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Letter

Photomechanical Deformation of Azobenzene-Functionalized Polyimides Synthesized with Bulky Substituents

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Supporting Information

ABSTRACT: Photomechanical effects realized in azobenzenefunctionalized polyimides have shown large deformation and an exceptional increase in photogenerated force output. Here, we synthesize and characterize the photomechanical output of a series of linear polyimide materials prepared with a bulky substituent, incorporated via the development of a new bis(azobenzene-diamine) monomer containing a 9,9-diphenylfluorene cardo structure (azoCBODA). All six azoCBODAcontaining polyimides are amorphous and exhibit high glass transition temperatures (T_g) ranging from 298 to 358 °C,



storage moduli ranging from 2.27 to 3.81 GPa (at 30 °C), and good thermal stability. The magnitude of the photoinduced mechanical response of the azobenzene-functionalized polyimide is correlated to the rotational freedom of the polyimide chains (resulting in extensive segmental mobility) and fractional free volume (FFV > 0.1).

Photomechanical responses of azobenzene-based polymeric systems of amorphous, crystalline, and liquid-crystalline nature have been investigated for the last 50 years.¹⁻⁶ Nevertheless, a holistic structure-property-performance understanding of macromolecular factors contributing to photomechanical outputs of polymeric materials remains incomplete.^{7–9} The photoinduced responses of these polymeric materials are triggered by either trans-cis isomerization or trans-cis-trans reorientation processes upon irradiation of 365 nm UV or blue-green light (440-530 nm), respectively. Exposure of these materials to UV light induces a trans-cis isomerization, resulting in a length reduction of the molecular axis of azobenzene from 9 Å (trans) to 5.5 Å (cis).¹⁰ In certain materials, distinctive mechanical effects can be observed by irradiation with blue-green light, near the isosbestic absorption of the isomeric forms of azobenzene.9,11 When linearly polarized blue-green light is incident on these materials, a small but measurable fraction of azobenzene can reorient orthogonal to the orientation of the electric field vector of the polarized light source, attributable to both the rotational freedom of the azo bond and the dichroic absorbance of both the trans and cis isomeric forms.¹² The local reorientation of azobenzene results in a highly stable, optically fixed shape in polymeric glasses, without a substantial concentration of the thermally sensitive cis isomer.^{13–22}

Photomechanical responses of azobenzene-functionalized liquid crystalline polymer networks (azo-LCNs) have been systematically studied and widely exploited. 15,16,21,23-29 Compared to the amorphous or crystalline azo-polymers, the director orientation of liquid crystal mesogens could be controlled, and azo-LCNs with polydomain, monodomain, twist-nematic, or splay orientation are prepared by the cell geometries. The various director orientations in the azo-LCNs induce particular shapes or surface responses upon exposure to the blue-green light.^{24,30,31}

Our prior work has also demonstrated that large photomechanical responses are possible in glassy azobenzenefunctionalized polyimides with high modulus and glass transition temperatures.^{13,14,32–37} In these studies, the effects of azobenzene concentration,¹³ crystallinity,¹⁴ free volume,³² prestretching,³³ backbone rigidity,³⁴ and light polarization³⁵ were investigated on the bidirectional bending, the magnitude of bending angles, and photogenerated stress^{13,14,32,33,35} as photomechanical responses of the azobenzene-functionalized linear and/or cross-linked polyimides. Photomechanical effects in both liquid crystalline³⁸⁻⁴² and amorphous^{43,44} polymers have also been examined theoretically.

Related to this work, the effect of backbone rigidity of the linear azo-polyimides on the photodirected bending response has been described,³⁴ and a recent simulation study on the stress relaxation dynamics of azo-polyimides has provided insights into the correlation of polymer structure and topology with the persistence of photomechanical strains, the control of which is critical to the broader utility of the material in shape-

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programmable systems.⁴⁵ However, the coupled effect of rigid and voluminous moiety in the photoresponsive azobenzenefunctionalized polymers, to our knowledge, has not been investigated. This coupled effect is important because such molecular bulkiness increases free volume that would be kinetically more invariant and less temperature dependent than free volume created by physical aging.³²

Polymeric materials prepared with the so-called cardo or "loop" pendants are structurally distinctive. The cardo group is comprised of a ring structure typically including a quaternary carbon ("spiro-carbon") that is shared by the main chain.⁴⁶ Besides dictating amorphous character, the inclusion of the cardo moieties in polymeric materials improves solubility in organic media, increases glass-transition temperatures, and extends thermal stability. Furthermore, the bulky nature of this group also increases the local free volume, a factor known to be critically important in allowing the photoisomerization of azobenzene in macromolecular systems.³² While the literature is replete with examples of thermally stable cardo polymers to exploit these features in applications that require solution processability,⁴⁷ gas permeability/permselectivity,^{48,49} improved ionic conductivity, alkali resistance of anion exchange membrane,^{50,51} high transparency, high refraction index/low birefringence, ^{52,53} low dielectric constant, ⁵⁴ or combinations of these properties, employing the cardo group to affect free volume in photomechanically active, azobenzene-functionalized polymeric materials has yet to be exploited.

