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A Simply Synthesized, Tough Polyarylene with Transient Mechanochromic Response

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Abstract: A simple, straightforward and high-yielding route to tough polyarylenes of type poly(*meta,meta,para*-phenylene) (P*mmp*P) is developed. P*mmp*P is already tough in its as-synthesized state at intermediate molar mass of M_w ~60 kg/mol and exhibits outstanding mechanical properties for further optimized molecular weight (M_w = 96 kg/mol, E = 0.9 GPa, ε = 300 %). Statistical copolymers with *para,para*-spiropyran (SP) are mechanochromic, whereby the tough behavior allows to investigate mechanochromism. Strained samples instantaneously lose color upon force release. DFT calculations show this phenomenon to be caused by i) the tough P*mmp*P matrix that allows build-up of sufficiently large forces to be transduced to SP, and ii) the relatively unstable corresponding merocyanine (MC) form arising from the aromatic comonomer. MC units covalently incorporated into P*mmp*P show a drastically reduced half life time of 3.1 s compared to 4.5 h obtained for SP derivatives with common 6-nitro substitution.

Polyarylenes have intrigued material scientists since the invention of transition metal catalyzed cross coupling reactions.[1,2] In 2007, Schlüter *et al.* introduced a high molecular weight (MW) Poly(*meta,para*-phenylene) P*mp*P by careful selection of catalyst, solvent mixture, concentration and temperature.[3] In their pioneering work a crude polymer of M_w = 83 kg/mol was synthesized and the MW further increased to M_w = 255 kg/mol by fractionation. After fractionation, this material showed a toughness close to that of aromatic polycarbonates (E = 1 GPa, ε = 122 %). This was a remarkable feat both from a synthetic as well as a material science point of view, because

polyarylenes are inherently more chemically stable than polycarbonates due to the exclusive presence of aryl-aryl bonds in the backbone. Subsequently, Schlüter *et al.* investigated various kinked polyarylenes, with some of them exhibiting toughness at high molecular weight after fractionation.[3–7]

Our interest in tough polyarylenes stems from their potentially ideal use as stable, tough yet amorphous matrices for covalent incorporation of mechanochromic dyes such as spiropyrans (SPs).[8–10] SPs isomerize to their colored merocyanine (MC) form under a number of external stimuli, including force, and can therefore be used as mechanical force sensors.[11–15] Compared to matrix polymers used so far in combination with covalently linked SPs, tough polyarylenes have several distinct advantages. Their toughness allows drawing samples and thus to transduce mechanical force to SP. Also, they are typically amorphous, hence mechanochromism can be investigated within an isotropic matrix not possible with semicrystalline polymers. Here we show that the nature and high strength of polyarylenes is of striking additional advantage in that high forces can be transduced to SP comonomers.

We found existing protocols for kinked polyarylene synthesis to be cumbersome, expensive and inefficient due to significant loss of polymer during fractionation.[3,4,7] Moreover, existing polyarylenes show limited solubility and high glass transition temperatures (T_g) of up to 160 °C, which required processing at too high temperatures for thermolabile SP copolymers. The design of new, tough polyarylenes satisfying all mentioned criteria required straightforward synthesis of monomers starting from inexpensive compounds. Therefore, we designed a new kinked polyarylene, Poly(*meta,meta,para*-phenylene) P*mmp*P. *Para*-bromination of 2,2'-biphenol **1** results in the solid monomer **2**, which can be conveniently purified by recrystallization. Suzuki polycondensation (SPC) with **3** gives the kinked polyarylene P*mmp*P with a "double *meta*-" linkage in its backbone (Scheme 1). High weight average molecular weights M_w ~ 56-96 kg/mol were obtained with almost all molecular weights showing a yield point. Details regarding retrosynthetic analysis, molecular and mechanical characterization are given in the Supporting Information.

