Polymer Synthesis

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Suzuki Polycondensation Put to Work: A Tough Poly(*meta*-phenylene) with a High Glass-Transition Temperature**

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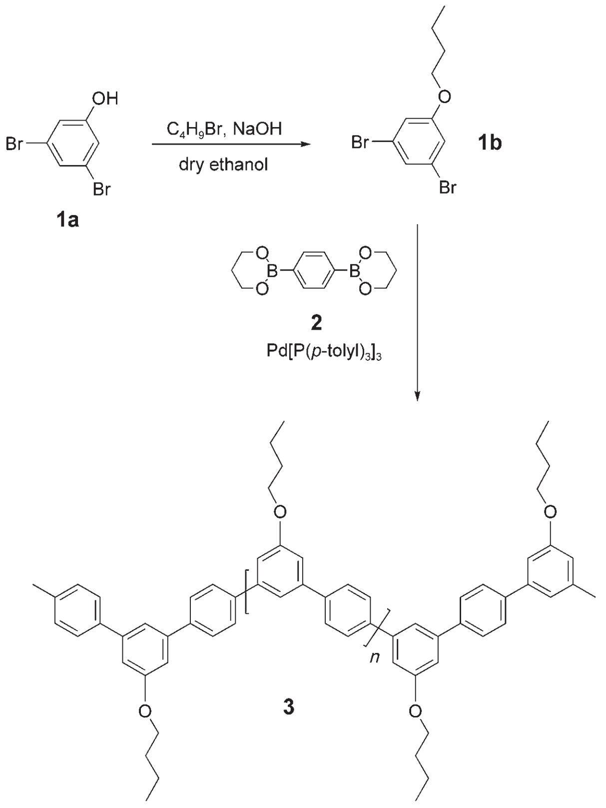
Since its discovery in the 1980s, polymerization based on the Suzuki cross-coupling reaction[1] has been developed into a key route for the synthesis of structurally defined polyarylenes now referred to as Suzuki polycondensation (SPC).[2,3] Most polymers prepared by this method are poly(*para*-phenylene)s, investigated principally because of their rigid-rod nature and useful electro-optical properties.[4,5] More recently, this route has found technical application in the production of organic light-emitting diodes (OLEDs) based on linear fluorene copolymers.[6]

Polyarylenes are chemically and thermally robust and interesting as polymeric materials per se. This, of course, is also true for the *meta*-linked polyphenylenes. Their kinked structure should not only impart enhanced processability to the polymer—as for the related *meta* analogues of aromatic polyamides (aramids) and thermotropic polyesters[7,8]—but also permit formation of highly amorphous materials because their macromolecular ordering kinetics are expected to be slow relative to typical processing time scales.

To our knowledge, only one report describes the use of the powerful Suzuki polycondensation for the synthesis of poly(*meta*-phenylene)s (P*m*Ps),[9] although other routes have also been pursued;[10–15] invariably, however, few details have been given regarding the properties of the materials produced. Here, we present the synthesis and material characteristics of one selected member of the P*m*P family, poly(3-butoxy-4′,5-biphenylene) (PB*m*P) (**3**). We found this polymer to exhibit a highly useful combination of properties, including convenient processability, a high glass-transition temperature, T_g. Polymer **3** also displays outstanding toughness, that is, capability to absorb mechanical energy, rivalling that of high-performance polycarbonates (PC), but shows improved resistance against environmental stress-cracking, a faiblesse of the latter engineering polymer.[16,17]

The synthesis of PB*m*P (**3**) started from the commercial dibromophenol **1a**, which was etherified with butyl bromide to give the dibromo monomer **1b** (Scheme 1). Together with its counterpart, the diboronic acid ester **2**, it was subjected to conventional SPC conditions, whereby the stoichiometric balance of the monomers was strictly observed. Polymer **3** was worked-up and fractionated by precipitation to yield three fractions on gram scale, whose quantities and molar masses are given in Table 1. The structural integrity of the polymer was confirmed by high-field NMR spectroscopy; representative ^{1}H and ^{13}C NMR spectra are shown in Figures 1 and Figure 2 with signal assignments. Detailed synthetic procedures and all analytical data are available in the Supporting Information.



Scheme 1. Synthesis of the poly(*meta*-phenylene) poly(3-butoxy-4′,5-biphenylene) (**3**).

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Table 1: Weight-average molar masses (M_w) and degrees of polymerization (P_w) from gel permeation chromatography of PB*m*P (**3**) and its three fractions referenced to polystyrene standards. The polydispersities are 3.3 for the as-obtained material and approximately 2 for the fractions.

