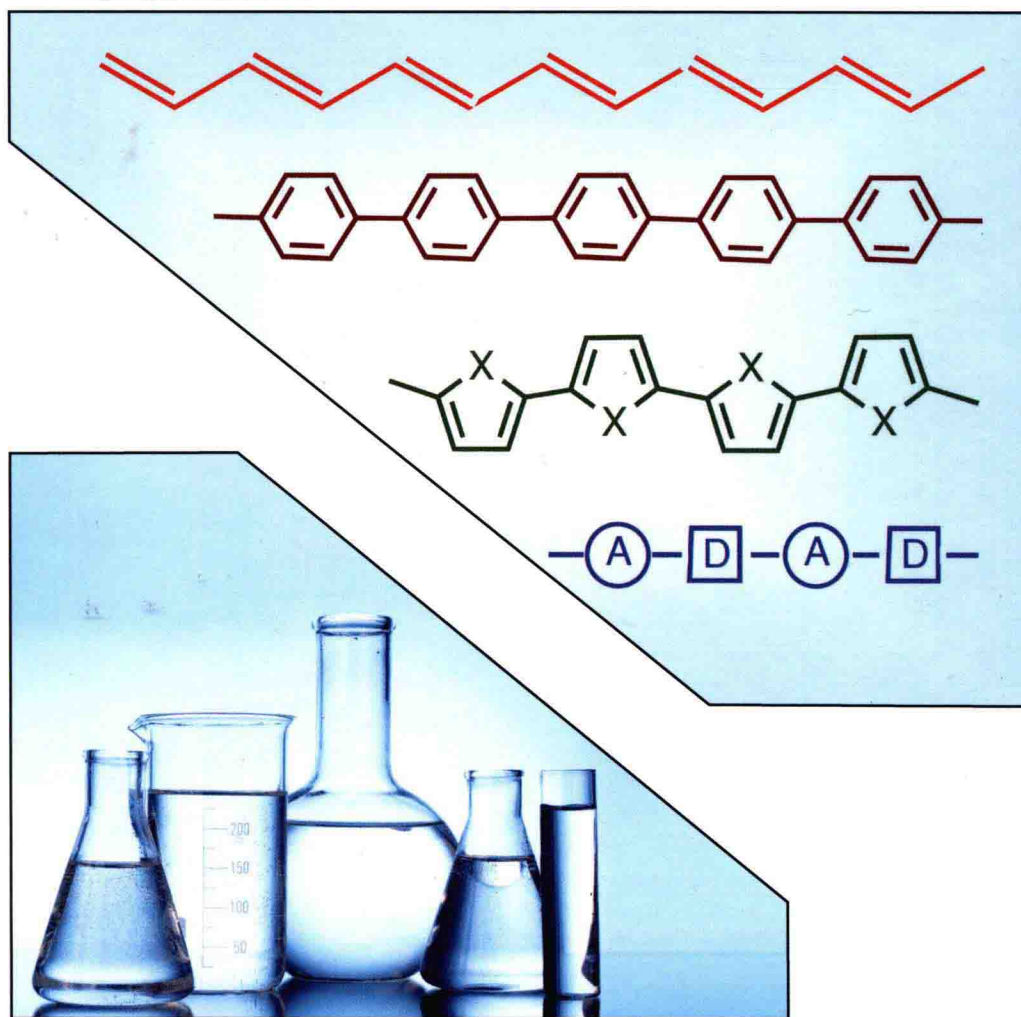


RSC Polymer Chemistry Series

Edited by Klaus Müllen, John R Reynolds and Toshio Masuda

# Conjugated Polymers

A Practical Guide to Synthesis



RSC Publishing

# ***Conjugated Polymers***

## ***A Practical Guide to Synthesis***

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RSC Publishing

RSC Polymer Chemistry Series No. 9

ISBN: 978-1-84973-799-9

ISSN: 2044-0790

A catalogue record for this book is available from the British Library

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Published by The Royal Society of Chemistry,  
Thomas Graham House, Science Park, Milton Road,  
Cambridge CB4 0WF, UK

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# Conjugated Polymers

## A Practical Guide to Synthesis

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*This book is dedicated to our spouses, Renate Müllen,  
Dianne Reynolds and Keiko Masuda, for the understanding and support  
they have given us in all that we do.*



# Preface

Why conjugated polymers? A convincing answer to this question can be given in three parts: conjugated polymers are fascinating species from i) a structural point of view due to the many ways of establishing an extended pi-conjugation; ii) a functional point of view due to their electronic and optical properties, which qualify them as active components of organic electronics; and iii) a research point of view due to their potential of fostering cross-disciplinary research.

Since we live in a material world there cannot be novel technology without new or improved materials, and they must be synthesized. Synthesis is both a matter of creative design and experimental skill, and no target structure can prove this claim better than conjugated polymers. The crucial role of synthesis is what has led to the concept of this book; not so much as a theoretical exercise “on-paper”, but as a practical, “hands-on” approach. It is intended to convince the reader of the beauty of conjugated polymer design and synthesis, but not set aside the technical difficulties and experimental pitfalls.