SPs have been covalently incorporated into various polymer architectures.[11,14,16,17] Notably, almost all of these systems use 6-nitro-SP derivatives. The nitro group lowers the energy of the corresponding MC form and hence facilitates SP → MC isomerization.[18] The previously reported main-chain alternating *para,para*-SP copolymers did not show toughness and hence the mechanochromic behavior of the *para*-linked SP without the nitro-substituent could not be investigated using uniaxial positive strain.[8–10]

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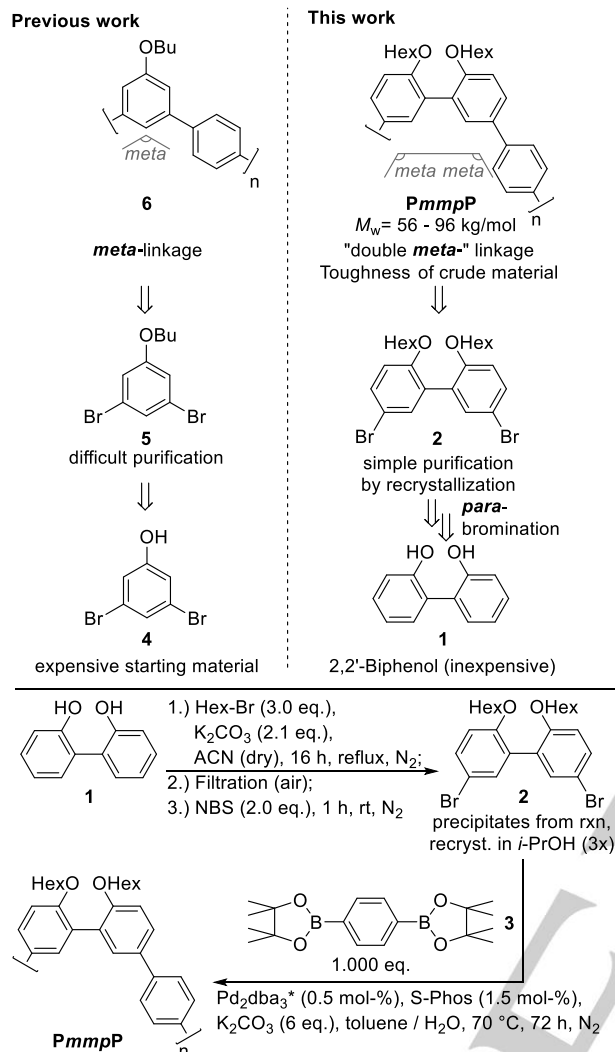
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Previous work

This work

6

meta-linkage

⇓

5

difficult purification

⇓

4

expensive starting material

P*mmp*P

M_w= 56 - 96 kg/mol

"double *meta*-" linkage
Toughness of crude material

⇓

2

simple purification
by recrystallization

para-
bromination

1

2,2'-Biphenol (inexpensive)

1

1.) Hex-Br (3.0 eq.),
K₂CO₃ (2.1 eq.),
ACN (dry), 16 h, reflux, N₂;
2.) Filtration (air);
3.) NBS (2.0 eq.), 1 h, rt, N₂

2

precipitates from rxn,
recryst. in *i*-PrOH (3x)

3

1.000 eq.

Pd₂dba₃* (0.5 mol-%), S-Phos (1.5 mol-%),
K₂CO₃ (6 eq.), toluene / H₂O, 70 °C, 72 h, N₂

P*mmp*P

Scheme 1. Top: Retrosynthetic analysis of P*mmp*P compared to previous work.[3] Bromination of 2,2'-biphenol leads to a "double *meta*-" linkage in the backbone. Bottom:Synthesis of P*mmp*P. * = non-commercial Pd₂dba₃.

