Living Polymerization

Tri- and Tetracarbanionic Initiators by a Lithium/Halide Exchange Reaction: Application to Star-Polymer Synthesis**

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Although well described by a mechanism involving the formation of ate complex intermediates, especially in the case of aryl halides, and routinely used for the preparation of simple organolithium reagents, lithium/halogen exchange reactions could never be successfully applied to the synthesis of precisely defined polylithium organic compounds.[1] Indeed polylithiations of multihalide organic molecules by reagents such as *tert*-butyllithium or *sec*-butyllithium are reported to result at best in moderate yields and to afford products with different degrees of substitution.[2–6] The reasons that are generally held responsible for the impracticality of polylithiation, especially when the halogen atoms to be substituted are attached to the same carbon atom or to adjacent carbon atoms, are twofold. α-Lithium halide eliminations and intermolecular couplings between the lithiated reagent and the halide-substituted species are two important competing reactions that have long prevented polylithiation reactions being considered practical. Another reason for the lack of attention paid to multiple metal/halide exchange is the fact that polylithiated compounds have limited solubility in most organic solvents, since they form rather insoluble aggregates.[7]

For instance, in polymer chemistry polylithiation has never been contemplated for the reasons mentioned above; had it been mastered and the experimental conditions worked out, polylithiation would be a viable and straightforward route to prepare multicarbanionic initiators for the synthesis of star-shaped polymers. So far the only possibility of generating such multicarbanionic initiators was lithiation by addition to multivinyl compounds, but the very small number of reports on this synthetic strategy indicates that it is not a convenient route. Indeed it requires the prior synthesis of multivinyl compounds that would not homopolymerize on addition of organolithium reagents.[8] These constraints explain why the only initiator of precise functionality ever synthesized by this method is the tricarbanionic compound of Quirk et al., which was obtained by addition of *sec*-butyllithium to a molecule containing three 1,1-diphenylethylene-type unsaturated moieties.[9]

We report here a novel approach to the preparation of polylithium organic compounds by lithium/halogen exchange and their use as initiators for the synthesis of miscellaneous star polymers by anionic means. This method relies on the metalation of poly(aryl halide)s whose halogen atoms are carried by separate aryl rings and not by adjacent carbon atoms as in previous cases. Unlike regular halogen/metal exchanges, metalation in our case could be conducted at room temperature and in apolar medium, since the polylithiated species formed were unexpectedly found to be soluble in the presence of σ/μ-coordinating ligands; this remarkable feature could be further exploited for star polymer synthesis.

To successfully demonstrate the viability of our method, we utilized commercially available bis(aryl halide) **1** and also designed two poly(aryl halide)s carrying respectively three (**2**) and four (**3**) halo groups, which were synthesized by using reported procedures.[10,11] Compound **2** was obtained from 4-bromoacetophenone diethyl ketal and acetyl chloride with samarium trichloride as catalyst, and **3** was prepared in excellent yields (> 90 %) by Diels–Alder reaction of 2,3,4,5-tetrakis(*p*-bromophenyl)cyclopentadienone and phenylacetylene with extrusion of carbon monoxide (see Supporting Information for the ^{1}H NMR spectra of **2** and **3**). Next, **1**, **2**, and **3** were treated with stoichiometric amounts of *sec*-butyllithium in benzene to generate **1′**, **2′**, and **3′**, the corresponding di-, tri-, and tetracarbanionic initiators (Scheme 1).

The formation of 2-bromobutane (**4**) was monitored by GC (see Supporting Information). In all three cases the yields were quantitative, and only 2-bromobutane and the corresponding protonated polyaryl compounds were formed as products. No coupling between 2-bromobutane and the polycarbanionic species **1′**, **2′**, or **3′** was ever detected, that is, in apolar medium no such side reactions occurred. However, the resulting polylithiated species were insoluble in benzene and therefore could not be used as such for

