Mechanistic insight in rhodium-mediated carbene polymerization
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Chapter 6

Potential Applications of Poly-Carbenes; Towards Polymeric Surfactants and Polymeric Solar Cells?
6.1 Introduction

In the previous chapters we focused mainly on elucidating the reaction mechanism of the Rh-mediated stereoregular carbene polymerization process. This Chapter deviates from the general mechanistic topic of this Thesis, and describes two functionalizations of the new, highly functionalized, stereoregular polymeric materials towards potential new applications of these polymeric materials. First, we will show that we can generate amphiphilic block copolymers that form micelles by initiating the EDA polymerization on a preformed PEG polymeric chain containing an alcohol end-group. These materials potentially find application as polymeric surfactants (e.g. in micro-emulsion/micelle reactors in (catalytic) dual-phase reactions or as controlled-release drug carriers), as compatibilizers in blends of polymers containing different side-group substituents, or as emulgators for mixtures of water and less polar solvents. Secondly, we investigated the synthesis of polymers from several different diazo compounds expected to produce polymers with electron-conducting properties. Such polymers potentially find application in new polymeric solar cells.

6.2. Amphiphilic block copolymers

Amphiphilic block copolymers can be made by combining a hydrophobic segment and a hydrophilic segment in one polymer chain. By self-assembly of these amphiphilic polymers, micelles or liposomes (bilayer vesicles) can be formed (see Figure 1). By forming micelles the two different polymer segments separate an internal nonpolar compartment from an external polar solution, while for liposomes the internal compartment and external solution are both of the same polarity. Both micelles and liposomes can be exploited by using the interior compartments as, for example, controlled-release drug carriers or as nanoreactors.

Figure 1. Micelle (left) and liposome (right).

Amphiphilic block copolymers are also of interest for their potential use as compatibilizers in blends of polymers containing different side-group substituents and as emulgators for different water-solvent mixtures (e.g. in paints). One of the most well-studied polymers to display such amphiphilic behavior is [poly{1,3-butadiene},ethylene oxide]{n}, in which the butadiene part is hydrophobic (and does not contain any functional groups, only the hydrocarbon backbone) and the ethylene oxide block polymer corresponds to the hydrophilic segment. When the hydrophobic compartments contain polar groups it can promote coordination of
Potential applications of poly-carbenes

catalysts and reactants, which has been shown to positively influence different catalytic reactions performed in micelles of these polymers. These polymers are challenging to make by known routes. The Rh-mediated carbene polymerization methodology described in the previous chapters of this Thesis potentially provides an easier, more straightforward method to synthesize such amphiphilic block copolymers. New amphiphilic block copolymers potentially have additional advantages imposed by the special properties of PEA, as explained below.

Scheme 1. Polymerization of ethyl diazoacetate (EDA) to form high molecular weight, stereoregular poly(ethyl 2-ylidene-acetate) (PEA).

PEA contains a polar ester moiety on every C-atom of the backbone. The polar groups are ordered in a syndiotactic manner. These features lead to self-aggregation of PEA into triple helices, thereby producing rigid thermotropic and lyotropic liquid crystalline polymers. Despite the presence of polar substituents, PEA polymers are not very polar. They readily dissolve in dichloromethane and chloroform, but not in alcohols or water. Apparently, the regular helical arrangement of the ester moieties around the polymeric chain reduces the dipolar effect of each individual ester moiety, leading to a mild polarity of PEA (partial cancelation of the total dipole moment of the polymer). Hence, despite the high number of polar ester moieties, PEA is a hydrophobic polymer which exhibits thermotropic and lyotropic liquid crystalline behavior. These combined properties make amphiphilic block copolymers based on PEA potentially interesting for several applications.

In this section the focus is on the synthesis and isolation of such polymers. We here show that it is indeed possible to obtain such amphiphilic block polymers employing the Rh-mediated carbene polymerization methodology developed in our group.

6.2.1. Chain transfer by PEG

To obtain an amphiphilic block polymer, a hydrophobic PEA chain should be combined with an hydrophilic polymer. We argued that this should be possible by making use of alcohol-mediated chain-transfer properties of the Rh-mediated carbene insertion polymerization methodology. As described in Chapter 2 and 4 (theoretical investigations in Chapter 5), chain-transfer on alcohol moieties is rather slow and quite high concentrations of alcohols are needed to affect efficient chain-transfer. Therefore it should be possible to simply mix alcohol-terminated poly(ethylene glycol) (PEG) in the carbene-polymerization reaction mixture. Previous studies already revealed that PEG is suitable as hydrophilic block of other amphiphilic block copolymers, inducing efficient micelle formation. Hence, we decided to use PEG as chain-transfer agent in the EDA
polymerization reaction. PEG contains two alcohol groups, tri-block copolymers can be expected (A in Figure 2). However, alcohol-mediated chain-transfer is a relatively slow process compared to carbene insertion propagation (see Chapters 4 and 5) and formation of di-block copolymers cannot be excluded. To exclusively obtain di-block polymers, methoxy poly(ethylene glycol) (mPEG) was also used (B in Figure 2).

In our previous studies the longest alcohol used to engage chain-transfer in carbene polymerization was butanol (C4-unit). Therefore, we first needed to investigate if long PEG-type polymers ($M_w$ 200-5000 Da) can be used at all in similar chain-transfer reactions.

Figure 2. Synthesis of amphiphilic block copolymers with A) EDA and PEG to form di-block polymers and tri-block polymers, B) EDA and mPEG to form di-block polymers.

We used the easily accessible [($\mu$-Cl)Rh(cod)]$_2$ complex as a catalyst for these initial experiments. As was shown in Chapter 2, this dinuclear complex easily breaks-up to form an active catalytic species in the presence of alcohols. PEG and mPEG were, just like in previous alcohol-mediated chain-transfer experiments with small alcohols, added in excess (between 5 eq.-12 eq.). PEG and m-PEG with different $M_w$ were added to the reaction mixture (PEG $M_w$ of 200 (PEG200), PEG $M_w$ of 600 (PEG600), PEG $M_w$ of 1500 (PEG1500), PEG $M_w$ of 3400 Da (PEG3400) and m-PEG $M_w$ of 550 (mPEG550) and 5000 Da (mPEG5000) to see if the different diffusion properties of short PEG ($M_w < 1500$ Da) compared to long PEG ($M_w > 1500$ Da) have an influence on the reaction. Also the different properties of block copolymers with varying block lengths are of interest. The reaction was carried out by combining the catalyst and the PEG in dichloromethane and subsequently adding EDA at room temperature. When using PEG with $M_w > 1500$ Da, we increased the reaction temperature to 40$^\circ$C in order to obtain a homogeneous reaction mixture. After a reaction time of 16h, the solvent was evaporated and the remaining solid was washed with MeOH and water. During work-up it became clear that separation of the excess PEG/mPEG and the formed polymers was challenging and was not accomplished by washing with MeOH and water only.
polymer fractions after washing still contained residues of PEA homopolymer and unreacted PEG/mPEG. Obtaining pure PEA-PEG copolymers was essential to be able to correctly interpret analytical results. To remove the excess of PEG/mPEG several separation techniques were used, including column chromatography with silica and alumina and size exclusion chromatography (SEC) with Sephadex and BioBeads. Furthermore, separation by dialysis with a membrane (pore size = 0.5 - 2 KDa) was tried for the polymerization reactions with PEG $M_N < 600$ Da. The fractions obtained by these different separation methods were analyzed by $^1$H NMR, IR, MALDI-ToF MS and GPC. All the data of these analysis still showed traces of unreacted PEG/mPEG in the polymer fraction. Nevertheless, the MALDI-ToF data indicated that chain-transfer by PEG/mPEG was indeed successful. The MALDI-ToF spectra show a peak pattern of 44 Da and 86 Da, for the copolymerization reactions with PEG200 and mPEG550, corresponding to a block copolymer (see Figure 3 and at the end of this Chapter). The signals overlap and make the peaks very broad. Similar results were obtained for PEG1500 but a peak pattern was less clear.

The spectrum in Figure 3 shows the presence of free PEG200, a large fraction of PEA homopolymer (containing only a 86 Da peak pattern of PEA) and a fraction of block polymers. The overlapping signals correspond to linear block copolymers, HO–(OCH$_2$CH$_2$)$_n$–(CH(COOEt))$_m$–H $+$ Na$^+$ and cyclic copolymers –O–(OCH$_2$CH$_2$)$_n$–(CH(COOEt))$_m$ $+$ Na$^+$ (see Figure 4).
Table 1. Assignment of a selection of the peaks of block copolymer PEA-PEG200: HO–(OCH₂CH₂)ₙ–(CH(COOEt))ₘ–H + Na⁺ and –O–(OCH₂CH₂)ₙ–(CH(COOEt))ₘ+ Na⁺.

