.* **2013**, *42*, 7468.
[18] O. Grimm, F. Schacher, *Polymers* **2018**, *10*, 645.
[19] A. Radu, S. Scarmagnani, R. Byrne, C. Slater, K. Tong Lau, D. Diamond, *J. Phys. D: Appl. Phys.* **2007**, *40*, 7238.
[20] G. Petriashvili, M. P. De Santo, L. Devadze, T. Zurabishvili, N. Sepashvili, R. Gary, R. Barberi, *Macromol. Rapid. Commun.* **2016**, *37*, 500.
[21] B. Seefeldt, R. Kasper, M. Beining, J. Mattay, J. Arden-Jacob, N. Kemnitzer, K. H. Drexhage, M. Heilemann, M. Sauer, *Photochem. Photobiol. Sci.* **2010**, *9*, 213.
[22] H. Zhou, C. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G. K. Auernhammer, R. Berger, H. J. Butt, S. Wu, *Nat. Chem.* **2017**, *9*, 145.
[23] W. Hu, C. Sun, Y. Ren, S. Qin, Y.u Shao, L. Zhang, Y.u Wu, Q. Wang, H. Yang, D. Yang, *Angew. Chem., Int. Ed.* **2021**, *60*, 19406.
[24] T. J. Gately, W. Li, S. H. Mostafavi, C. J. Bardeen, *Macromolecules* **2021**, *54*, 9319.

[25] B. Yang, M. Yu, H. Yu, *ChemPlusChem*. **2020**, *85*, 2166.
[26] H. Cui, H. Liu, S.i Chen, R. Wang, *Dyes Pigm*. **2015**, *115*, 50.
[27] A. Abdollahi, Z. Alinejad, A. R. Mahdavian, *J. Mater. Chem. C* **2017**, *5*, 6588.
[28] A. Gonzalez, E. S. Kengmana, M. V. Fonseca, G. G. D. Han, *Mater. Today Adv.* **2020**, *6*, 100058.
[29] X. Fang, H. Zhang, Y. Chen, Y. Lin, Y. Xu, W. Weng, *Macromolecules* **2013**, *46*, 6566.
[30] C. C. Huang, M. X. Du, B. Q. Zhang, C. Y. Liu, *Macromolecules* **2022**, *55*, 3189.
[31] K. E. Smith, S. S. Parks, M. A. Hyjek, S. E. Downey, K. Gall, *Polymer* **2009**, *50*, 5112.
[32] E. Samoylova, L. Ceseracciu, M. Allione, A. Diaspro, A. C. Barone, A. Athanassiou, *Appl. Phys. Lett.* **2011**, *99*, 201905.
[33] W. Tian, J. Tian, *Langmuir* **2014**, *30*, 3223.
[34] Y. Xue, J. Tian, W. Tian, P. Gong, J. Dai, X. Wang, *J. Phys. Chem. C* **2015**, *119*, 20762.
[35] L. Wang, Y. Liu, X. Zhan, D. Luo, X. Sun, *J. Mater. Chem. C* **2019**, *7*, 8649.
[36] Y. Li, Y. Liu, D. Luo, *J. Mater. Chem. C* **2019**, *7*, 15166.
[37] F. M. Raymo, S. Giordani, *J. Am. Chem. Soc.* **2001**, *123*, 4651.
[38] C. Li, A. Iscen, L. C. Palmer, G. C. Schatz, S. I. Stupp, *J. Am. Chem. Soc.* **2020**, *142*, 8447.