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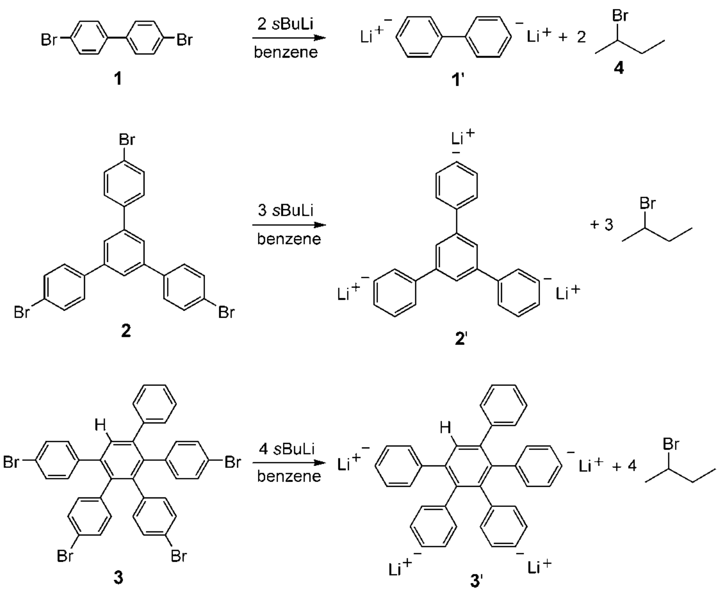


Scheme 1. Synthesis of dilithiated (**1′**), trilithiated (**2′**), and tetralithiated (**3′**) initiators.

initiation purposes; the investigated monomers (styrene, butadiene, 1,1-diphenylethylene) failed to react with these aggregates. Various additives were therefore employed to solubilize the polycarbanionic species. The ligand that proved most efficient at solubilizing these carbanionic aggregates regardless of their functionality was lithium 2-methoxyethoxide (**5**). This σ/μ ligand was previously employed by Teyssié et al. to prevent lithium enolates from aggregating in apolar medium and thus bring about a living anionic polymerization of methacrylic monomers.[12] A ratio of [lithium 2-methoxyethoxide] to [C_6H_4Li groups] of four was necessary to obtain fully soluble initiators in benzene (see Supporting Information). In these attempts at solubilizing **1′**, **2′**, and **3′**, **5** was prepared separately by reaction of *sec*-butyllithium with 2-methoxyethanol, but in the subsequent polymerization experiments **5** was simply generated in situ by addition of *sec*-butyllithium prior to lithium/halide exchange by **1**, **2**, or **3**.

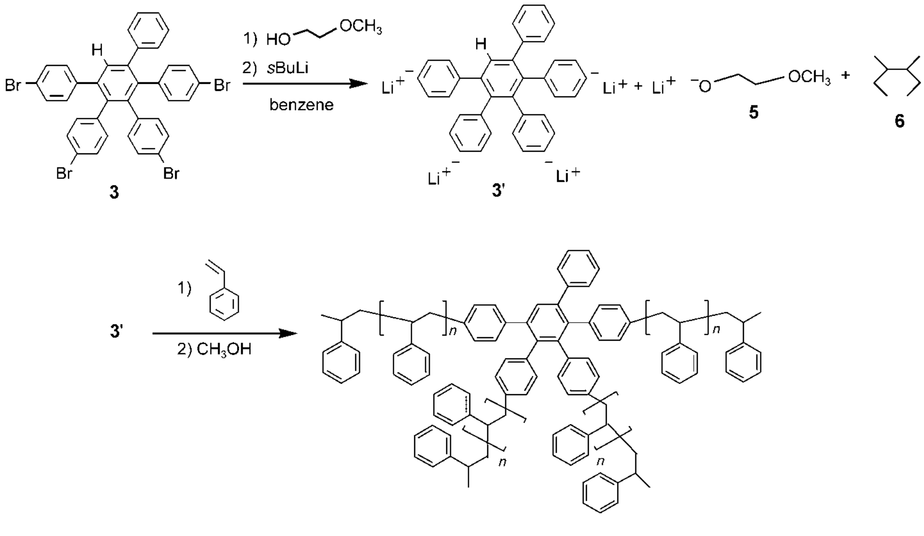
Before triggering polymerization by monomer addition, we managed to neutralize **4** that resulted from the lithium/halide exchange reaction; even though **4** is inert enough not to react with poly(aryl lithium)s **1′**, **2′**, and **3′**, it is sufficiently electrophilic to deactivate the growing carbanionic chains of polystyrene or polybutadiene. Indeed, in a separate experiment conducted under stoichiometric conditions in benzene, we observed such deactivation of polystyryllithium anions by **4** in the presence of *N*,*N*,*N′*,*N′*-tetramethyethylenediamine, when **4** completely disappeared within less than 30 min. To neutralize **4** prior to monomer addition one equivalent of *sec*-butyllithium was added and the formation of 3,4-dimethylhexane (**6**) was monitored by GC (see Supporting Information). After checking that the neutralization of **4** was complete, the polymerization of styrene or butadiene could be triggered by addition of the corresponding monomer (Scheme 2). On deactivation of the living carbanionic chains by ethylene oxide after complete monomer consumption, ω-hydroxy three- and four-armed polystyrene and polybutadiene stars could be isolated from **2′**, **3′** as initiators. α,ω-Dihydroxy telechelic polymers were obtained from **1′**.