Because of the voluminous nature and concurrent influence on macromolecular rigidity, the thermally robust 9,9-diphenylfluorene motif is selected for this work. The 9,9-diarylfluorene diamine (azoCBODA) monomer (7, Scheme S1, Supporting Information) was synthesized via a 4-step route, starting with an aromatic nucleophilic substitution reaction in which 9,9bis(4-hydroxyphenyl)fluorene (1) was treated with 1-fluoro-4nitrobenzene (2) in the presence of potassium carbonate to yield 9,9-bis[4-(4-nitrophenoxy)phenyl]fluorene (3). Compound 3 was then chemically reduced to 9,9-bis[4-(4aminophenoxy)phenyl]fluorene (4) by hydrazine in ethanol. The condensation reaction of 4 and formally 2 equiv of 4nitrosoacetanilide (5) in acetic acid yielded 6, a protected precursor containing two azobenzene units. Finally, the azoCBODA monomer (7) was obtained by deprotection of 6 via deacetylation under acidic conditions.

Scheme 1 outlines the synthesis of azoCBODA-containing homopolyimides (azoCBODA-XXXX, where XXXX stands for one of the following dianhydrides: PMDA, BPDA, BTDA, ODPA, 6FDA, and BPADA). Briefly, azoCBODA (7) and a dianhydride (8) were dissolved under nitrogen atmosphere in N.N-dimethylacetamide (DMAc) (5 wt % concentration) at room temperature for 24 h to generate poly(amic acid) (PAA; 9). The resulting PAA precursor was poured onto glass slides and cured in a vacuum oven following the protocol: vacuum evaporation of DMAc at 50 °C/48 h and heat-treated at 100 °C/1 h, 150 °C/1 h, 175 °C/1 h, 200 °C/1 h, 250 °C/1 h, and 300 °C/1 h to form the imidized-polymer film, which was released by soaking in methanol. The obtained azoCBODA-XXXX films are tough, creasable, and soluble in NMP and DMAc but not in THF (except -OPDA and -BPADA). The film thickness was approximately 20–100 μ m.

Thus, the resulting azoCBODA-XXXX materials enable us to systematically correlate the resulting photomechanical response to the material properties such as thermal stability, free volume, and rotational freedom of the local chains. Accordingly, the Scheme 1. Synthesis of the Azobenzene-Functionalized, Cardo-Based, Linear Polyimides 10a-f



polyimide materials were characterized by various techniques. The results from both wide-angle X-ray scattering (Figure S1, Supporting Information) and polarized optical microscopy (Figure S2) confirmed that all the azo-polyimides examined here are amorphous. The control materials, similarly prepared by the reaction of the linearly compact azoBPADA (see Figure 2 for chemical structure), also yields amorphous azopolyimides.

The heat resistance of the azoCBODA polyimides was examined by TGA at a heating rate of 10 °C/min, and the results are summarized in Table S1 (Supporting Information). All azoCBODA-based polyimides examined here show good thermal/thermo-oxidative stability, with 5 wt % weight loss temperatures ($T_{\rm d5\%}$) ranging between 425 and 447 °C in nitrogen and 455-481 °C in air. Notably similar to our previous observation,³⁴ the $T_{d5\%}$ values of these materials in air are found to be ~30-49 °C higher than measurements in a nitrogen atmosphere (Table S1). In general, polymers are more stable (higher degradation temperatures) in nitrogen than in air. These unusual results (a TGA example is provided in Figure S3) are explained by the oxidization of the azo bonds, possibly via azoxy and/or nitro formation, resulting in weight gain in air and offsetting the weight loss due to the usual thermo-oxidative degradation processes that occurred concurrently.