A good case can be made by first taking a look at the device and then work backwards to the synthesis of the functional molecules. Technologies and also the underlying materials stand in competition with each other. Organic electronics face the fact that inorganic semiconductors, such as silicon, have beautiful properties and are thus strong contenders. One may think of the high charge carrier mobilities and the vanishing exciton binding energy. What stands against that is the “designable” structural and functional versatility of their organic counterparts, highlighted by the ease of their synthesis and processing. Even in the organic field, conjugated polymers must compete with small organic molecules, which can be made structurally perfect and can be processed by vacuum techniques.

Whatever material is considered, organic synthesis is generally performed in solution. The active function of an organic electronic device, however, cannot



be understood or even tailored by restricting one's attention to the dilute solution. It is rather a matter of solid thin films and their interfaces. An important criterion, when judging the function of an organic field effect transistor (OFET) as a switch, is high charge carrier mobility. This depends upon the solid state packing and thus the supramolecular order of the semiconductor. Likewise, "bright" emission from an organic light emitting diode (OLED) requires different layers with defined interfaces to keep the charge recombination zone away from the metal electrode; and this, next to high film quality, depends upon the orthogonal solubility of the different conjugated polymers used. The situation in an organic photovoltaic device (OPV) is, from a morphological point of view, even more complex. What is needed in such a device is a nanophase separation of electron donor and electron acceptor components to ensure, after charge separation, efficient percolation of holes and electrons. It is the complexity of the underlying functional processes that explains why physics, engineering and materials science are so important – or at least have the last say when it comes to device performance and stability.

Again, the whole endeavor starts with synthesis and this shall be considered in greater detail now. Even the more distant reader will be aware of "classical" conjugated polymer structures, such as poly(*p*-phenylene) (PPP), poly(phenylenevinylene) (PPV) and polythiophene (PT). Here the "usual suspects" are incorporated as building blocks: benzene, thiophene or a C=C double bond. It does not need much imagination, however, to dream up structural modifications, which brings us to the unbelievable manifold of design opportunities. When we take a closer look at the nature of the building blocks, benzene can be replaced by larger polycyclic aromatic hydrocarbons (PAHs) that also leave us with different ring positions as coupling points. Hydrocarbons can be replaced by their heterocyclic analogues, which is particularly important for the electron donor or acceptor character of the final macromolecule. The search for even more repeat units can have different driving forces, empirical or theoretical, and is often coupled to device results. This can also explain why the community sometimes follows fashion. Presently, donor units, such as bridged dithiophenes, and acceptor units, such as benzothiadiazole or diketopyrrolopyrrole, seem to be particularly popular. When different building blocks are incorporated there are many ways of doing this, statistically or in a defined sequence. Conjugated polymers with an alternating array of donor and acceptor repeat units have been studied as low band gap materials for efficient light harvesting in OPV. Another important structural modification becomes possible by an increase in the dimensionality of the macromolecules when going from a (linear) chain to a step ladder or even full ladder polymer. A logical extension then is a true two-dimensional pi-system, such as a graphene sheet, which has recently attracted immense attention. Finally, all these polymer architectures possess inherent rigidity that can severely limit solubility and thus solution processability. Alkyl substitution is therefore a mandatory step. There is of course, the danger of compromising extended conjugation when the additional substituent causes torsion of the building blocks about the interring bonds, and substituents may be considered

to “dilute” electronic properties. Nevertheless, alkyl substituents can also have beneficial effects by directing supramolecular order during film formation. This is also true when more complex topologies are targeted, such as diblock or multiblock copolymers made from rod or coil segments. The latter aspect is not only relevant for electronic reasons – bringing electron rich and electron poor domains into close proximity to one another – but also for morphological reasons, where phase separation can be enforced at the desired length scale.

All these design opportunities concern the macromolecular structure – prior to processing – and they are, indeed, decisive for key electronic and optical features, such as, for example, the wavelength of absorption and emission or their function as n-type *vs.* p-type semiconductors. One might go as far as to claim that, based on these subtle structure–property relationships, (opto)electronic properties can be “synthesized”. Or one might even go a step further and encode desired supramolecular characteristics to introduce weak intermolecular forces during molecular design, although in this case structure–property relationships are much less well developed. Here is, however, a very critical point: all these design opportunities are easily sketched on paper but do not necessarily translate easily into a glass flask. This brings us to the key issue of this book: the synthesis of conjugated polymers.