Analysis by GC and size exclusion chromatography (SEC) indicated the complete consumption of initiators. No peak attributable to residual **1**, **2**, or **3** could be detected in the low molar mass region, and the only trace seen was a narrow and monomodal peak corresponding to the expected star or linear polymer in the high molar mass region (Figure 1).

Such narrow molar mass distribution ($\bar{M}_w/\bar{M}_n < 1.1$) reflects a rate of initiation by **1′**, **2′**, or **3′** comparable to that of propagation (Table 1). The structure of the polymer formed and specially the star character could be established first by ^{1}H NMR analysis on polybutadiene samples with low degrees of polymerization (see Supporting Information). From the ratio of the integrals of the signal for the aromatic core ($\delta = 6.8$–7.3 ppm) to that for the methylene protons of the $-CH_2OH$ chain ends ($\delta = 3.7$ ppm) the actual functionality of the various samples prepared could be determined: functionalities close to three and four for the three- and four-arm polybutadiene stars, respectively, and close to two for the telechelics were obtained.

Characterization of both linear and star polystyrene and polybutadiene samples by SEC with a light-scattering detector (SEC-LS) also showed an excellent agreement between experimental and expected values of molar masses.

Further evidence for the three- and four-arm star structures was obtained by comparing the intrinsic viscosity $[\eta]$ of our samples with that of linear polymers. Indeed, a classical



Scheme 2. Synthesis of four-armed polystyrene stars.

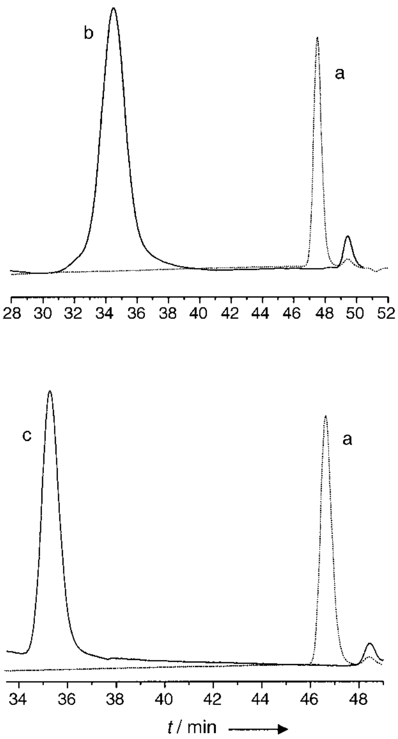
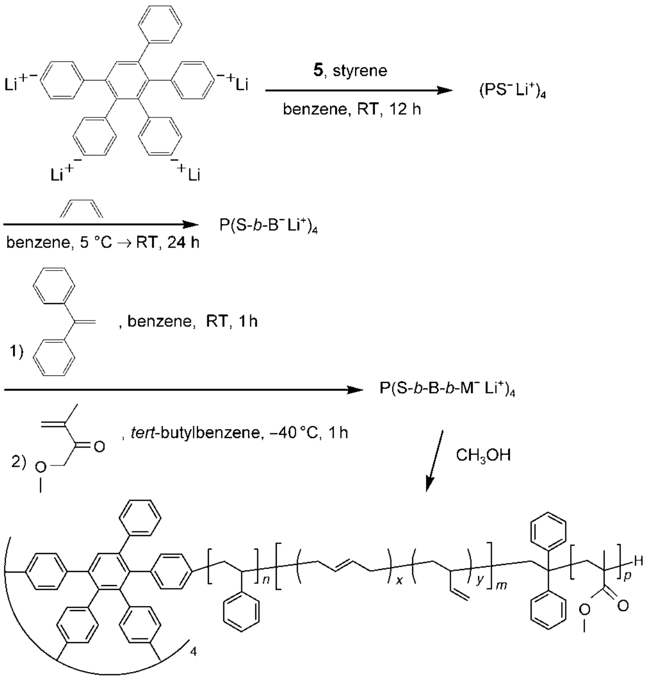