The mechanochromic response of P*mmp*P with 2 mol-% copolymerized *p,p*-SPBr₂ is shown in Figure 1 (M_w = 134 kg/mol, Đ = 5.5). For the first time, copolymers with *p,p*-SPBr₂ were mechanochromic under positive strain. Yet more remarkable is the observation that samples immediately lost their color upon force release. Figure 1 shows that repeated switching was possible for 25 times. This is a marked difference compared to SP-based mechanochromic systems reported so far showing persistent colors.[10,13,17]

We hypothesized the reason for the observed transient mechanochromic behavior of P*mmp*P with instantaneous loss of color upon force release is two-fold. Firstly, covalent incorporation of SP through *para*-linkages compared to commonly used *ortho*-linked SP mechanophores leads to a rather inefficient molecular lever and transduction of mechanical force to the weak C-O bond. The replacement of the commonly used nitro-group in 6-position by phenyl ring of comonomer **3** further adds up to this effect, as the electronic effect of the phenyl ring destabilizes the MC form compared to the nitro group.[18] In order to be able to observe

mechanochromism regardless, the high strength of P*mmp*P of up to 50 MPa at yield is probably key (see Supporting Info). Secondly, once MC forms under the conditions of the stress-strain experiment, it is only stable under the applied force due to the discussed substitution pattern, but immediately isomerizes back to SP when the force is released. This behavior of a rather unstable MC form leads to the observed transient mechanochromic response.

To further corroborate this assumption and get more insight into the uncommon mechanochromic behavior of the SP copolymer, density functional theory (DFT) calculations were performed. Bond breaking under the action of an external force F_{ext} mostly is a stochastic process as it is initiated by thermal fluctuations.[19–22] Only in case of extremely rapid pulling, thermal effects are overcome and the force corresponding to the maximal derivative of the potential gets visible. The force needed to break a bond thus depends on the loading rate $\alpha = dF_{ext}/dt$. We modeled two SP derivatives, one having the SP substitution pattern as in P*mmp*P and "*para*,*para*- pulling direction", and one with the commonly used 6-nitro group (SP-NO₂) and "*para, ortho*-pulling direction".[23,24]

The structures are depicted in Figure 2. Calculations were performed within the projector augmented wave method as implemented in the GPAW package.[25,26] The exchange-correlation energy was approximated as devised by Perdew, Burke, and Ernzerhof.[27]
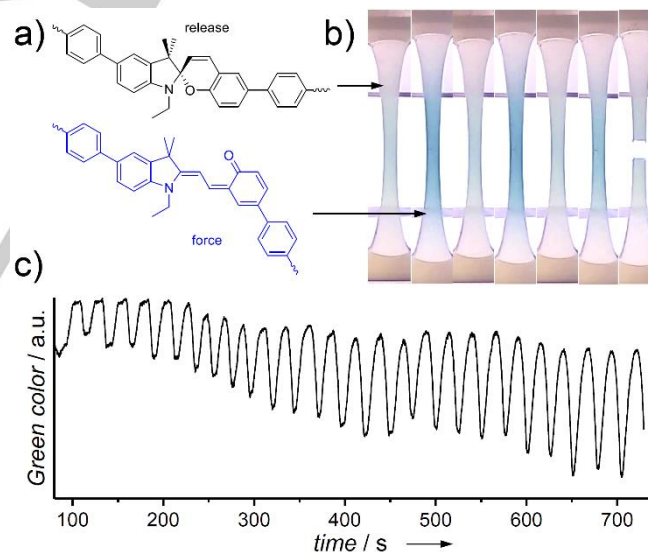
Figure 1. Tensile experiment of P*mmp*P containing 2 mol-% *p,p*-SPBr₂. a) Structures of SP (top) and MC (bottom) in the P*mmp*P matrix. b) Pictures of repeated strained and released samples. Pictures were adjusted for brightness and contrast. c) Intensity of green color in the mid-section of the specimen during repeated force build-up and release. The time scale corresponds to the change in force as shown in Fig. S5.