<table>
<thead>
<tr>
<th>Linear copolymer (Da)</th>
<th>Cyclic copolymer (Da)</th>
<th>Rep. units PEA (m)</th>
<th>Rep. units PEG (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2413.0</td>
<td>2411.0</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>2455.1</td>
<td>2453.5</td>
<td>26</td>
<td>4</td>
</tr>
<tr>
<td>2499.1</td>
<td>2497.1</td>
<td>26</td>
<td>5</td>
</tr>
<tr>
<td>2541.6</td>
<td>2539.1</td>
<td>27</td>
<td>4</td>
</tr>
<tr>
<td>2585.1</td>
<td>2583.1</td>
<td>27</td>
<td>5</td>
</tr>
<tr>
<td>2671.1</td>
<td>2669.2</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>2673.2</td>
<td>2671.2</td>
<td>27</td>
<td>7</td>
</tr>
<tr>
<td>2713.2</td>
<td>2711.2</td>
<td>29</td>
<td>4</td>
</tr>
</tbody>
</table>

Formation of unsaturated block copolymers HO–(OCH₂CH₂)ₙ–(CH(COOEt))ₘ–C(COOEt)=CH(COOEt) + Na⁺ is an alternative explanation for the signals ascribed to the cyclic polymers, and cannot be excluded.

The amphiphilic nature and emulsifying properties of the PEA-PEG block copolymers are most likely the reason for the difficult separation of the PEG, PEA and block copolymer fractions. The PEA-PEG block copolymers have very similar properties to both PEG and PEA, and readily aggregates with both. This limits the effectiveness of any separation technique. PEA-PEG copolymers with longer PEG segments (Mₘ > 1500) show higher concentrations of free PEG and PEA in the analytical data, probably due to the tendency of long PEGs to have a greater affinity to form aggregates than those with short PEG segments. Due to the aggregation behavior, the large structures are not separated into individual polymer chains during chromatography, therefore elution of the different polymers happens simultaneously and a mixture is collected. Increasing the solvent polarity leads to less aggregation, probably due to stronger interactions between dissolved PEG and the polar solvent, hence leading to somewhat better separations. However, even in a highly polar eluent such as acetonitrile, separation of PEA-PEG copolymers to obtain these separately, from free PEA and PEG could not be achieved.
6.2.2 Emulsifying properties of PEA-PEG block copolymers

While the abovementioned difficulties to purify PEA-PEG copolymers from PEA and PEG homopolymers are unfortunate, they also reveal the emulsifying and amphiphilic properties of the block copolymers. Hence, we decided to briefly investigate these properties of the obtained polymer mixtures. We anticipated that mixing the block copolymers with water and organic solvents should lead to emulsification despite the presence of the homo-PEG and homo-PEA impurities. Indeed, when the copolymer mixture was combined with DCM and small amounts of water, opaque white mixtures were formed; this emulsification occurs with all copolymers (see Figure 5), except for PEA-PEG200.

![Figure 5. Left: PEA-PEG1500 in water, middle: PEA-PEG1500 in DCM, right: PEA-PEG1500 in water and DCM which forms an emulsion.](image)

Interestingly, emulsions of PEA-PEGs 1500 and 3400 and PEA-mPEG5000 were stable even after standing for several days at room temperature. The comparatively poor emulsifying property of PEA-PEG200 is possibly due to the small ratio of the hydrophilic part compared to the hydrophobic chain in this copolymer. Future investigations should reveal whether the above emulsions are based on reversed micelles or vesicles, and should further focus on the use of these aggregates as micro reactors. It would also be interesting to investigate the use of the block copolymers as compatibilizers in polymer blends.

6.2.3 Conclusions PEA-PEG block copolymers

PEG can function as a chain-transfer agent and block copolymers of PEA-PEG are formed, as was confirmed by MALDI-ToF and GPC analysis. As expected, these block polymers show amphiphilic properties and act as emulsifiers of water and dichloromethane. The nature of these emulsions (reversed micelles or vesicles) is currently not clear. The emulsions obtained when using PEA-PEG copolymers with a PEG-block > 200 Da are surprisingly stable.

Separation of the copolymers from homo-PEA and homo-PEG proved to be highly challenging. This is likely due to properties of the PEA-PEG block copolymers. They have very similar properties to both PEG and PEA, and likely readily aggregate with both, thus limiting the effectiveness of any separation technique. On the other hand, this is a desirable property when aiming for applications of these block copolymers as...
compatibilisers in polymer blends. These future applications, as well as the potential use of micelles or vesicles in DCM/water emulsions as nano-reactors in two-phase catalytic reactions, is a topic for future research.

6.3. Side-chain π-π electron transfer hopping in poly-carbenes?

Other potential applications of poly-carbenes may arise from their unique structure, for example their potential use as conducting polymers. While the main-chain of these polymers is saturated (hence poorly conducting), these polymers have the unique property of having a functionality attached to every carbon atom of the polymeric backbone. This places these functionalities in a very close position. When using aromatic functionalities, this allows for efficient π-π stacking effects, both within a chain and among different polymeric chains. We wondered if we could use this feature to prepare polymers with special properties, like conductivity through the side-chains of these polymers. Such a property may find potential application in solar cells completely based on polymers. Therefore we decided to prepare a series of new polymers in which the design encompasses side-chain conducting properties, and we explored their properties. We also briefly investigated their potential use as electron transport materials in polymer-polymer solar cells.

In fact, the development of new, cheap and efficient polymer-based organic solar cells strongly depends on the discovery of new, improved polymeric materials with efficient electron-injection and effective electron- and hole-transport properties. The development of such solar cells is crucial for future sustainable energy production. Most commercial solar cells are Si-based and have a power conversion efficiency of nearly 25%. However, the high price of these Si-based devices, primarily due to the requirement of high purity crystalline semiconductors, is a strong motivation to develop cheaper alternatives such as polymeric solar cells. However, current polymer-polymer solar cells have an even low power efficiency, due to the unavailability of polymers with electron-accepting capability. We hypothesized that with proper modifications, resulting in electron-accepting properties of the polymers, the highly functionalized, stereoregular carbene polymers may contribute to a potential solution to this challenge. These polymers offer a new approach of electron transfer in the polymer. Instead of common electron-transfer through a conducting polymer backbone, we expect that the close proximity of the side-groups in poly-carbenes may allow electron-transfer via π-π stacking of the side-groups of the polymer. We anticipated that this may be beneficial for the development of polymeric solar cells based on the bulk-heterojunction principle (vide infra).

In the next sections we will first explain why specific monomers were chosen to form potential electron-accepting polymers (section 6.3.1). Next the characterization of the polymers formed is described (section 6.3.2). We also briefly investigated their potential for use as electron-accepting polymers in polymeric solar cells (section 6.3.3). The
description of this last section starts with a brief explanation of polymeric solar cells and the general requirements of the electron-accepting materials in these devices. In the remaining part of this section we compare the electron-accepting properties of the new polymers with those of known materials used in polymeric solar cells.

6.3.1. Monomer selection

The polymerization of BnDA leads to polymers with special properties. \(^1\)H NMR of these polymers show shielding effects. These arise from \(\pi-\pi\) stacking interactions as shown in Scheme 2.\(^1\) The self-assembled \(\pi-\pi\) stacks of the aromatic rings generate inter and intra-chain interactions between the aromatic rings.\(^2\) Because of this stacking effect, electrons can potentially hop between different phenyl groups, either inter- or intra-chain, creating many different pathways for electron transport. It is important to note that the \(\pi-\pi\) stacking of the PBnA passes through the side chains as opposed to the \(\pi-\pi\) stacking that passes through the backbone of the polymer.

Although the electron transport of PBnA should be feasible in theory, one important property is missing in PBnA: it is not a good electron-accepting material. Therefore, accepting substituents have to be incorporated into the polymer.

![Scheme 2. Polymerization of BnDA to PBnA and a schematic representation of the chain interactions in PBnA.](image)

We chose fluoro- and cyano-groups as electron-accepting substituents to influence the electron-accepting properties of the polymers. Hence, we synthesized the new diazo compounds CNBnDa (A), \(\text{F}_3\text{BnDa} \text{ (B)}\) and \(\text{F}_5\text{BnDa} \text{ (C)}\) (see Scheme 3). These are highly electronegative and relatively small. They were polymerized with [(\(L\)-pro)Rh(Me\(\text{cod}\))] in chloroform.\(^3,20\) Copolymerization with BnDA was also carried out to increase the solubility of the obtained polymer. Furthermore, we hoped that the addition of BnDA to \(\text{F}_3\text{BnDa}\) would have an additional effect, perhaps allowing the synthesis of alternating copolymers. It is known that preorganization through \(\pi-\pi\) stacking occurs between hexafluorobenzene and other aromatic rings like benzene, toluene and \(p\)-xylene when mixed in a 1:1 ratio.\(^21,22\) This pre-organization is also observed in radical polymerization of styrene and pentafluorostyrene, allowing the
Chapter 6

synthesis of close-to alternating copolymers.\(^{23}\) Formation of alternating copolymers from BnDA and F\(_5\)BnDA would be interesting. Previous studies have shown that alternating donor/accepting polymers in solar cells have a smaller band-gap, as a result of the high-lying HOMO of the donor being combined with the low-lying LUMO of the acceptor.\(^{24,25,26}\) A similar effect can be expected in alternating copolymers formed by copolymerization of BnDA and F\(_5\)BnDA. This pre-organization could be established by a shift of the peaks in the \(^1\)H NMR spectra. A 1:1 mixture of the monomers was measured by \(^1\)H NMR experiments and indeed the peak of the \(-\mathrm{O}-\mathrm{CH}_2-\)R and the benzyl show a small shift (between 0.02-0.2 ppm, see Table 2). This small shift indicates a weak \(\pi-\pi\) stacking in solution caused by preorganization of the monomers, which could lead to alternating copolymers in the polymerization reaction.