The thermomechanical properties of the azoCBODA polyimides determined by DMA (Figure S4, Supporting Information) are summarized in Table 1. These azo-polyimides show high storage moduli with a range of 2.28 to 3.81 GPa at 30 °C and glass transition temperatures ranging from 298 to 358 °C. The trend for T_g (or T_α) is PMDA > BPDA > BTDA > 6FDA > ODPA > BPADA. Our recent report has shown a strong correlation of the photomechanical response of polyimide materials to the loss modulus, specifically to the prevalence and magnitude of the β -transitions associated with

sample code	E' (GPa) at 30 °C	T_{β} (K)	T_{α} (K)	T_{β}/T_{α}	MW_{ru}^{a} (g/mol)	MW _{ru} ratio ^b	density (g/cm ³)	FFV (calcd) ^c
azoCBODA-OPDA	3.02	333	587	0.567	1016	0.829	1.27	0.125
azoCBODA-BPDA	3.63	331	598	0.553	1000	0.815	1.27	0.120
azoCBODA-PMDA	3.81	348	631	0.552	924	0.754	1.26	0.132
azoCBODA-6FDA	3.34	355	616	0.576	1150	0.938	1.31	0.132
azoCBODA-BTDA	3.21	348	621	0.560	1028	0.838	1.28	0.114
azoCBODA-BPADA	2.27	318	571	0.557	1226	1	1,20	0.157

^{*a*}Molecular weight of a repeat unit. ^{*b*}Normalizing MW_{ru} by $MW_{ru} = 1226$ of azoCBODA BPADA; the ratio value is inversely proportional to the effective chromophore (azobenzene) number density. ^{*c*}Calculated fractional free volume.

segmental mobility.³⁶ Evident in Figure 1, the materials examined here all exhibit a very broad β transition ranging



Figure 1. Plot of loss modulus vs temperature for the azo-CBODA-XXXX polyimides.

from 0 °C to more than 200 °C in the case of the azoCBODA-PMDA. Our prior examination reported ratios of the β - to α transition temperatures $[T_{\beta}(K)/T_{\alpha}(K)]$ of 0.69–0.74 for linear and cross-linked azo-polyimides.³⁶ The ratio of $[T_{\beta}(K)/T_{\alpha}(K)]$ is a good indicator of intermolecular correlation of glass transition and thermal expansion.⁵⁵ Typical ratios for polyimides range from 0.65 to 0.8.⁵⁶ The ratio of $[T_{\beta}(K)/T_{\alpha}(K)]$ for the azo-CBODA polyimides examined here is smaller, spanning 0.55–0.58 (Table 1). The association of the cardo group on this value is evident when comparing azoBPADA-6FDA (0.72)³⁶ to the analogous azoCBODA-6FDA (0.576). A similar observation has been reported in the polyimide literature for analogous cardo vs noncardo materials (0.59 vs 0.71).^{57,58} These results further confirm that while the cardo group can sterically hinder the long-range mobility of the polymer chain it concurrently lowers the activation barrier to accessing and influencing the segmental mobility in these materials. Accordingly, we postulate that during irradiation the free volume (or fractional free volume, *vide infra*) in the material associated with the inclusion of the cardo-fluorene group in the immediate vicinity may enable additional mobility of the chromophore units through the rotation of the neighboring 1,4-phenylene rings.^{59,60}

The photomechanical outputs of these materials were examined by irradiating the cantilevers of the various materials as a function of exposure time under linearly polarized blue light parallel to the long axis (E//x) at 60 mW/cm² intensity.⁶¹ Bending is induced as a result of a photoinduced strain gradient (absorption gradient) across the thickness of the cantilever. The magnitude of the bending angle is largely indicative of the photoinduced mechanical response of the material.³⁴

The photomechanical response of the azoCBODA-OPDA cantilever is depicted as a series of snapshots in Figure S5(a), Supporting Information, that shows bending angle from 0° to ~90° in 30 min. The temporal response plots for the photoinduced deflection of cantilevers composed of six azoCBODA-XXXX polyimides are depicted in Figure S5(b). Essentially, these azo-polyimides have shown large-magnitude bending responses (~45–70°), regardless of the dianhydride's structure. Noteworthy is the smaller bending angle of azoCBODA-BPADA that is likely caused by its having lower chromophore concentration due to having the highest molecular weight repeating unit (MW_{ru}). As shown by the data in Table 1, the MW_{ru} of azoCBODA-BPADA is 10–20%



Figure 2. Photomechanical responses of two comparative series of azopolyimides: (a) azoBPADA-PMDA (i), azoBPADA-BPDA (ii), and azoBPADA-OPDA (iii) and (b) azoCBODA-PMDA (i), azoCBODA-BPDA (ii), and azoCBODA-OPDA (iii). All materials (~20 μ m thickness) were exposed to 60 mW/cm² 445 nm light polarized parallel to the long axis of the cantilever (*E*//*x*).