Figure 1. SEC eluograms of (PS)$_4$ polystyrene and (PB)$_4$ polybutadiene stars. a) Protonated version of **3′**. b) Polystyrene star. c) Polybutadiene star.

means to probe starlike architectures and their actual functionality is to determine $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$. As can be seen in Table 1, the calculated g' values are close to those predicted by theoretical models.[13] These results thus confirm that the target structures were actually obtained and validate the pertinence of our novel approach to star synthesis by anionic means.

After demonstrating the efficiency of these di-, tri-, and tetracarbanionic initiators for the synthesis of polystyrene and polybutadiene telechelics and stars, (ABC)$_n$ ($n = 2$–4) linear and star block terpolymers were derived by sequential anionic polymerization of styrene (S), butadiene (B), and methyl methacrylate (M) with **1′**, **2′**, or **3′** as initiator. These novel architectures—P(S-*b*-B-*b*-M)$_2$ pentablock terpolymers from **1′**, P(S-*b*-B-*b*-M)$_3$ and P(S-*b*-B-*b*-M)$_4$ star block terpolymers from **2′** and **3′**, respectively—were prepared by the same sequence of monomer addition as for the synthesis of P(S-*b*-B-*b*-M) linear block terpolymers (Scheme 3).[14]



Scheme 3. Reaction scheme for the synthesis of SBM star block terpolymers.

Since lithium 2-methoxyethoxide (**5**) was present as an additive to solubilize **1′**, **2′**,or **3′**, methyl methacrylate could be polymerized under living conditions, as disclosed by Teyssié et al.,[12] from polybutadienyllithium anions. Prior to the addition of M, polybutadienyllithium anions were end-capped with 1,1-diphenylethylene (DPE) to reduce the probability of side reactions at the ester group of M while initiating its polymerization. The reaction medium was also diluted with *tert*-butylbenzene and the temperature decreased to −40 °C to further prevent the above-mentioned side reactions. Upon addition of M, the color of the medium changed from the characteristic red of diphenylethyllithium carbanions to colorless. By taking an aliquot before introduction of each type of monomer, the formation of these SBM-based architectures could be easily followed by SEC (see Supporting Information).

The absolute molar mass of the first PS block could be determined by SEC-LS; as for PB and PM blocks their respective molar masses were deduced by ^{1}H NMR spectroscopy, given the known molar masses of their precursors (Table 2,

Table 1: Characterization of PS and PB samples synthesized from initiators **1′**, **2′**, and **3′**.

	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_{n(\text{theo})}$[c]	f[d]	g'[e]	$g'_{(\text{theo})}$ Zimm–Stockmayer[f]	Berry[g]	Grest[h]
PS$_2$	11200	1.12	12000	1.9	–	–	–	–
PS$_3$	90800	1.08	89000	3.0	0.805	0.91	0.88	0.99
	131000	1.13	128000	3.0	0.846	0.91	0.88	0.99
PS$_4$	38400	1.08	39500	3.9	0.75	0.83	0.79	0.79
	98600	1.08	120000	3.9	0.79	0.83	0.79	0.79
PB$_3$	32500	1.03	30000	3.0	–	–	–	–
PB$_4$	16400	1.05	17200	3.9	–	–	–	–