Table 2. \(^1\)H NMR of the BnDA, F\(_5\)BnDA and a 1 to 1 mixture of both.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>CH (ppm)</th>
<th>(-\mathrm{O}-\mathrm{CH}_2-)R (ppm)</th>
<th>Bn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BnDA</td>
<td>4.80</td>
<td>5.21</td>
<td>7.37</td>
</tr>
<tr>
<td>F(_5)BnDA</td>
<td>4.81</td>
<td>5.30</td>
<td>-</td>
</tr>
<tr>
<td>Mix</td>
<td>4.80*</td>
<td>5.19 (F(_5)BnDA) and 5.27 (BnDA)</td>
<td>7.35</td>
</tr>
</tbody>
</table>

* The CH protons of BnDA and F\(_5\)BnDA form one peak

We first investigated the homopolymerization of CNBnDa (A), F\(_3\)BnDa (B) and F\(_5\)BnDa (C). The obtained yields and \(M_n\) of the new homopolymers are low (Table 3, entries 1-3), most likely due to the poor solubility of the polymers in chloroform and DCM leading to precipitation during the polymerization.\(^{27}\) Next we also investigated the copolymerization of CNBnDa (A), F\(_3\)BnDa (B) and F\(_5\)BnDa (C) with BnDa. These reactions lead to higher polymer yields and higher \(M_n\) polymers, probably because the
Potential applications of poly-carbenes
copolymers are much better soluble in chloroform and DCM than the above homopolymers. It is not very clear if these copolymers are random or alternating copolymers, but most likely they are random. Their characterization and the characterization of the homopolymers, is described the next section.

Table 3. Polymerization and characterization of the acceptor carbene polymers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_n$ (kDa)$^a$</th>
<th>DPI$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CNBnDA (A)</td>
<td>PCNBnA</td>
<td>14.0</td>
<td>4.2</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>F$_3$BnDA (B)</td>
<td>PF$_3$BnA</td>
<td>14.5</td>
<td>8.0</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>F$_3$BnDA (C)</td>
<td>PF$_3$BnA</td>
<td>29.5</td>
<td>6.9</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>A / BnDA (1:1)</td>
<td>P(CNBnA-co-BnA)</td>
<td>32.5</td>
<td>310</td>
<td>2.7</td>
</tr>
<tr>
<td>5</td>
<td>B / BnDA (1:1)</td>
<td>P(F$_5$BnA-co-BnA)</td>
<td>22.4</td>
<td>283</td>
<td>2.9</td>
</tr>
<tr>
<td>6</td>
<td>C / BnDA (1:1)</td>
<td>P(F$_3$BnA-co-BnA)</td>
<td>25.0</td>
<td>278</td>
<td>2.7</td>
</tr>
</tbody>
</table>

$^a$ SEC analysis calibrated against polystyrene samples.

6.3.2 Characterization of the polymers
The ratio of the different monomers present in the polymers was estimated by integration of the corresponding peaks in the $^1$H NMR spectra. The substituents on the benzyl-ring did not influence the ratio of the monomers (almost 1:1 ratio, see Table 4), which makes alternating organization of the polymer certainly possible.

Table 4. Monomer ratio in the copolymer, determined with $^1$H NMR.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio in the polymer (RBnA/BnA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CNBnA-co-BnA)</td>
<td>0.49/0.51 (CNBnA/BnA)</td>
</tr>
<tr>
<td>P(F$_5$BnA-co-BnA)</td>
<td>0.42/0.58 (F$_5$BnA/BnA)</td>
</tr>
<tr>
<td>P(F$_3$BnA-co-BnA)</td>
<td>0.51/0.49 (F$_3$BnA/BnA)</td>
</tr>
</tbody>
</table>

There was no indication of block copolymer formation, since the NMR spectra did not show separate peaks for the CH, CH$_2$ and benzyl of the BnA and acceptor monomer. The chemical shifts differ from those in the homo-polymers, but the NMR spectra did not give conclusive evidence for formation of either random or alternating copolymers, however all signals of the two monomers overlap in the NMR spectra. All 2D NMR techniques attempted proved useless to distinguish between these two possibilities.

As in the corresponding homo-polymers, π-π stacking in the polymer is also observed in the copolymers. Shielding effects (upfield shifts)$^{28,29}$ observed in the $^1$H NMR spectra of PBnA for the CH$_2$ signal caused by the electron density of the benzyl-rings (see Figure 6) are smaller in the polymer analogs with electron-withdrawing groups. The F$_5$, F$_3$ and CN substituents, both in the homopolymer and in the copolymers, mask such shielding effects on the CH$_2$ peak and deshielding is observed as a result of the electron withdrawing groups (see Table 5).$^{30}$
Figure 6. Schematic overview of the effect of the electron density: more shielding effect of the high electron density part above the benzyl-groups in PBnA compared to the benzyl-groups in PF$_5$BnA and more deshielding effect of the electron poor part outside the benzyl-ring of PBnA compared to PF$_5$BnA.

Table 5: $^1$H NMR chemical shifts of the polymers and copolymers at room temperature in CDCl$_3$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>-O-CH$_2$R (ppm)</th>
<th>CH (ppm)</th>
<th>Bu (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PF$_5$BnA</td>
<td>5.12</td>
<td>3.2</td>
<td>7.65-7.35</td>
</tr>
<tr>
<td>2</td>
<td>PCNBnA</td>
<td>5.08</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PF$_3$BnA</td>
<td>4.97</td>
<td>3.51</td>
<td>6.85 and 7.18</td>
</tr>
<tr>
<td>4</td>
<td>P(F$_3$BnA-co-BnA)</td>
<td>4.85</td>
<td>3.42</td>
<td>7.18</td>
</tr>
<tr>
<td>5</td>
<td>P(F$_5$BnA-co-BnA)</td>
<td>4.83</td>
<td>3.54</td>
<td>6.72 and 7.13</td>
</tr>
<tr>
<td>6</td>
<td>P(CNBnA-co-BnA)</td>
<td>4.76</td>
<td>3.59</td>
<td>7.12</td>
</tr>
<tr>
<td>7</td>
<td>PBnA</td>
<td>4.74</td>
<td>3.62</td>
<td>7.05-7.14</td>
</tr>
<tr>
<td>8</td>
<td>P(EA-ran-BnA)</td>
<td>3.9 and 4.9</td>
<td>3.4</td>
<td>7.2</td>
</tr>
<tr>
<td>9</td>
<td>PEA$^2$</td>
<td>4.1</td>
<td>3.2</td>
<td>-</td>
</tr>
</tbody>
</table>

The CH peak in PBnA is shifted downfield. Also this effect is masked in both in the homopolymers and copolymers with F- and CN-substituents. Here the CN- and F-substituents effectively have a deshielding effect on the CH moiety of the backbone (see Figure 5). For PCNBnA and PF$_3$BnA the effects are smaller than in PF$_5$BnA. The (de)shielding effects of the copolymers are an average of PBnA and their corresponding homopolymers. These shifts confirm self-aggregation of these polymers into π-π stacked assemblies of (co)polymers. Due to this stacking the polymers can form nanostructures, which is, at least potentially, beneficial for efficient charge transport in bulk heterojunction polymeric solar cells.

The thermal stability of the new (co)polymers was investigated with thermogravimetric analysis (TGA). TGA measurements show stable polymers up to 300°C, which is typically an indication of stereoregular polymers (see Figure 6).$^{20}$ (atactic materials have a decomposition temperature of ~180°C).$^{22}$ Only PCNBnA has a decomposition temperature of 250°C. This lower temperature is probably due to disordered packing induced by the cyano substituents. For all three copolymers the curve falls in-between the curves of the two corresponding homopolymers without any overlap. From this we can conclude that in the copolymerization reaction no homopolymers nor block copolymers are formed.
The polymers were further analyzed by Differential Scanning Calorimetry (DSC) to measure their degree of crystallinity and to get information about their liquid crystallinity (as reported for PEA and PBnA). Unexpectedly, PCNBnA and PF₅BnA (and their copolymers with PBnA) did not reveal any crystalline to liquid-crystalline transition in DSC (Table 5). The transition observed for PF₅BnA has a lower enthalpy value compared to PBnA. Give the unexpected absence of this transition for PCNBnA and PF₅BnA, the DSC data are again inconclusive for either formation of alternating or random copolymers in case of P(CNBnA-co-BnA) and P(F₅BnA-co-BnA). The lower Tc and much lower crystallinity of P(F₃BnA-co-BnA) compared to both PBnA and PF₃BnA may suggest the formation of a random copolymer. The higher Tc of P(F₅BnA-co-BnA) compared to PBnA is perhaps indicative for formation of an alternating copolymer.

Table 6. Thermal properties of the (co)polymers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCNBnA</td>
<td>80</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PF₅BnA</td>
<td>112</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>PF₃BnA</td>
<td>110</td>
<td>190</td>
<td>172</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>P(CNBnA-co-BnA)</td>
<td>59</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>P(F₅BnA-co-BnA)</td>
<td>84</td>
<td>201</td>
<td>195</td>
<td>0.003</td>
</tr>
<tr>
<td>6</td>
<td>P(F₃BnA-co-BnA)</td>
<td>75</td>
<td>147</td>
<td>130</td>
<td>0.006</td>
</tr>
<tr>
<td>7</td>
<td>PBnA¹</td>
<td>52</td>
<td>181</td>
<td>154</td>
<td>20</td>
</tr>
</tbody>
</table>

* Tm and Tc were determined from the heat flow curves, while the Tg was derived from the reversing heat flow curves.