PB*m*P (**3**) sample	Amount [g]	$M_w[\times 10^{-3}]$	P_w
as obtained	3.57	83	370
fraction 1	1.08	255	1140
fraction 2	1.42	85	380
fraction 3	0.98	27	120

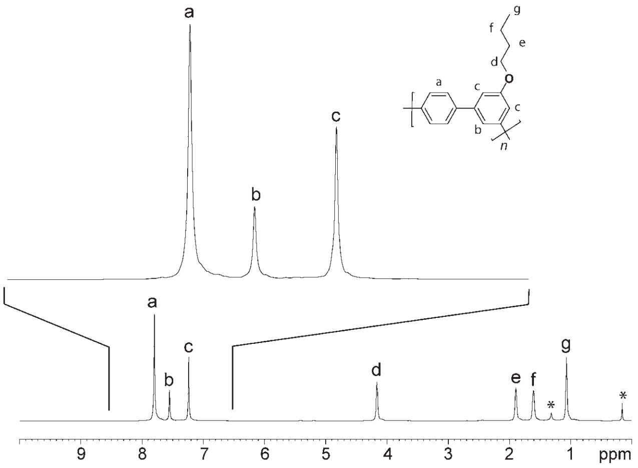

Figure 1. ^{1}H NMR spectrum (700 MHz) of polymer **3** (fraction 1) in $CDCl_3$ with signal assignment to illustrate the level of structural integrity. The inset shows the enlarged aromatic region. Solvent signals are marked (*).

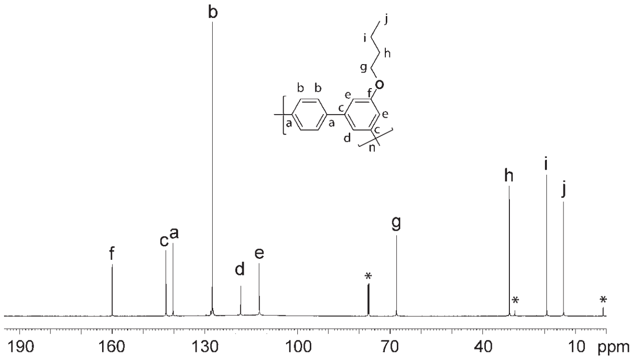

Figure 2. Representative ^{13}C NMR spectrum (176 MHz) of polymer **3** (fraction 1) in $CDCl_3$ with signal assignment. Solvent signals are marked (*).

Thermogravimetric analysis (TGA) of the various polymer fractions revealed that the present samples displayed rapid weight loss above 310 °C. We note, however, that heating the present samples caused discoloration at temperatures exceeding 180 °C, possibly due to residual traces of catalyst.

Differential scanning calorimetric (DSC) analysis of once-molten polymer samples is presented in Figure 3a. This data indicate a pronounced, typical molar-mass-dependent[18] glass temperature, T_g, in the elevated range from 149 to 166 °C for **3** of M_w of 27×10^3 to 255×10^3. These values significantly surpass those of traditional bulk amorphous polymers such as atactic polystyrene (a-PS) and poly(methyl methacrylate) (PMMA) ($T_g \approx 100$ °C) and compare favorably with that of high-performance polycarbonates ($T_g \approx 150$ °C).[19]