In order to obtain the force needed for the transition from SP to MC, we applied a two-dimensional Constrained Geometries Simulate External Force (COGEF) method, where the energy barriers in dependence of F_{ext} are determined (see supporting info for details).[22,28]

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We found two energy barriers with an instable intermediate state along the transition, which belong to the C-O cleavage (increasing of bond length b) and the *cis-trans* isomerization by rotation of the dihedral angle β (see Fig. 2a,b). Figure 2c depicts the rate determining total energy barriers in forward $\Delta G_{f,\text{total}}(F_{\text{ext}})$ and backward $\Delta G_{b,\text{total}}(F_{\text{ext}})$ direction which are relative to the energies of the SP and MC forms, respectively. For small forces the barrier for β rotation is decisive, while for large forces it is C-O bond breaking. While this behavior is similar in both SP derivatives, the transition happens at much lower external force for SP-NO$_2$ compared to SP in PmmpP. Fig. 2c also shows that the forward barrier for nitro is smaller than for polyarylene in a large force range. The transition rates k can be obtained from the barriers using the Eyring equation[20,29]

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G}{k_B T}\right), \tag{1}$$

where k_B is the Boltzmann and h the Planck constant. From these the probabilities for the presence of each isomer at fixed force and temperature T can be determined through solving the corresponding coupled rate equations for the probabilities $P_S(F_{\text{ext}})$ with $S = \text{SP, IN, MC}$ (see supporting info for details). Coloration happens as soon as the C-O bond breaks. Therefore the probability for the colored form is $P_c = 1 - P_{\text{SP}} = P_{\text{IN}} + P_{\text{MC}}$. The average force for coloration F is then obtained as

$$F = \int_0^\infty \frac{dP_c(F_{\text{ext}})}{dF_{\text{ext}}} F_{\text{ext}} \, dF_{\text{ext}} \tag{2}$$

By assuming a constant loading rate α, integral (2) can be evaluated and leads to $F(\alpha)$ as shown in Figure 2d. The rupture forces for SP in PmmpP are larger compared to SP-NO$_2$ within a wide range of loading rates except for very large values of $\alpha \geq 10^5$ nN/s. This is a result of the higher forward energy barrier for SP in PmmpP for low external forces that is decisive for small loading rates (Fig. 2d). Only for very high loading rates external forces $F_{\text{ext}} \geq 0.7$ nN are reached and SP in PmmpP isomerizes faster than SP-NO$_2$. The sharp increase of the rupture force for SP-NO$_2$ and the deeper understanding of the force-dependent energy barriers obtained from the method of calculation are subject of future studies.

Here, we estimate the loading rate to be less than $\alpha = 1$ nN/s such that the rupture force for SP in PmmpP is larger by more than a factor of two. This explains why SP in PmmpP isomerizes at larger mechanical stress than the commonly used SP-NO$_2$. Figure 2c also shows that the backward barrier of SP-NO$_2$ is substantially higher than that of SP in PmmpP. As the SP isomer is energetically favored, discoloration happens spontaneously with a theoretical half time of 4.5 h for SP-NO$_2$, but only with 3.1 s for SP in PmmpP, which is in excellent agreement with the fast de-coloration observed in the experiment.

Next to these unique electronic substituent effects, the high strength and elongation at break enabling transient mechanochromic response, the SP in PmmpP additionally benefits from the strong absorption of UV light of PmmpP (see supporting info), which may reduce photo-bleaching as a major drawback of SP-based materials considerably.[30–32]

In conclusion, we designed a simple and high-yielding synthetic route to polyarylenes of type PmmpP with *meta,meta,para*