Figure 7. TGA of the homo- and copolymers, A) PCNBnA B) PF₅BnA C) PF₃BnA.
The liquid crystalline phase of the (co)polymers was also investigated by optical microscopy, equipped with a hot stage. In agreement with the DSC data, but nonetheless unfortunately, only PF$_3$BnA reveals a liquid crystalline phase transition (see Figure 8). Compared to PEA and PBnA, this LC phase seems to be less well-defined (based on the above DSC data).

![Figure 8. Liquid crystalline phase transition of PF$_3$BnA at A) 194°C and B) 330°C.](image)

6.3.3 Potential application in polymeric solar cells?

A potential application of the above new polymers is their use as electron-accepting polymers in polymeric solar cells. Before we compare the properties of the materials with those of known materials used in bulk hetero-junction polymeric cells, we first give a brief description of the principles of such solar cells. Afterwards, the electron-conducting properties of the new polymers are describe concisely to determine whether or not these polymer can be applied in polymer-polymer solar cells.

6.3.3.1. Brief description of a polymeric solar cell device and the basic properties of its components

*Solar cell principles*

A solar cell is based on electron transfer from a donor material to an acceptor material, which is initiated by absorption of light. This electron transfer can happen when a photon gets absorbed by a photoactive polymer, which leads to the excitation of an electron from the HOMO to the LUMO. The electron will subsequently be donated to the LUMO of the accepting material only when the LUMO of the accepting material is lower in energy than the LUMO of the donating material. This is the driving force of the charge transfer. The band-gap (= HOMO-LUMO) of the material (see Figure 9) represents the lowest energy required to excite an electron.
Photons with energies equal or higher than this band-gap will be absorbed. Materials with smaller band-gaps will absorb more photons, which can lead to more efficient charge generation and a lower power output. Furthermore, when $\Delta E$ is small the efficiency of charge transfer will be high. This electron-excitation process will form an electron-hole pair, called an exciton. By charge separation of these excitons, the hole will travel through the donor material and the electrons through the acceptor material to reach the electrodes, which leads to current generation. It is important to note that the productive distance for electron-hole separation is limited, 5-20 nm. A smaller distance will lead to recombination of the charges without producing current. To obtain materials with these distances blends of acceptor and donor materials are made, so called bulk heterojunctions. In these materials the donor-acceptor interface can be easily reached by the excitons and therefore the focus is on this type of systems. Furthermore, the polymer blend should dissolve easily, to be able to form thin films for different processing techniques and analysis.
An efficient bulk-heterojunction depends on the availability of a liquid crystalline phase. The polymer folds into the thermodynamically most stable conformation during annealing, which in a liquid-crystalline phase is expected to lead to an arrangement that facilitates charge transfer and transport.\textsuperscript{12,13,47} The selection of the donor and acceptor materials is based on different properties and will be discussed in the next section.

**Donor material in heterojunctions**

To facilitate light absorption, the donor material should contain conjugated motifs based on sp\(^2\)-hybridized carbon atom systems (see Figure 11). This delocalization of electrons occurs due to $\pi-\pi^*$ transitions between the bonding and anti-bonding p\(_z\)-orbitals. Furthermore, to absorb more photons, the band-gap in the donor material should be small. Charge transport in these donor materials occurs by carriers, which can be intra-molecular (moving along the polymer chain) or inter-molecular (moving between two different chains). High regioregularity, the ability to form $\pi-\pi$ stacking between the different polymer chains and a high molecular weight will improve the charge transport and absorption.

**Acceptor material in heterojunctions**

The acceptor material should accept the excited electron of the donor material and it should therefore have a lower lying LUMO compared to the LUMO of the donating material (see Figure 9). The acceptor material should also have fast charge transfer properties to transport the electron to the electrode.\textsuperscript{48} This can occur in the same way as in the donor material via a conjugated system.

**Solar cell example**

One of the most efficient polymer-based solar cells is currently a mixture of poly-(3-hexyl thiophene) (P3HT) (see Figure 12A) as donor material and 1-(3-methoxy carbonyl)propyl-1-phenyl[6,6]C\(_{61}\) (PCBM) (see Figure 12B) as acceptor material. This blend has a liquid crystalline phase, which leads indeed to folding the polymers into the thermodynamically most stable conformation during annealing.\textsuperscript{49,50,51,52} However, this photoactive material has a limited power conversion efficiency of 6%.\textsuperscript{13,11,53,54,55}
The P3HT material used is based on thiophene rings that can readily delocalize electron density as well as participate in π-π stacking. The hexyl-side groups on the thiophene have two purposes, to increase the solubility of the polymers, since polythiophenes typically have poor solubility, and to form lamellar-stacking motifs. Due to the two types of stacking in this molecule a higher structural order can be formed. These structures improves the efficient hole mobility, a key property to optimize for donor materials. In the P3HT-PCBM system, the acceptor (PCBM), is a C60-based molecule, a its highly conjugated system, which can easily accept electrons and has fast charge transfer, furthermore it has a good solubility, making it a suitable acceptor material. There are only a few electron-accepting polymers known, poly[2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene)] (CNPPV) and poly(9,9-diocetylfluorene-co-benzothiadiazole) (F8BT) are two of the rare examples, nevertheless the results of power conversion efficiencies are lower compared to the P3HT-PCBM material. This low conversion is due to the less effective charge transfer in these polymer mixtures. In these mixtures perfect charge transfer only takes place at the interface, therefore the morphology is important. In the next section we compare some of the basic requirements of electron-accepting polymers used in polymeric solar cells with the corresponding properties of the new (co)polymers described above. For this we will make a direct comparison with the known P3HT-PCBM system.

6.3.3.2. Determination of the acceptor properties of the new (co)polymers

The properties of the polymers obtained by Rh-mediated carbene polymerization are potentially interesting for applications in polymeric solar cells; high molecular weight, high stereoregularity, good air-stability and the ability to form nanostructures by π-π stacking. A drawback of the homo-polymers is their rather low solubility, while a potential drawback of the copolymers is the fact that they do not reveal a clear liquid crystalline behavior. Nonetheless, we investigated the prospects of these new (co)polymers, containing accepting benzylic substituents, for potential application in polymer-polymer solar cells. For this reason we studied the electron-accepting properties of these new materials by means of cyclic voltammetry and UV-vis, EPR and fluorescence spectroscopy. Due to the low solubility, the homopolymers could only be analyzed by UV-vis spectrometry. We also investigated their chemical reduction. These
data are compared to the known P3HT-PCBM combination in existing polymeric solar cells. We first investigated the band-gap and the LUMO of the new acceptor polymers. This was measured by two different methods: UV-vis spectroscopy and cyclic voltammetry.

**UV-vis spectroscopy**

By calculating the band-gap ($E_{\text{opt}}^{\text{HOMO-LUMO}}$, see Figure 8), an indication is given about the minimum energy needed to excite an electron and it can be calculated by the formula $E_{\text{opt}}^{\text{HOMO-LUMO}} = h\nu_{\text{onset}}$. In solar cells, photons with at least this energy or higher, will be absorbed by molecules containing π-electrons to excite an electron. Hence, more photons will be absorbed for materials with smaller band-gaps.\(^6\) In Table 7 the $\lambda_{\text{onset}}$ measured with UV-vis absorption spectroscopy are given, and the corresponding $E_{\text{opt}}^{\text{HOMO-LUMO}}$ values estimated from these measurements are reported as well.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{\text{opt}}^{\text{HOMO-LUMO}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P3HT</td>
<td></td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>PCBM</td>
<td></td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>PCNBnA</td>
<td>242</td>
<td>334</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>PF$_5$BnA</td>
<td>263</td>
<td>292</td>
<td>4.3</td>
</tr>
<tr>
<td>5</td>
<td>PF$_3$BnA</td>
<td>269</td>
<td>287</td>
<td>4.3</td>
</tr>
<tr>
<td>6</td>
<td>P(CNBnA-co-BnA)</td>
<td>243</td>
<td>330</td>
<td>3.8</td>
</tr>
<tr>
<td>7</td>
<td>P(F$_5$BnA-co-BnA)</td>
<td>263</td>
<td>286</td>
<td>4.3</td>
</tr>
<tr>
<td>8</td>
<td>P(F$_3$BnA-co-BnA)</td>
<td>268</td>
<td>283</td>
<td>4.4</td>
</tr>
<tr>
<td>9</td>
<td>PBnA</td>
<td>258</td>
<td>279</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Unfortunately, the new (co)polymers have larger estimated band-gaps than P3HT and PCBM. This already makes them less suitable for application in polymeric solar cells. The homopolymers show a smaller band-gap compared to the copolymers, probably due to the fact that more electron-withdrawing groups are present. PCNBnA and P(CNBnA-co-BnA) have the lowest band-gap, this can be explained by an extra absorption band at a red shifted wavelength.