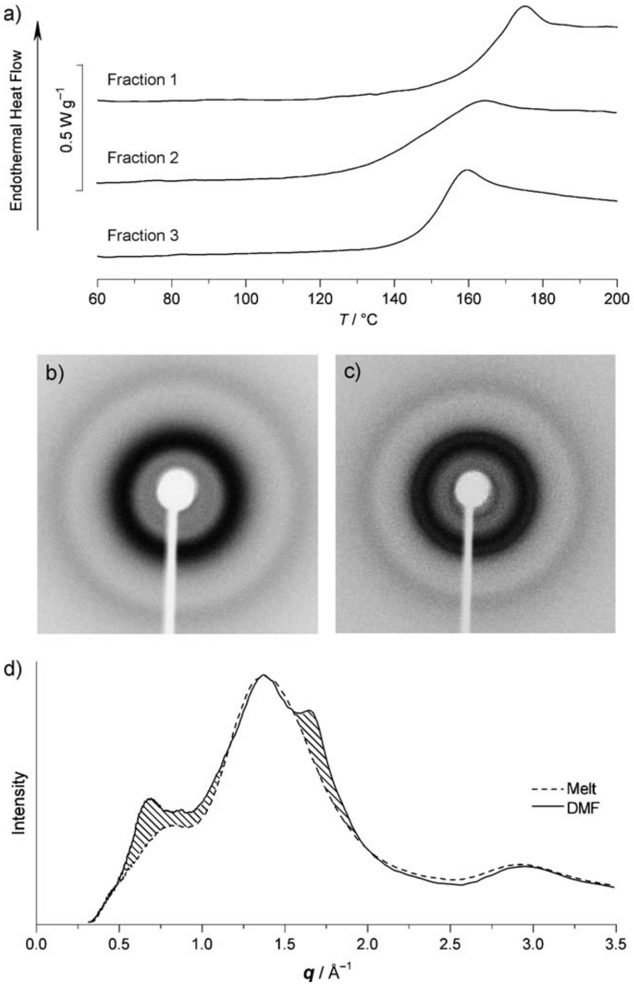

Figure 3. a) DSC thermograms of once-molten PB*m*P (**3**) fractions 1–3 revealing pronounced glass-transition temperatures. b) WAXS pattern of a melt-compression molded film of PB*m*P (**3**) (fraction 1) revealing its largely amorphous nature. c) WAXS pattern of the same polymer solidified by slow evaporation of dimethylformamide from a 1 % solution, indicative of crystalline order. Reflections were found corresponding to lattice spacings of 3.9, 7.6 and 9.1 Å. d) Plot of X-ray intensity vs. scattering vector ***q*** for the samples in (b) and (c).

Wide-angle X-ray scattering (WAXS) indicated that melt-compression-molded samples of PB*m*P were largely amorphous (Figure 3b). It should be noted, however, that as a result of to the particular chemical route employed PB*m*P (**3**) is a regioregular macromolecule that under the appropriate experimental conditions (e.g. slow cooling, slow precipitation from solution or in flow fields) should be able to form an ordered phase, similar to PC.[20] Solidification of the polymers from dimethylformamide (DMF) by evaporation of the solvent at room temperature yielded slightly birefringent films, indeed indicative of the presence of some crystalline order, consistent with their WAXS patterns (cf. Figure 3c). Standard analysis[21] of the radially integrated (0.3–3.5 Å^{-1}) patterns yielded a degree of crystallinitiy of approximately

5 % (Figure 3 d). DSC thermograms of such samples featured endothermic transitions in the range from 185–210 °C, which we attribute to melting of crystalline PB*m*P.

Owing to their relatively low molar masses, melt-compression-molded films of PB*m*P fractions 2 and 3 displayed such brittleness that their mechanical properties could not be tested in a reliable manner. In stark contrast, films of the high-molar-mass fraction 1 were flexible and tough and could be deformed well past the yield point. In Figure 4, results are presented of room-temperature tensile deformation tests of these polyarylene films (thickness ≈150 μm). For comparison, stress–strain curves are presented also of melt-compression-molded films of similar thickness of common a-PS, PMMA, and PC. The PB*m*P films, although of a somewhat lower stiffness, featured a nominal stress at break similar to the above polymers, but, remarkably, exhibited a macroscopic elongation at break that surpasses those of the highly brittle former two bulk polymers, and approaches that of PC, which is reputed for its toughness (cf. Table 2, Figure 4).

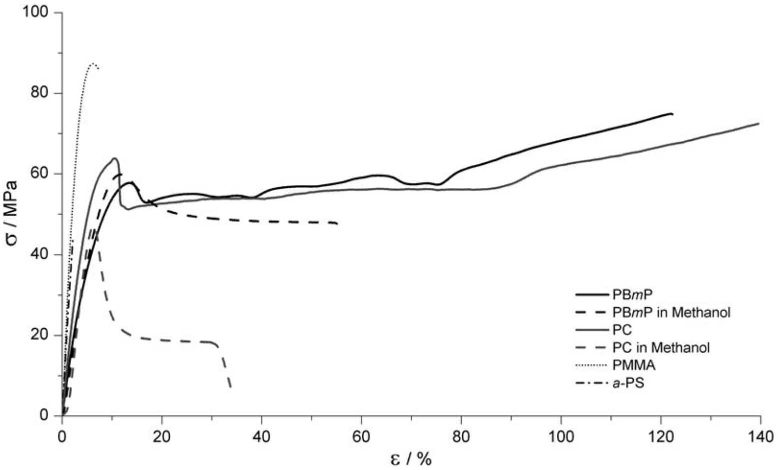

Figure 4. Stress–strain curves, recorded at room temperature of melt-compression molded films of PB*m*P (**3**) (fraction 1). For reference purposes, corresponding curves of a-PS, PMMA, and PC are also shown, illustrating the excellent mechanical properties of the new polyarylene (cf. Table 2). Also plotted are stress–strain curves of PB*m*P and PC samples recorded while immersed in methanol, showing the superior resistance of the former polymer against environmental stress-cracking induced by this liquid.