[a] Determined by SEC in THF with a multiangle laser light scattering detector. The dn/dc value was taken equal to that of linear polystyrene (dn/dc = 0.183 cm^3 g^{-1} in THF). [b] Derived from refractometric detector. [c] $\bar{M}_{n(\text{theo})} = M_{\text{styrene}} \times ([\text{Styrene}]/[\text{C}_6\text{H}_4\text{Li groups}]) \times n$ ($n = 2$, 3, or 4). [d] Average functionality of the samples as determined by ^{1}H NMR spectroscopy. [e] Experimental values of $g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$. [f] $g'_{\text{R.W.}} = (2/f)^{1.5}[0.396(f-1)+0.196]/0.586$[13a] (R.W. = random walk). [g] $g' = g'_{\text{R.W.}}{}^{0.5} = [(3f-2)/f^2]^{0.5}$.[13b] [h] $g' = K'F^{\beta}$ ($K = 2.37$, $\beta = -0.789$).[13c]

Table 2: Characterization of P(S-*b*-B-*b*-M)$_2$ pentablock and P(S-*b*-B-*b*-M)$_3$ and P(S-*b*-B-*b*-M)$_4$ star block terpolymer samples.

	PS		P(S-*b*-B)		P(S-*b*-B-*b*-M)		Microstructure
	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_w$[b]	[% 1,2-(B)][d]
(SBM)$_2$	30000	1.09	35000	1.1	41000	1.2	60
(SBM)$_3$	2800	1.08	5700	1.1	7500	1.1	75
(SBM)$_4$	6100	1.05	12100	1.1	16100	1.2	70

[a] Determined by SEC in THF by using a multiangle laser light scattering detector. The d*n*/d*c* value of PS was 0.183 cm^{3}g^{-1} in THF. [b] Derived from refractometric detector. [c] Determined by ^{1}H NMR spectroscopy from the molar mass of the polystyrene block, assuming 100% efficiency in the initiation of the second and third blocks. [d] Calculated from ^{1}H NMR spectra.

Figure 2). In all cases narrow molar mass distributions were observed for the three types of structures, that is, the growth of the three blocks occurred under living conditions. In some instances, P(S-*b*-B-*b*-M)$_{3,4}$ star block terpolymers were contaminated with P(S-*b*-B)$_{3,4}$ precursors (less than 10%) but the latter could be easily removed by fractionation through a silica column.

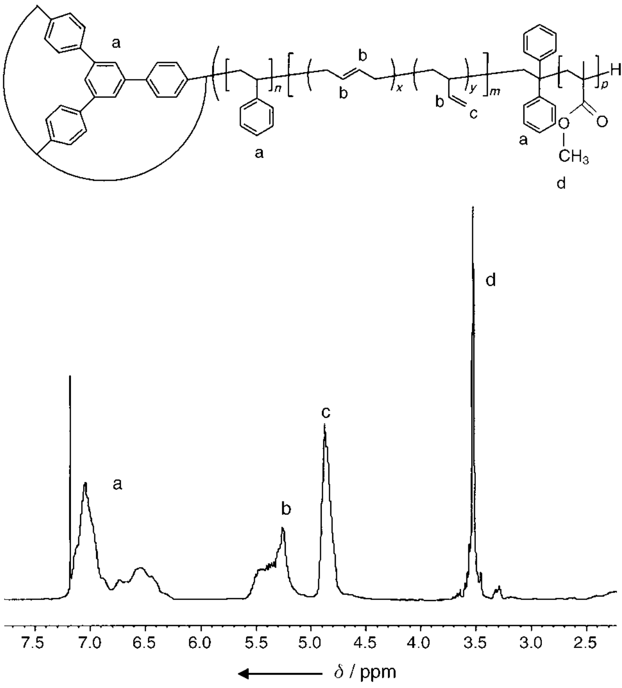


Figure 2. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of P(S-*b*-B-*b*-M)$_3$ star block terpolymer.