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higher than those of other azoCBODA polyimides. This rationale is corroborated by a comparative UV–vis result (Figure S6, Supporting Information) that azoCBODA-BPADA has the lowest absorbance change for its azobenzene trans–cis photoisomerization relative to two other members of this series under the same conditions. Finally, the relaxation processes of the six azoCBODA cantilevers were monitored after 1 h exposure to the blue light. All samples exhibit fast relaxation in 30 min and almost full recovery in 2 h (Figure S5(c)).

To illustrate the influence of the inclusion of the bulky substituent to the azoCBODA polyimides, Figure 2 compares the photomechanical response of analogous polyimides synthesized with the linearly compact azobenzene-containing bisphenol A diamine (BPADA) employed in our prior studies.³⁴ This diamine was polymerized with three dianhydrides (PMDA, BPDA, and OPDA). As also evident in our prior study, varying the dianhydride structure strongly affects the observed photomechanical response. We have previously attributed this effect to the relative influence of dianhydrides' aromaticity on the backbone rigidity of the polyimide, which results in a notable increase in moduli and a distinct difference in photoresponse (Figure 2(a)). In comparison, when the same three dianhydrides are polymerized with the azoCBODA diamine, the resulting photomechanical response is indistinguishable (Figure 2(b)).

These results indicate that regardless of the contribution of the dianhydride precursors on rigidity the incorporation of the azoCBODA unit enables more efficient transduction of photonic energy into molecular motion. We attribute this to the correlation of the influence of the CBODA group on both the local free volume as well as the relative mobility of the azobenzene chromophore within the material.

Free volume (V_f) is defined as an empty space between the (macro)molecules (i.e., amount of microporosity among the polymer chains) and affects the range of polymer chain motion.⁶² Empirically, free volume has been estimated as the difference between specific volume (V_{sp}) and occupied volume (V_{occ}), which is 1.3 times the van der Waals volume (V_w) when V_w is computed based on Bondi's principle of group contributions.⁶³⁻⁶⁵ To notionally correlate polymer properties, fractional free volume (FFV), a dimensionless parameter (eq 1) that is defined as the ratio of free volume to specific volume, is generally used:

$$FFV = \frac{V_{sp} - V_{occ}}{V_{sp}} = \frac{(V_{sp} - 1.3V_{w})}{V_{sp}}$$
(1)

The FFV values for the azoCBODA polyimides are summarized in Table 1. For comparison, the calculated FFV values of three polyimides, with BPA constituting either the dianhydride (in Ultem) or the diamine (azoBPADA-OPDA and -PMDA)³⁴ structure, are also included in Table S2 (computation details are provided as Supporting Information).

The azoCBODA polyimides with cardo-fluorene substituent show FFV (0.114-0.157) larger than those of Ultem (0.077) and the two azoBPADA polyimides (0.045-0.101).

The FFV calculations confirm that the incorporation of the cardo moiety strongly influences free volume. Photoinduced isomerization or reorientation of the azobenzene chromophore in these materials is comparatively less encumbered by the local macromolecular environment.

The influence of the cardo functional group on the mechanical properties of these materials is multipronged. The

photogenerated stress measurable from azoCBODA-PMDA is contrasted to the analogous material, azoBPADA-PMDA in Figure 3. Without optimization or other processing enhance-



Figure 3. Photogenerated contractile stresses of two structural similar azopolyimides containing cardo (blue trace) and no cardo (red trace) moieties under tensile mode during continuous irradiation by linearly polarized blue light, 30 mW/cm², parallel to the long axis (E//x); 6 mm × 1 mm × 0.02 mm gauge.

ments, the azoCBODA-PMDA sample produces almost 250 kPA of stress upon irradiation. This increase in photogenerated force is largely attributable to the concurrent influence of the cardo group on the modulus (stiffness) of the samples, enabling greater force generation.

In summary, we report here the synthesis of a novel series of azobenzene-functionalized polyimides that have been intentionally prepared with bulky substituents. The inclusion of these substituents is shown to strongly increase the fractional free volume in these materials. Accordingly, the resulting macromolecular environment in and around the azobenzene chromophores is conducive to more efficient photoisomerization or reorientation and, in so doing, enabled comparatively larger photoinduced deformation as well as force generation. In this way, this report details a distinct method to prepare materials that yield both large deformation and force. Subjecting these materials to physical aging³⁰ or drawing³¹ would further enhance the photomechanical output of these materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.7b00854.

Scheme S1, Tables (S1 & S2), Figures (S1–S6), and preparative details for azoCBODA diamine monomer (PDF)

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Notes

The authors declare no competing financial interest. [‡]Also with UES Inc.

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