backbone that are tough without prior purification and at intermediate molecular weight. Our rational monomer design employs inexpensive and readily available 2,2' biphenol as a
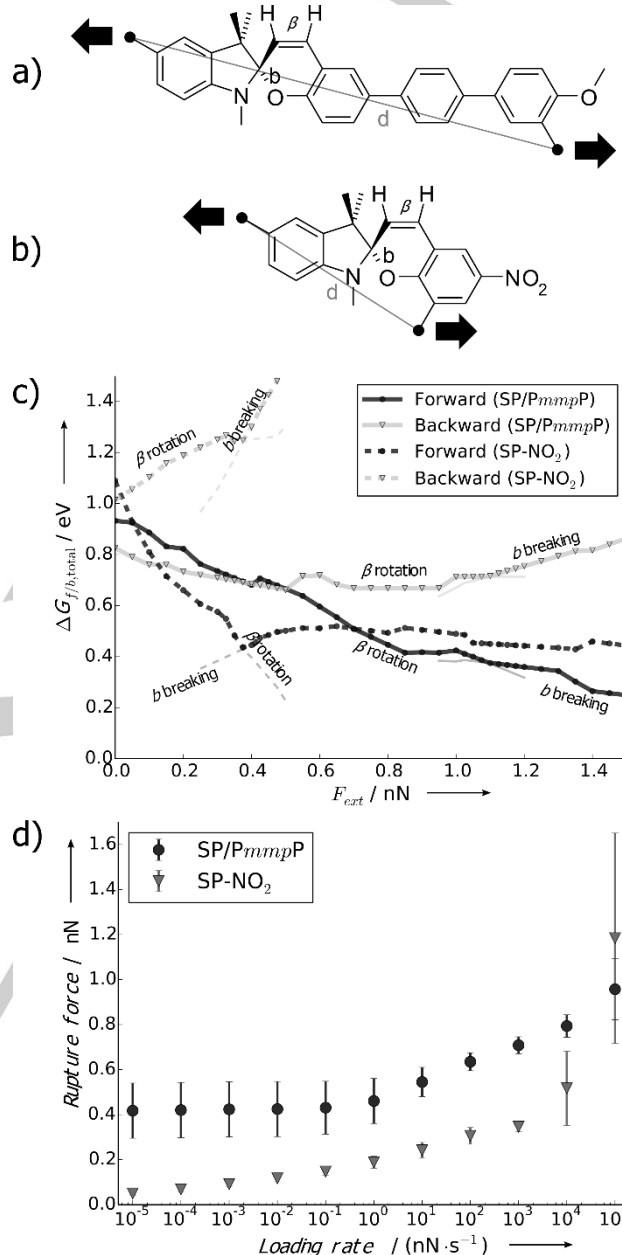

Figure 2. a), b) Chemical structures of SP derivatives modelled with arrows indicating pulling directions. The definitions of the pulling distance d, the bond distance b and the dihedral angle β between olefinic protons are indicated. c) Gibbs energy barriers in dependence of the external force corresponding to the polyarylene and nitro-substituted spiropyran. d) Force needed for coloration F in dependence of the loading rate α for the two SP derivatives.

starting material, from which solid monomers can be made in high purity by simple recrystallization in multigram scale. The availability of highly pure and solid monomers allowed for high molecular weight polycondensates to be made, which further improved mechanical properties to outstanding values. Copolymers of PmmpP with spiropyran are mechanochromic under positive uniaxial strain, but lose color instantaneously after

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force release. With this transient response enabling the direct visualization stress in polymeric materials without delay, engineering both the substitution pattern of covalently incorporated SP units as well as the polymer matrix allows to tailor-make smart materials for specific applications.

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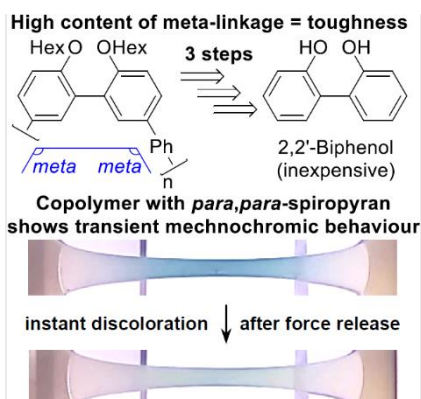[32]   G. Ballet, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. Mol. Cryst. Liq. Cryst.* **1997**, *298*, 75–82.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

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A simple and high-yielding synthesis to high molecular weight, tough poly(*meta,meta,para*-phenylene) is reported. Statistical copolymers with *para*,*para*-spiropyran showed a transient mechanochromic response, the origin of which is explained in detail.

High content of meta-linkage = toughness
HexO OHex **3 steps** HO OH
meta meta Ph n 2,2'-Biphenol (inexpensive)
Copolymer with *para,para*-spiropyran shows transient mechnochromic behaviour
instant discoloration ↓ after force release

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