**CV**

Besides UV-vis, the band-gap can also be estimated electrochemically, using cyclic voltammetry (CV). The oxidation process and the reduction process can be measured by CV. The material is dissolved in a solvent containing a salt as supporting electrolyte and the potential is measured of the working electrode. The current is recorded and the onset of the oxidation wave and onset of the reduction wave is estimated (CV spectra at the end of this Chapter). These numbers are closely related to $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$.\(^6,67,68\)
Potential applications of poly-carbenes

\[ E_{\text{HOMO}} = -(E_{\text{ox onsets}} - E_{\text{fc}}) - 4.8 \text{ eV}^* \]

\[ E_{\text{LUMO}} = -(E_{\text{red onsets}} - E_{\text{fc}}) - 4.8 \text{ eV}^* \]

\[ E_g^{CV} = E_{\text{LUMO}} - E_{\text{HOMO}} \]

The \( E_{\text{LUMO}} \) of the acceptor material can be compared to the \( E_{\text{LUMO}} \) of the donor material. When \( E_{\text{LUMO-donor}} > E_{\text{LUMO-acceptor}} \) charge transfer can take place and the transfer is more efficient when the band-gap is small.

A thin film of the copolymers was applied to the working electrode using drop-casting, thus allowing measurements on ‘solid’ polymer samples. This makes it less comparable with the UV-vis measurements, which measures the energies in solution. The band-gap values measured by CV (Table 8) are depicted in Figure 13. The energies are compared to the energies of the P3HT-PCBM system to estimate the value of the energies of the copolymers.

**Table 8.** Electrochemical measurements and HOMO, LUMO and band-gap calculation (at onset potential).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( E_{\text{ox}} ) (V)</th>
<th>( E_{\text{red}} ) (V)</th>
<th>( E_{\text{HOMO}} ) (eV)</th>
<th>( E_{\text{LUMO}} ) (eV)</th>
<th>( E_g^{CV} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CNBnA-co-BnA)</td>
<td>3.35</td>
<td>-0.12</td>
<td>-7.77</td>
<td>-4.30</td>
<td>3.5</td>
</tr>
<tr>
<td>P(F5BnA-co-BnA)</td>
<td>3.57</td>
<td>-0.27</td>
<td>-8.00</td>
<td>-4.16</td>
<td>3.8</td>
</tr>
<tr>
<td>P(F3BnA-co-BnA)</td>
<td>3.34</td>
<td>-0.04</td>
<td>-7.72</td>
<td>-4.34</td>
<td>3.4</td>
</tr>
<tr>
<td>P3HT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCBM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) The potential values in this table are versus Ag/Ag\(^+\) reference electrode.

Figure 13. Schematic diagram of the HOMO and LUMO levels of the copolymers compared to P3HT and PCBM, 1: P(CNBnA-co-BnA), 2: P(F5BnA-co-BnA), 3: P(F3BnA-co-BnA).

\(^*\) \( E_{\text{fc}} \) is the half potential of the ferrocene standard and -4.8 eV is the ferrocene value, with respect to the vacuum level, which is defined as being zero.
The CV data clearly indicate that electron-transfer to the copolymer is possible when P3HT is used as donor material. However, comparing the LUMO of the copolymers with the LUMO of the PCBM, the energies are relatively low. These lower energy levels lead to less efficient charge transfer and is therefore less suitable for solar cells.

Noticeable, P(F$_3$BnA-co-BnA) appears to be a better electron-acceptor than P(F$_5$BnA-co-BnA) while the opposite would be expected. Perhaps, the chains in P(F$_3$BnA-co-BnA) are more closely packed due to less steric hindrance, and therefore electron-transfer to this polymer is easier. Another possibility is a difference in configuration of P(CNBnA-co-BnA) and P(F$_3$BnA-co-BnA) compared to P(F$_5$BnA-co-BnA). This last polymer may have an alternating configuration of the F$_5$Bn and Bn monomer-units (which may be more difficult to reduce), while P(CNBnA-co-BnA) and P(F$_3$BnA-co-BnA) are likely random (perhaps easier to reduce). This would be in agreement with the DSC data, and perhaps explains the quite unexpected electrochemical behaviour of these copolymers.

**Chemical reduction**

The acceptor properties of the copolymers were further investigated by chemical reduction of the material and electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy is commonly used to study the charge delocalization in (aromatic) molecules in solution. One-electron reduction is expected to generate an unpaired electron delocalized over the polymer chain, which can be detected by EPR. Hence, to see if the copolymers are capable of accepting electrons, P(CNBnA-co-BnA) and P(F$_3$BnA-co-BnA) were mixed with cobaltocene, a relatively strong reducing agent, and the EPR spectra of these mixtures were measured. The EPR spectra (Figure 14) indeed show spectra with g-values close to 2.00, consistent with electron-transfer to the polymers.

![Figure 14. EPR spectra of P(CNBnA-co-BnA) and P(F$_3$BnA-co-BnA).](image)
Potential applications of poly-carbenes

Emission quenching
A way to measure the potential of light-induced electron-transfer from the donor material to the acceptor material is by measuring the quenching of the emission of P3HT with the acceptor polymer. PCBM can completely quench the emission of P3HT, as well as PPV (poly(p-phenylene vinylene)).\footnote{69,70} If the newly synthesized copolymers are good acceptors, then the emission of P3HT and PPV should be quenched by our copolymers as well. Unfortunately, when P3HT or PPV were mixed with copolymers in a 1:1 M solution the same emission spectra were observed as in absence of the copolymers, thus indicating that emission quenching does not occur. Therefore, no electron transfer occurs either within the life-time of the exited states of P3HT and PPV. Hence, while the above measurements indicate that the copolymers are acceptor polymers, their band-gap is larger than that of PCBM and electron-transfer from the donor material to these polymers is too slow to allow light-induced electron transfer required for use in polymeric solar cells. Despite our expectations and initial indications of their acceptor behaviour, these polymers are not suitable for application in polymeric solar cells.

6.3.3. Conclusions about potential application of polycarbenes in polymeric solar cells
Six new types of electron-accepting polymers are synthesised via the Rh-mediated carbene polymerization with the goal to use them in polymer-polymer solar cells as the electron-accepting part. Benzyl groups substituted with electron-withdrawing F, F\textsubscript{3} and CN, were used as electron acceptor in homopolymers and (most likely random) copolymers with BnA and between these (substituted) benzyl rings, π-π stacking was observed in NMR experiments. These polymers are indeed capable of accepting electrons, as was shown with cyclic voltammetry, chemical reduction and EPR detection of the reduced form of the polymers. The level of the LUMO’s of these polymers (obtained using UV-vis spectroscopy) show that all copolymers can in principle accept electrons from P3HT as a donor material. However, band-gaps of the new copolymers are rather large, which already make them less suitable for application in polymeric solar cells compared to PCBM in known polymeric solar cells. While this problem can be in principle solved by using different substituents on the benzyl groups, we also encountered another, more serious problem of using these systems as acceptor materials in polymeric solar cells: Emission quenching of P3HT and PPV by the copolymers is not observed at all. Hence, electron-transfer from the donor material to these polymers is too slow to allow light-induced electron transfer, thus making the current materials unsuitable for application in polymeric solar cells. These characteristics may well (in part) be caused by a lack of order of these (most likely random) copolymers. The homopolymers are expected to have a higher order parameter of the conducting side-groups. However, unfortunately this also leads to a higher crystallinity with thus associated poor
solubility. This also makes the current homo-polymers unsuitable for application in this area, because this severely complicates the study and processing of these polymers. Nonetheless poly-carbenes with different substituents may still have interesting potential for future applications in this research area. Screening of more differently substituted monomers will be necessary to obtain such polymers having the optimal properties.

6.4 Overall conclusions

Amphiphilic block copolymers can be generated using Rh-mediated carbene polymerization in the presence of hydrophyllic PEG as a chain-transfer agent in production of hydrophobic PEA. These new “polymeric soaps” are potentially of interest for application in micro-emulsion/micelle reactors in (catalytic) dual-phase reactions, as controlled-release drug carriers, as compatibilizers in blends of polymers containing different side-group substituents, or as emulgators for mixtures of water and less polar solvents. A complication of this method is purification of the synthesized amphiphilic polymers.

Application of poly-carbenes as acceptor materials in polymer-polymer solar cells using benzylic diazo compounds with different cyano- and fluoro-substituents proved not possible. However, screening of other, differently substituted monomers may eventually lead to (co)polymers with the optimal properties for such applications. Hence, more effort is required to advance this potential application area.

6.5 Acknowledgements

Iris Krom and Medea Kosian are acknowledged for their contributions to this Chapter. Prof. Dr. T. J. Dingmans is acknowledged for analyzing the liquid crystalline phase of the polymers. Petra Aarnoutse is thanked for MALDI-ToF mass spectrometry analysis of the polymers.
Potential applications of poly-carbenes

Figure 15. $^1$H NMR spectrum (300 MHz) of syndiotactic PEA-PEG. Inset shows unfunctionalized atactic PEA.

Figure 16. MALDI-ToF spectrum of copolymerization of PEA-mPEG550, with an enlarged area of MS 3400-3800 Da.
Table 9. Of peaks of PEA-mPEG550 CH₃(OC₂H₄)_nO(CH(COOEt))_mH + Na.