An undesirable feature of amorphous polymers is their tendency to become increasingly brittle in the course of time.[22–24] The latter phenomenon—commonly referred to as "aging"—typically manifests itself in a significantly increased yield stress and reduced elongation at break.[25,26] Gratifyingly, accelerated aging studies revealed that storage of films of PB*m*P fraction 1 at 110 °C for periods of up to 1 month caused only a gradual increase in yield strength of 28 % at 5.4 MPa per decade, accompanied by only a modest reduction of the elongation at break of 15 %. These results compare favorably with those of PC under similar experimental conditions.[26]

Table 2: Direct comparison of some mechanical properties of PB*m*P (**3**) with those of PC, PMMA, and a-PS.

Polymer	Young's modulus [GPa]	Yield stress [MPa]	Tensile strength [MPa]	Strain at break [%]	Strain energy [$\mathrm{MJ\,m^{-3}}$]
PB*m*P	1.0	57.7	75.0	122	71.8
PC	2.3	63.8	78.3	160	96.3
PMMA	3.2	87.3	87.3	7	4.9
a-PS	2.4	–	44.1	2	0.5

Another major drawback of most glassy polymers is the sensitivity of their mechanical properties to specific solvents, generally referred to as environmental stress-cracking.[16,17] Most interestingly, in tensile tests carried out with samples immersed in methanol, PB*m*P displayed a superior resistance to this unwanted feature when compared to PC (cf. Figure 4). This beneficial property may be of relevance in, for instance, medical applications, where sterilization at elevated temperatures and contact resistance against alcohols are critical requirements.

The chemical structure of the poly(*meta*-phenylene) **3** presented here can be easily varied and, thus, it may serve as a model for a new family of high-performance materials. From a synthetic point of view, it should be possible to widely vary both the structure of the backbone and the lateral substituent(s), as well as to create random copolymers. Furthermore, P*m*Ps may be designed to fold up into helices, whose length is determined by the degree of polymerization and whose pore diameter is defined by the distance between consecutive *meta* units in the backbone. Specifically, in regard to helix length, such polymers are likely to be superior to their extensively explored congeners, the monodisperse foldamers.[27]

Experimental Section

Reference materials: Atactic polystyrene (a-PS; $M_w = 350 \times 10^3$) and poly(methyl methacrylate) (PMMA; $M_w = 250 \times 10^3$) were obtained from Polysciences and polycarbonate (Makrolon LQ-2847) from Bayer MaterialScience. Prior to use, the polymers were dried at 70 °C under vacuum for at least 48 h.

Films: Films of all materials were prepared by melt-compression molding at 210 °C under a pressure of about 50 MPa, yielding homogeneous samples of a thickness of about 150 μm.

Thermal analysis: Thermogravimetric analysis (TGA) was conducted in air at a scan rate of 2 $\mathrm{K\,min^{-1}}$ with a Mettler Toledo TGA/SDTA851^e instrument. Differential scanning calorimetry (DSC) was carried out with a Mettler Toledo DSC822^e instrument under N_2 atmosphere at a scan rate of 10 $\mathrm{K\,min^{-1}}$. The sample weight was ca. 5 mg. All samples were first heated to a temperature of 240 °C, then cooled down to room temperature at a rate of 10 $\mathrm{K\,min^{-1}}$, prior to recording the glass-transition temperatures reported here.

Mechanical properties: Mechanical testing was performed at room temperature with an Instron tensile tester (model 4411). For this purpose films were prepared as indicated above, from which standard dog-bone-shaped samples were cut. The sample gauge length was 11.8 mm and the cross-head speed was 10 mm min^{-1}. In a second set of experiments, the resistance against environmental stress-cracking of PB*m*P and reference PC was examined by carrying out tensile tests of similar samples while the samples were immersed in a bath filled with methanol.

Wide-angle X-ray scattering: WAXS patterns were recorded with a Diffraction Xcalibur PX from Oxford Instruments (Scotts Valley, USA), using Mo$_{K\alpha}$ radiation ($\lambda = 0.71$ Å).

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