When talking about conjugated polymer synthesis, an initial question concerns the availability and purity of the suitably functionalized building blocks. Thereby, the required synthetic efforts can be quite different and demands by the community can lead to the commercial availability of starting compounds. Closely connected to this is the question of the polymerization reaction, that is to say how the building blocks are subjected to a repetitive coupling. Remarkably enough, while step-growth methods have long been the “classical” polymerization mode, chain-growth methods have recently been realized as well. This of course holds promise for establishing “living” end-groups and offers new opportunities for block copolymer synthesis. Transition metal-catalyzed reactions developed in organic and organometallic chemistry have had a huge impact on conjugated polymer synthesis, and this holds true for methods not only of carbon-carbon, but also carbon-heteroatom (*e.g.* nitrogen) connections. Many of these commonly used pathways are addressed as “named reactions” honoring their inventors and, indeed, these inventions can hardly be overestimated. These reactions allow the connection of aromatic ring systems to a polymer chain *via* homo- or hetero-atom couplings, and there the reader will readily envisage how important the above mentioned strictly alternating incorporation of donor and acceptor moieties is. Apart from aromatic building blocks, vinylene and ethynylene elements can be introduced as well. Here it is rewarding to compare transition-metal catalysis with older procedures, such as connective double-bond formation.

Is it thus sufficient, when targeting a particular polymer structure, to check the literature for the right building blocks and the best mode of coupling? The answer is definitely no, and there are at least two reasons for that. The first one, even if somewhat discouraging for a physicist who feels that the synthetic plan looks quite easy, concerns the experimental conditions. A typical case is

rigorous exclusion of oxygen and water since these can affect catalyst activity and trigger unwanted side-reactions. The choice of reaction temperature and time should be mentioned here as well. The second reason is that the nature of the building block and the chosen synthetic method must be carefully adjusted. Thus, steric hindrance may slow down the growth of the macromolecule so much that side reactions come into play, which can either stop further growth or induce side reactions. The issue of side reactions, even if occurring as minor processes, is critical. A typical case is the so-called Wessling Zimmermann synthesis of PPV, which played an important role for the development of light emitting devices based upon conjugated polymers in the early nineties. This advance in the synthetic procedure was achieved *via* a precursor polymer, which was finally transformed into the conjugated chain *via* a 1,2-elimination process. Failure to accomplish this quantitatively will, of course, lead to an interrupted pi-conjugation. Even more severe is the fact that side reactions can lead to (ketonic) defects that act as traps for the excited states of the light emitting device. Let us come back to the question of the mechanism of the polymer forming reaction. In a step-growth polycondensation, high molecular weights can only be achieved for high degrees of conversion and thus the coupling of intermediate oligomers. Even if limitations imposed by solubility can be excluded, mismatch of the stoichiometries must be avoided, and this relates to the absence of side reactions.

Conjugated polymer synthesis, in order to be meaningful, requires an even higher level of sophistication, and this raises the question of how we describe its molecular structure. We commonly denote the prevailing repeat units, written in parenthesis, and then add “*n*” for the number of repeat units, even if it is often not specified. There are ample cases, particularly in recent literature, where the molecular weight and the polydispersity of an individual polymer play a decisive role in the device performance, such as charge carrier mobility. This, by the way, can readily be understood when considering the above mentioned ordered packing of polymer chains. Then, it is clear that further features come into play, such as the mode of end-capping. Impurities, as has been mentioned, can serve as traps not only for excitons, but also for charges, and structural irregularities do not only interrupt pi-conjugation, but also hamper regular packing. It follows that the above way of denoting a polymer is in urgent need of careful specification. Otherwise, the whole research field is in danger of criticism, such as “*they measure very precisely, but they do not precisely know what they measure*”.

This book is intended to show the beauty of conjugated polymer synthesis without ignoring the difficulties and obstacles. While organic electronics are often tempted to follow the fascination of device fabrication, this book takes the opposite direction in a synthesis-first approach. This approach requires imagination, but also scrupulous optimization of experimental conditions combined with careful proof of structural perfection.

Considering the above, a strong plea is made herein to activate the good old virtues of organic synthesis, and these will certainly prove their value when, for example, pushing the limits of molecular weight or handling a low band gap

polymer with its inherent chemical instability. There are, however, still many open territories for conjugated polymer synthesis. The new challenges could concern a complex combination of properties, such as making a charge transporting polymer also responsive to stimulus-driven switching or by connecting a conjugated polymer segment to a biomacromolecule for recognition and self-assembly processes. Furthermore, while we have so far focused on the power of solution synthesis, performing synthesis in the (bulk) solid state or on a surface could create significant advantages as one could not only build in the supramolecular order, but also avoid the additional difficulties of controlling solution processing. Whether synthesis is structure or method oriented, knowledge or application driven, or whether it targets new polymer structures or up-scales established ones, it finds room everywhere. But it is not always easy. However, we believe that this book will help to make it easier – and more successful.

Last but not least, we would like to thank all the authors who actively do research in the forefront of the conjugated polymer field for their excellent contributions. Thanks are also due to Professor Ben Zhong Tang, Editor-in-Chief of this book series for his continuous support and to Ms. Leanne Marle at the RSC office for her clerical assistance.

Klaus Müllen  
On behalf of the Editors



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