<table>
<thead>
<tr>
<th>Peak (Da)</th>
<th>Rep. units PEA (m)</th>
<th>Rep. Units PEG (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3423.6</td>
<td>33</td>
<td>12</td>
</tr>
<tr>
<td>3425.6</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>3427.6</td>
<td>31</td>
<td>16</td>
</tr>
<tr>
<td>3465.6</td>
<td>34</td>
<td>11</td>
</tr>
<tr>
<td>3467.6</td>
<td>33</td>
<td>13</td>
</tr>
<tr>
<td>3469.0</td>
<td>32</td>
<td>15</td>
</tr>
<tr>
<td>3471.6</td>
<td>31</td>
<td>17</td>
</tr>
<tr>
<td>3511.1</td>
<td>33</td>
<td>14</td>
</tr>
<tr>
<td>3515.6</td>
<td>31</td>
<td>18</td>
</tr>
<tr>
<td>3555.6</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>3557.6</td>
<td>32</td>
<td>17</td>
</tr>
<tr>
<td>3595.6</td>
<td>35</td>
<td>12</td>
</tr>
<tr>
<td>3597.6</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>3599.6</td>
<td>33</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 10. ¹H NMR chemical shifts of the polymers and copolymers at elevated temperatures.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>CH ppm</th>
<th>CH₂ ppm</th>
<th>Bn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PF₅BnA</td>
<td>3.78</td>
<td>5.53</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PF₃BnA</td>
<td>3.77</td>
<td>5.16</td>
<td>6.78 and 7.34</td>
</tr>
<tr>
<td>3</td>
<td>PCNBnA</td>
<td>3.54</td>
<td>5.11</td>
<td>7.26-7.40</td>
</tr>
<tr>
<td>4</td>
<td>P(F₃BnA-co-BnA)</td>
<td>3.73</td>
<td>5.05</td>
<td>7.21-7.35</td>
</tr>
<tr>
<td>5</td>
<td>P(F₃BnA-co-BnA) a</td>
<td>3.84</td>
<td>5.05</td>
<td>6.67 and 7.16-7.32</td>
</tr>
<tr>
<td>6</td>
<td>P(CNBnA-co-BnA) a</td>
<td>3.88</td>
<td>5.00</td>
<td>7.17</td>
</tr>
<tr>
<td>7</td>
<td>PBnA</td>
<td>3.94</td>
<td>4.97</td>
<td>7.09</td>
</tr>
<tr>
<td>8</td>
<td>PBnA a</td>
<td>3.96</td>
<td>4.97</td>
<td>7.09</td>
</tr>
</tbody>
</table>

*Measured in C₆D₄Cl₂ a at 100 °C and b at 80 °C.
Potential applications of poly-carbenes

Figure 17. Cyclic voltammograms in acetonitrile with Bu₄NPF₆ as the electrolyte, solid lines are the measurements without ferrocene and the dashed lines are with ferrocene: A) P(CNBnA-co-BnA), B) P(F₅BnA-co-BnA), C) P(F₃BnA-co-BnA).
6.6 Experimental section

General remarks

The reactions to obtain the monomers and the intermediates where preformed in a normal atmosphere. The polymerization reactions are performed in a flame dried schlenk under nitrogen. Dichloromethane distilled from calcium hydride en diethyl ether distilled from sodium benzophenone ketyl. Chloroform (stabilized by ethanol; 0.5-1.5%w/v) was purchased from Biosolve and used as such. The synthesis of [Rh(cod)(μ-Cl)]₂ and [(L-pro)Rh(co)] has been reported previously. BnDA was synthesized from glycine benzyl ester hydrochloride according to literature procedures. The starting materials where purchased from commercial suppliers and used without further purification. The different NMR experiments where preformed on a Bruker DRX 400 spectrometer (400 and 100 MHz for 1H and 13C NMR, respectively) and the experiments at high temperature where preformed on the Bruker DRX 300 spectrometer (300 and 75 MHz for 1H and 13C NMR, respectively) and when mentioned on the Varian Inova 500 spectrometer (500 and 100 MHz for 1H and 13C NMR, respectively). Solvent shift reference for 1H-NMR spectroscopy: CDCl₃, δH 7.26 ppm; 13C-NMR reference: CDCl₃, δC 77.36 ppm.

Abbreviations used are: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, cod = 1,5-cyclooctadiene, pro = proline, PEG = polyethylene glycol. Molecular weight distributions were measured using size-exclusion chromatography on a Shimadzu LC-20AD system with two PLgel 5 μMIXED-C (300 nm x 7,5 mm) columns (Polymer Laboratories) in series and a Shimadzu RID-10A refractive-index detector, using dichloromethane as mobile phase at 1 ml/min at 35°C and for PEA-PEG using THF as mobile phase at 1 ml/min. Polystyrene standards in the range of 760-1 880 000 g/mol (Aldrich) were used for calibration. TGA experiments were obtained with a Perkin-Elmer TGA7 with a heating rate of 10 °C/min under a nitrogen atmosphere. DSC was performed using a DSC Q1000 in the modulated mode. The heating rate was 10 °C/min. Tg and Tc was determined from the heat flow curves, while the Tc was derived from the reversing heat flow curves. Cyclic voltammograms where obtained with an autolab pgstad10 under a nitrogen flow using a silver electrode as working electrode and platinum for the reference and control electrode. The UV-vis spectra where obtained scanning between 180-1100 nm in a 1cm glass cuvet. FTIR spectra (dilute solution in CHCl₃) were recorded in the transmittance range of 4000-800 cm⁻¹ on a Perkin-Elmer instrument using 0.1 mL glass cells. MALDI-ToF mass spectra of oligomeric products were obtained in reflection mode on a Shimadzu Biotech Axima instrument using a matrix of DCTB in acetonitrile with addition of Na⁺. Samples were dissolved in acetonitrile at a concentration of 5 mg.mL⁻¹. Solutions of DCTB (20 mg.L⁻¹) and NaTFA (10 mg.L⁻¹) were prepared. Matrix, sample and salt additive were mixed in a ratio of 2:2:1.

General procedure: Synthesis of (PEA-PEG) block copolymers.

To a dichloromethane (25 mL) solution of (m)PEG (12.5 g) and the catalyst [Rh(cod)(μ-Cl)]₂ (50 mg; 0.2 mmol Rh) was added EDA (1.23 g; 10 mmol) at room temperature. The mixture was stirred for 16 h. Volatiles were removed in vacuo and polymeric products were precipitated by addition of methanol (50 mL). Suspensions were centrifuged at 2250 rpm for a duration of 4 minutes. The pellets were washed with methanol and stirred for 16 h in 1:1 methanol/water. After centrifugation (2250 rpm, 4 min) and removal of the methanol/water supernatant, the white pellets were washed again with 100% methanol and dried in vacuo. Combined supernatants were concentrated in vacuo and purified by preparative size exclusion chromatography (SEC) and...
Potential applications of poly-carbenes

pseudo-reversed phase flash chromatography. Purified supernatants were further characterized as detailed below.

**Sephadex G25 Preparative Size Exclusion Chromatography.** Sephadex G25 preparative SEC was carried out using a preparative SEC column (length: 53.6 cm; internal diameter: 3.37 cm; total volume: 478 cm$^3$) packed with Sephadex G25 (crosslinked dextran). Chromatography was monitored using a BioRad Econo UV detector measuring at a wavelength of 254 nm and a sensitivity of 0.5 AUFS (Absorption Units Full Scale). An acetonitrile eluent was used. Flow was effectuated using 0.3 bar of air-pressure. Sephadex G25 beads (100 g) were allowed to swell in excess acetonitrile overnight. After swelling, the bead slurry was poured into the column and allowed to settle under 1.3 bar air-pressure. After settling, flow was stopped and a solution (1-4 mL) of crude oligomeric PEA-PEG in a minimal amount of eluent was slowly added to the gel bed. The column outlet was connected via silicone tubing to the UV detector and eluents were passed through the cell before collection. Fractions were collected manually.

**BioBeads SX-1 Preparative Size Exclusion Chromatography.** For BioBeads SX-1 preparative SEC, a preparative SEC column (length: 84 cm; internal diameter: 2.8 cm; total volume: 540 cm$^3$) packed with BioBeads SX-1 (crosslinked polystyrene-1%-divinylbenzene) was used. The detection system applied to monitoring SEC was identical to that described above for Sephadex G25. THF was used as eluent. A standard flow of 1.20 ml.min$^{-1}$ was used during elution, effectuated by a fitted BioRad Econo flow adaptor unit coupled to a BioRad Econo pump. A slurry was made of BioBeads SX-1 beads (100 g) in excess THF and was poured into the column. The beads were allowed to swell overnight. After connection of the pump and flow adaptor, the column was flushed with THF at a flow of 1.20 ml.min$^{-1}$ for 1 h. After flushing, flow was stopped and the column was charged with a solution (1-2 mL) of crude PEA-PEG in a minimal amount of THF. Elution was continued at the standard flow. Fractions were passed through the UV detector system and collected manually.

**Dialysis (PEG Mn>600).** Cellulose acetate membrane tubes (Float-a-Lyzer, Spectrum Labs; dry packaged, treated with glycerol; volume: 10 mL; pore size: 3.5-5 kDa). Crude copolymer (500 mg) was shaken in 15% aqueous ethanol (7 mL) until homogeneity. The emulsion was brought into the membrane and placed in water (1L) and stirred for several days. The dialysate was changed after two days. A sample (30 mL) of dialysate was evaporated and analyzed by $^1$H NMR for presence of free PEG. The system was stirred further at RT over two weeks. Free PEG was still present, verified by $^1$H NMR analysis.