In summary, halogen/lithium exchange reactions have been successfully applied to generate di-, tri-, and tetracarbanionic species from bis-, tris- and tetrakis-bromoaryl compounds. The use of a σ/μ ligand was instrumental in obtaining polycarbanionic initiators soluble in apolar medium, and the subsequent preparation of various well-defined star-shaped (co)polymers. These are the first examples of three and four-armed polystyrene and polybutadiene stars synthesized by the "core-first" method using anionic polymerization. Analysis of the macromolecular architectures obtained by SEC-LS, ^{1}H NMR spectroscopy, and viscometry all endorse the star character and functionalities of three and four for the samples derived from **2′** and **3′**, respectively. The efficiency of the latter was even exploited to synthesize P(S-*b*-B-*b*-M)$_3$ and P(S-*b*-B-*b*-M)$_4$ star block terpolymers. The phase separation and morphologies that develop in such materials are currently under investigation and will be compared with those reported for linear SBM copolymers.[15] The synthesis of a compound carrying ten bromoaryl moieties by Diels–Alder reaction between a diarylacetylene and a tetraphenylcyclopentadienone is contemplated. Such halogen/metal exchange chemistry is ripe to be applied for the derivatization and/or the selective "construction" of C−C bonds in polycyclic aromatic hydrocarbons.[16]

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[1] a) H. Gilman, F. W. Moore, *J. Am. Chem. Soc.* **1940**, *62*, 1843–1846; b) G. Wittig, *Angew. Chem.* **1958**, *70*, 65.

[2] a) R. West, P. C. Jones, *J. Am. Chem. Soc.* **1969**, *91*, 6156–6161; b) R. West, P. A. Carney, I. C. Mineo, *J. Am. Chem. Soc.* **1965**, *87*, 3788–3789.

[3] a) R. West, E. G. Rochow, *J. Org. Chem.* **1953**, *18*, 1739–1742; b) C. Chung, R. J. Lagow, *J. Chem. Soc. Chem. Commun.* **1972**, 1078–1079.

[4] a) F. J. Landro, J. A. Gurak, J. W. Chinn, R. M. Newman, R. J. Lagow, *J. Am. Chem. Soc.* **1982**, *104*, 7345–7346; b) J. A. Gurak, J. W. Chinn, R. J. Lagow in *Chemistry for the Future* (Ed.: H. Grünewald), Pergamon, New York, **1982,** pp. 107–113.

[5] a) J. R. Baran, R. J. Lagow, *J. Am. Chem. Soc.* **1990**, *112*, 9415–9416; b) J. R. Baran, C. Hendrickson, D. A. Laude, R. J. Lagow, *J. Org. Chem.* **1992**, *57*, 3759–3760.

[6] C. Tsitsilianis, G. Vogiagis, J. K. Kallitsis, *Macromol. Rapid Commun.* **2000**, *21*, 1130–1135.

[7] A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 268–276.

[8] N. G. Vasilenko, E. A. Rebrov, A. M. Muzafarov, B. Eßwein, B. Striegel, M. Möller, *Macromol. Chem. Phys.* **1998**, 199, 889–895.

[9] R. P. Quirk, Y. Tsai, *Macromolecules* **1998**, *31*, 4372–4375.

[10] K. J. Cheng, Z. B. Ding, S. H. Wu, *Synth. Commun.* **1997**, *27*, 11.

[11] J. F. Wolfe, F. E. Arnold, *Macromolecules* **1981**, *14*, 909.

[12] J. S. Wang, R. Jérôme, P. Bayard, M. Patin, P. Teyssié, *Macromolecules* **1994**, 27, 4635.

[13] a) B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **1949**, *17*, 1301; b) G. C. Berry, *J. Polym. Sci. Polym. Phys. Ed.* **1971**, *9*, 687; c) G. S. Grest, L. J. Fetters, J. S. Huang, D. Richter, *Advances in Chemical Physics*, Wiley, New York, **1996**, 94.

[14] V. Krappe, R. Stadler, I. Voigt-Martin, *Macromolecules* **1995**, *28*, 4558.

[15] R. Stadler, C. Auschra, J. Beckman, U. Krappe, I. Voigt-Martin, L. Leibler, *Macromolecules* **1995**, *28*, 3080.

[16] M. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267.