**Dialysis (PEG Mn<600)** Benzoylated cellulose membrane (Sigma Aldrich; wet packaged, treated with glycerol; flat width: 32 mm; pore size: 0.5-2 kDa). Sample preparation and dialysis were carried out as described for PEG Mn > 600.

In cases where more than 4 mL of eluent was needed to dissolve the oligomers (particularly with larger PEA-PEGs) the oligomer fraction was passed over the column in several batches.
Synthesis of PEA-PEG200. PEA-PEG200 was synthesized in accordance with the general procedure. Purification was attempted using BioBeads SX-1 SEC followed by flash chromatography on 40-63 μm neutral silica in CH₃CN eluent (column length: 7 cm; internal diameter: 2 cm; total volume: 22 cm³). A second purification attempt was done by using Sephadex G25 SEC instead of BioBeads SX-1 SEC. No purification was achieved. ¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ 4.09 (2 H, m, CH₂CH₃, PEA), 3.63 (0.16 H, m, CH₂O, PEG), 3.17 (0.74 H, m, CH₃, PEA), 1.22 (3 H, m, CH₂CH₃, PEA) ppm. FTIR (CHCl₃, dilute solution) (cm⁻¹): 1100-1200 (C-O PEG, PEA); 1740 (C=O, PEA), 3000 (C-H PEG, PEA). GPC (THF): MALDI-ToF-MS: See main text.

Synthesis of PEA-mPEG550. PEA-mPEG550 was synthesized following the general procedure. Purification of this copolymer was attempted using the same methods as described for PEA-PEG200. No purification was achieved. ¹H-NMR (CDCl₃, 300 MHz, 25 °C): δ 4.07 (2H, m, CH₂CH₃, PEA), 3.64 (0.05 H, m, CH₂O, PEG), 3.16 (0.64 H, m, CH₃, PEA), 1.21 (3 H, m, CH₂CH₃, PEA) ppm. FTIR (CHCl₃, dilute solution) (cm⁻¹): ca. 1100 (C-O, mPEG), 1200 (C-O, PEA); 1740 (C=O, PEA), 2250; 3000 (C-H mPEG, PEA). GPC (THF): See Table 3.5 MALDI-ToF-MS: See at the end of this Chapter.

Synthesis of PEA-PEG600. Synthesis of PEA-PEG600 was carried out as described in the general procedure. Purification of the copolymer was carried out using Sephadex G25 SEC. In addition, BioBeads SX-1 SEC and flash chromatography over 40-63 μm neutral silica in CH₃CN (column length: 7 cm; internal diameter: 2 cm; total volume: 22 cm³) have been attempted. No purification was achieved. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 4.07 (2 H, m, CH₂CH₃, PEA), 3.64 (0.77 H, m, CH₂O, PEG), 3.17 (0.35 H, m, CH₃, PEA), 1.24 (3 H, m, CH₂CH₃, PEA) ppm. FTIR (CHCl₃, dilute solution) (cm⁻¹): ca. 1100 (C-O, PEG); ca. 1240 (C-O, PEA); 1740 (C-O, PEA), 2250; 3000 (C-H PEG, PEA). GPC (THF): MALDI-ToF-MS: See main text.

Synthesis of PEA-PEG1500. Synthesis of PEA-PEG1500 was synthesized following the general procedure. Attempts at purification of this copolymer were made using BioBeads SX-1 SEC and Sephadex G25 SEC. Additional methods investigated were flash chromatography on 40-63 μm neutral silica in CH₃CN (column length: 7 cm; internal diameter: 2 cm; total volume: 22 cm³); flash chromatography on 40-63 μm neutral silica in CH₃CN followed by CHCl₃ on 60-200 μm silica and flash chromatography on 60-200 μm neutral silica using a CH₃CN/H₂O gradient from 0 to 15% water content. Elution was started with 100% CH₃CN and water content was slowly increased in 5% increments until all fractions had eluted. No purification was achieved. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 4.15 (2 H, m, CH₂CH₃, PEA), 3.64 (0.77 H, m, CH₂O, PEG), 3.17 (0.35 H, m, CH₃, PEA), 1.24 (3 H, m, CH₂CH₃, PEA) ppm. FTIR (CHCl₃, dilute solution) (cm⁻¹): ca. 1100 (C-O, PEG); 1240-1200 (C-O, PEA); 1740 (C-O, PEA), 2250; 3000 (C-H PEG, PEA). GPC (THF): MALDI-ToF-MS: See main text.

Synthesis of PEA-PEG3400. The general synthetic procedure was used in the synthesis of PEA-PEG3400. Purification was attempted using two extractions (THF and DMF) followed by BioBeads SX-1 SEC and flash chromatography on 40-63 μm neutral silica in CH₃CN (column length: 21 cm; internal diameter: 1.75 cm; total volume: 50.5 cm³). Other methods attempted include extractions with acetone and diethyl ether and flash chromatography over 60-200 μm
Potential applications of poly-carbenes

neutral silica in CH$_3$CN. No purification was achieved. $^1$H NMR (CDCl$_3$, 300 MHz, 25 $^\circ$C): $\delta$ 4.13 (2 H, m, CH$_2$CH$_3$, PEA), 3.65 (0.60 H, m, CH$_2$O, PEG), 3.18 (0.29 H, m, CH, PEA), 1.24 (3 H, m, CH$_2$CH$_3$, PEA) ppm. FTIR (CHCl$_3$, dilute solution) (cm$^{-1}$): 1150-1100 (C-O, PEG), ca. 1200 (C-O, PEA), 2900-2800 (C-H, PEG), ca. 3000 (C-H, PEA), 3500-3000 (O-H, PEG).

Synthesis of PEA-mPEG5000. PEA-mPEG5000 was synthesized in accordance with the general synthesis procedure. Purification methods investigated include BioBeads SX-1 SEC, extractions with THF, DMF, acetone and diethyl ether and flash chromatography over 40-63 $\mu$m and 60-200 $\mu$m neutral silica using CH$_3$CN/H$_2$O gradients ranging from 0 to 25% H$_2$O on various column lengths between 5 and 21 cm. No purification was achieved. $^1$H NMR (CDCl$_3$, 300 MHz, 25 $^\circ$C): $\delta$ 4.08 (2 H, m, CH$_2$CH$_3$, PEA), 3.65 (0.78 H, m, CH$_2$O, PEG), 3.16 (0.70 H, m, CH, PEA), 1.25 (3 H, m, CH$_2$CH$_3$, PEA) ppm. FTIR (CHCl$_3$, dilute solution) (cm$^{-1}$): ca. 1100 (C-O, PEG), ca. 1200 (C-O, PEA), 1750 (C=O, PEA), 2250; 3050-3000 (C-H, PEG, PEA), ca. 3100.

Preparation of polymers A, B and C. The polymers were obtained in 4 steps, first the corresponding benzylalcohol was synthesized (step 1), followed by the synthesis of the benzylglycine hydrochloride (step 2) and then the preparation of the diazo acetate (step 3). Step 4: polymerization with [(L-pro)Rh(cod)] (I) as catalyst.

$p$-cyanobenzylalcohol A-1. To a solution of cyanobenzaldehyde (20 mmol) in 50 ml of ethanol was added NaBH$_4$ (20 mmol) and (NH$_4$)$_2$CO$_3$ (20 mmol), the mixture was stirred at room temperature. After 30 minutes the reaction mixture was filtered over a flash column of celite and the filtrate was concentrated under reduced pressure to obtain the pure product. Yield 85%. $^1$H NMR (CDCl$_3$) $\delta$ 7.60-7.43 (dd, 4H, aromatic), 4.72 (s, 2H, CH$_2$), 3.26 (br s, 1H, OH) ppm.

$p$-cyanobenzylglycine hydrochloride A-2. Boc-glycine (19 mmol) was added slowly to a solution of p-cyanobenzylalcohol A-1 (17 mmol), DIC (17 mmol) and DMAP (1,7 mmol) in 20 ml DCM at 0 $^\circ$C. The mixture was stirred for 16 hours at room temperature. The precipitate was filtered off. The organic phase was washed with saturated NaHCO$_3$ solution (2 X 20 ml) and brine (2 X 20 ml). The organic phase was dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. Without further purification the product was dissolved in 20 ml 1,4-dioxane and 10 ml of 4 M HCl in dioxane was added at 0 $^\circ$C. The mixture was stirred at room temperature. After 16 hours the mixture was concentrated under reduced pressure. The residue was then washed with Et$_2$O. Yield 97%. $^1$H NMR (CD$_3$OD): $\delta$ 7,79-7,61 (dd, 4H, aromatic), 5,39 (s, 2H, CH$_2$), 3,97 (s, 2H, CH$_2$) ppm.

Pentafluorobenzylglycine hydrochloride B-2. Pentafluorobenzylglycine hydrochloride was obtained with the same procedure as used for p-cyanobenzylglycine hydrochloride using pentafluorobenzylalcohol B-1. Yield 52%. $^1$H NMR (CD$_3$OD): $\delta$ 5,45 ppm (s, 2H, CH$_2$), 3,91 ppm (s, 2H, CH$_2$).

2,4,5-Trifluorobenzylglycine hydrochloride C-2. 2,4,5-Trifluorobenzylglycine hydrochloride was obtained with the same procedure as used for p-cyanobenzylglycine hydrochloride using
Chapter 6

2,4,5-trifluorobenzylalcohol C-1. Yield 56%. $\text{H NMR (CD}_3\text{OD)}: \delta 7.53-7.47 (m, 1H, aromatic), 7.31-7.24 (m, 1H, aromatic), 5.33 (s, 2H, CH$_2$), 3.92 (s, 2H, CH$_2$).

$p$-Cyanobenzylidrazoacetate (p-CNBnDA) A-3. 20 ml of DCM was added to a solution of $p$-cyanobenzylglycine hydrochloride A-2 (16 mmol) in 15 ml H$_2$O, to the mixture was added drop wise NaNO$_2$ (16 mmol) in 2 ml H$_2$O at 0°C and after that 0.1 ml H$_2$SO$_4$ in 0.9 ml H$_2$O was added drop wise at 0°C. After stirring the mixture for 2 hours at room temperature the water and organic phase were separated the water phase was extracted with DCM (2 X 20 ml). The combined organic phases were washed with saturated NaHCO$_3$ solution (4 X 20 ml). The organic phase was dried with anhydrous MgSO$_4$ and concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleumether/ethyl acetate 1:1 as eluent to give the diazo in 59% yield. $\text{H NMR (CDCl}_3): \delta 7.66-7.44 (dd, 4H, aromatic), 5.24 (s, 2H, CH$_2$), 4.86 (s, 1H, CH) ppm.

Pentafluorobenzyldiazocacetate (F$_5$BnDA) B-3. F$_5$BnDA was obtained with the same procedure as used for p-CNBnDA using pentafluorobenzylglycine hydrochloride B-2. Stirred for 4 hours at room temperature and purified by column chromatography using silica geld and hexane/ethyl acetate 3:1 as eluent to give the diazo in 81% yield. $\text{H NMR (CDCl}_3): \delta 5.30 (s, 2H, CH$_2$), 4.81 (s, 1H, CH) ppm.

Poly(p-cyanobenzyl 2-yldeneacetate) (PCNBnA). p-CNBnDA B-3 (2 mmol) was added to a yellow solution of catalyst (I) (0.04 mmol) in 5 ml chloroform. The mixture was stirred for 16 hours at 40°C. Subsequently the solvent was removed under reduced pressure and methanol was added to the residue. The precipitate was centrifuged and washed with methanol until the washings were colourless. The resulting white powder was dried under reduced pressure. $\text{H NMR (CD}_2\text{Cl}_2,150\text{oC): } \delta 7.40-7.26 (bs d, H$_4$, aromatic), 5.11 (bs s, 2H, CH$_2$), 3.62 (bs s, 1H, CH) ppm. No $^{13}$C NMR spectrum obtained.

Poly(pentafluorobenzyl 2-yldeneacetate) (PF$_5$BnA). PF$_5$BnA was obtained with the same procedure as used for PCNBnA using F$_5$BnDA B-3. The mixture was stirred at room temperature. $\text{H NMR (CD}_2\text{Cl}_2,100\text{oC): } \delta 5.53 (bs s, 2H, CH$_2$), 3.78 (bs s, 1H, CH). $^{13}$C NMR (CD$_2$Cl$_2$) (in a 1 cm Ø NMR tube at 500 Hz), 169.86 (C=O), 146.71 – 136.48 (C$_q$ aromatic), 108.74 (C$_q$ aromatic), 53.36 ppm (CH$_2$), 44.29 (CH) ppm.

Poly(2,4,5-trifluorobenzyl 2-yldeneacetate) (PF$_3$BnA). PF$_3$BnA was obtained with the same procedure as used for PCNBnA using F$_3$BnDA C-3. The mixture was stirred at room temperature. $\text{H NMR (CD}_2\text{Cl}_2,80\text{oC): } \delta 7.34 (bs s, 1H, aromatic), 6.78 (bs s, 1H, aromatic), 5.16 (bs s, 2H, CH$_2$), 3.77 (bs s, 1H, CH). $^{13}$C NMR (CD$_2$Cl$_2$) in a 1 cm Ø NMR tube at 500 Hz): $\delta$ 170,76.
Potential applications of poly-carbenes

(C=O), 157.01 – 145.87 (C-F aromatic), 118.98 (C\textsubscript{q} aromatic), 117 (C-H aromatic), 105.55 (C-H aromatic), 59.94 (CH\textsubscript{2}) and 45.22 (CH) ppm.

Poly(p-cyanobenzyl 2-ylideneacetate-co-benzyl 2-ylideneacetate) (P(CNBnA-co-BnA)). A mixture of p-CNBnDA A-3 (2 mmol) and BnDA (2 mmol) was stirred for 15 min and added to a yellow solution of catalyst (I) (0.04 mmol) in 5 ml chloroform. The reaction mixture was stirred for 16 hours at room temperature. Subsequently the solvent was removed under reduced pressure and methanol was added to the residue. The precipitate was centrifuged and washed with methanol until the washings were colourless. The resulting white powder was dried under reduced pressure.

\( ^{1}H\) NMR (CDCl\textsubscript{3}), 7.12 (bs s, aromatic), 4.78 (bs s, CH\textsubscript{2}), 3.59 (bs s, CH) ppm.

\( ^{13}C\) NMR (CDCl\textsubscript{3}), 170.78 (C=O both CNBnA and BnA), 140.20 (C\textsubscript{q} aromatic CNBnA), 134.96 (C\textsubscript{q} aromatic BnA), 131.92-128.31 (CH aromatic CNBnA), 128.31-127.67 (CH aromatic BnA), 118.23 (C\textsubscript{q}CŁN CNBnA), 111.63 (C\textsubscript{q} aromatic-CŁN, CNBnA), 67.31 (CH\textsubscript{2}BnA), 65.71 (CH\textsubscript{2}CNBnA), 45.13 (CH both CNBnA and BnA) ppm.

Poly(pentafluorobenzyl 2-ylideneacetate-co-benzyl 2-ylideneacetate) (P(F\textsubscript{5}BnA-co-BnA)).

P(F\textsubscript{5}BnA-co-BnA) was obtained in the same way as P(CNBnA-co-BnA) using F\textsubscript{5}BnDA.

\( ^{1}H\) NMR (CDCl\textsubscript{3}): 7.19 (bs s, aromatic), 4.88 (bs s, CH\textsubscript{2}), 3.44 ppm (bs s, CH) ppm.

\( ^{13}C\) NMR (CDCl\textsubscript{3}, 100\textsubscript{϶}C): 170.53 (C=O both F\textsubscript{5}BnA and BnA), 147.73-139.35 (C\textsubscript{q} aromatic F\textsubscript{5}bA), 135.65 (C\textsubscript{q} aromatic BnA), 128.11 (CH aromatic BnA) 109.65 (C\textsubscript{q} aromatic F\textsubscript{5}BnA), 67.16 (CH\textsubscript{2}BnA), 53.53 (CH\textsubscript{2}F\textsubscript{5}BnA), 45.82 (CH both F\textsubscript{5}BnA and BnA) ppm.

Poly(2,4,5-trifluorobenzyl 2-ylideneacetate-co-benzyl 2-ylideneacetate) (P(F\textsubscript{3}BnA-co-BnA)).

P(F\textsubscript{3}BnA-co-BnA) was obtained with the same procedure as used for P(CNBnA-co-BnA) using F\textsubscript{3}BnDA.

\( ^{1}H\) NMR (CDCl\textsubscript{3}): 7.13 (bs s, aromatic), 6.72 (bs s, aromatic), 4.83 (bs s, CH\textsubscript{2}), 3.54 (bs s, CH) ppm.

\( ^{13}C\) NMR (CDCl\textsubscript{3}): 170.86 (C=O both F\textsubscript{3}BnA and BnA), 156.67-145.32 (C\textsubscript{q} aromatic F\textsubscript{3}BnA), 135,15 (C\textsubscript{q} aromatic BnA), 128.06 (CH aromatic BnA), 119.10 (C\textsubscript{q} aromatic F\textsubscript{3}BnA), 67.13 (CH\textsubscript{2}BnA), 59.48 (CH\textsubscript{2}F\textsubscript{3}BnA), 45.06 (CH both F\textsubscript{3}BnA and BnA) ppm.

6.7 References and notes

5  B. Lonetti, A. Tsigkri, P. R. Lang, Macromolecules, 2011, 44, 3583-3593.
9  When the solid part obtained after evaporation of the solvent in the EDA polymerization with solid PEG/PEG (M\textsubscript{w} > 1000 Da) was extracted with DCM at r.t. to obtain the
PEG-PEA copolymers, the fractions also contained un-polymerized PEG/m-PEG. PEA is not soluble and does not form emulsifications and PEG is soluble in water.

G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Nat. Mat., 2005, 4, 864-868.


This is based on comparison of the H NMR spectra of PEA and copolymers of EA and BnA. The shielding effect was not observed in these spectra.


Yield remains low, even when the temperatures are elevated.


The NMR experiments are also performed with higher temperature, to improve the solubility. The measurement give comparable results (see table 10 at the end of this Chapter).


Potential applications of poly-carbenes

51 J. Huang, G. Li, Y. Yang, Appl. Phys. Lett., 2005, 87, 112105

The reduction signals are reduced by addition of ferrocene probably due interaction of the ferrocene and the benzyl rings of the copolymers. Therefor ferrocene is used as external standard instead of internal. Also the measurements are irreversible, which suggest a change in the electronic structure after reduction and oxidation. The first onset of the reduction wave is used in the calculation, because this value represents the lowest energy excitation possible.