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Linear High Molecular Weight Ladder Polymer via Fast Polycondensation of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane with 1,4-Dicyanotetrafluorobenzene[a]

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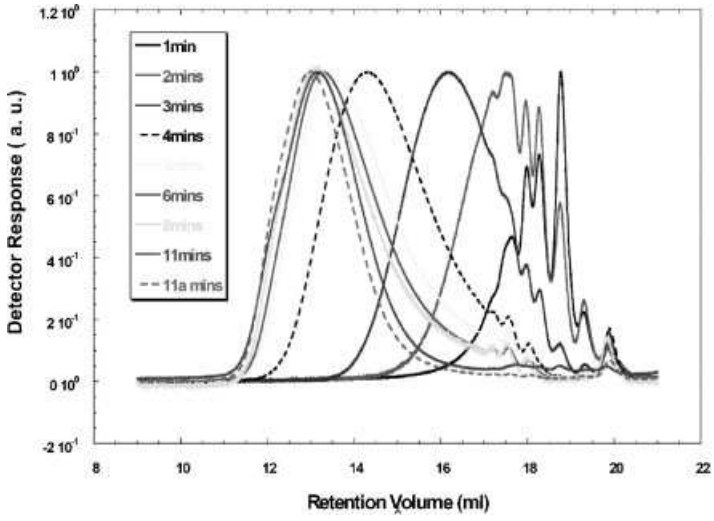
A high molecular weight ladder polymer based on 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane and 1,4-dicyanotetraflurobenzene has been synthesized by polycondensation under high-intensity mixing conditions at about 155 °C and cyclic-free products were obtained in high yield with low molecular weight distribution (1.7–2.3). The reaction could be completed within a few minutes. The polymer properties were characterized by GPC, ^{1}H NMR, ^{13}C NMR, F NMR, FT-IR, and MALDI-TOF MS. In addition, the mechanical properties, apparent surface areas and gas permeability are also reported. This procedure can also be used for the synthesis of other ladder polymers by irreversible polycondensations of tetraphenols with activated tetrafluoro aromatics.



Introduction

In the past 3 years, a British research group[1–5] reported on the syntheses of a number of glassy polymers of intrinsic microporosity (PIM) via irreversible polycondensations of tetraphenols with activated tetrafluoro or tetrachloro aromatics. The reaction conditions comprised polymerization at 8% monomer concentration (monomer/DMF: w/w) at 65 °C for 72 h. These polymers have attracted great interest as outstanding advanced polymeric materials for a variety of applications, including membrane-based gas separation, adsorption of small molecules, and heterogeneous

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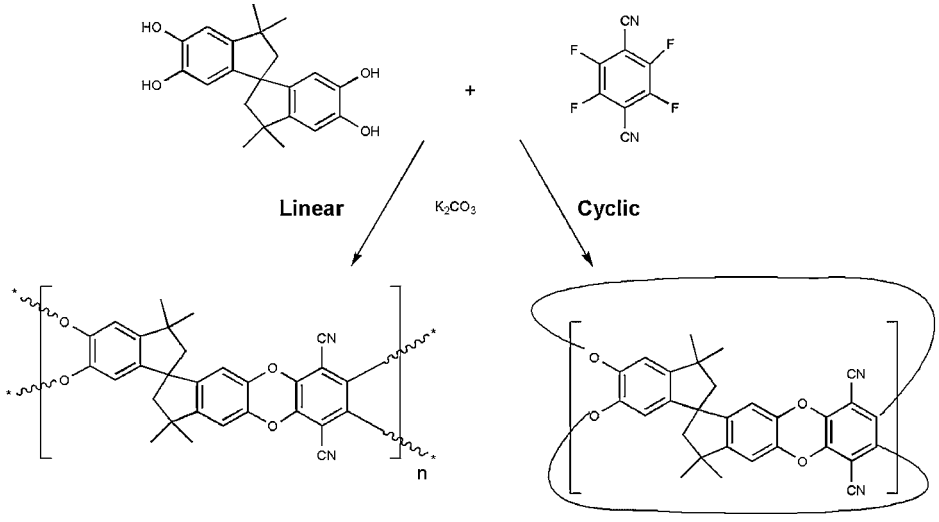
catalysts, due to a contorted zig-zag structure and loose chain packing capable of generating very high-free volume. To date, several ladder polymers with molecular weights high enough for film-forming capability have been reported, especially two that are referred to by the British group as PIM-1 and PIM-7.[4] More recently, Kricheldorf et al. further investigated PIM-1, which has been the most widely studied PIM (see Scheme 1) based on 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI) and 1,4-dicyanotetrafluorobenzene (DCTB).[6,7] Under seemingly similar reaction conditions as those reported by the British group, they concluded that the majority of the product was cyclic which resulted in low molecular weight polymer and high polydispersity indices up to 15. The best result reported was $\overline{M}_n = 18\,000$ and a PDI of 5.2. This is contrary to the finding of the British group, which reported $\overline{M}_n$ of 170 000 Da and PDI of 1.7. It is well known that cyclization competes with every chain-growth step at all stages of polycondensations[8] and high temperature or high concentration conditions have been shown to favor the decrease in cyclic oligomers.[9] However, according to our experiments and a previous report,[7] high temperature and high concentration resulted in an explosion-like polycondensation in this reaction system, yielding a crosslinked product. In this paper, a successful synthetic approach to a high molecular weight linear ladder polymer with few low molecular weight cyclic species prepared at elevated high temperature and high concentration conditions is presented.

Results and Discussion

It has been observed in classic polycondensation reactions of bisphenols and bifluoro aromatics for the production of poly(aryl ethers) that a large amount of macrocyclic oligomers were formed.[8,9] During the initial stages of the reaction, the bisphenol reacted with sodium or potassium carbonate (or hydroxide) to give a number of salt precipitates which hindered stirring of the reaction mixture. The cyclic compounds were formed in the reaction mixture as a result of the high dilution conditions created by poor solubility of the salt. This implies that the rate-controlling step in the reaction is the dissolution of the salt. Miyatake and Hlil found that the cyclization problem in this kind of reaction system can be ameliorated by using a high-speed homogenizer. The high-intensity mixing increased the surface area of the salt, hence aiding its dissolution.[9] Very high molecular weight polyformals with low molecular weight distributions were obtained in a few minutes.

In contrast with the typical reactions to synthesize linear poly(aryl ethers), the formation of this specific ladder polymer is more complicated. As can be seen in Scheme 1, both monomers have four reactive groups. Thus, the solubility of the tetraphenol salt is even lower than that of a bisphenol and cyclics are formed more easily. In addition, the presence of multiple reactive groups in one monomer increases the possibility of crosslinking. It was also observed that the polymer or cyclics will precipitate out from the reaction mixture (if DMAc or DMF are used as solvent) if their molecular weight is higher than 10 000 Da. At this point, it is not easy for the common step-growth polymerization reaction to proceed further, because the cyclics form more easily due to lower monomer and oligomer concentration. In addition, crosslinking takes place rapidly because OH and F groups stretch out randomly from the surface of the precipitated polymer whose chains fold, coil, and pack together, and react randomly with other OH and F groups. We found that



Scheme 1. Synthetic route to the ladder polymer.

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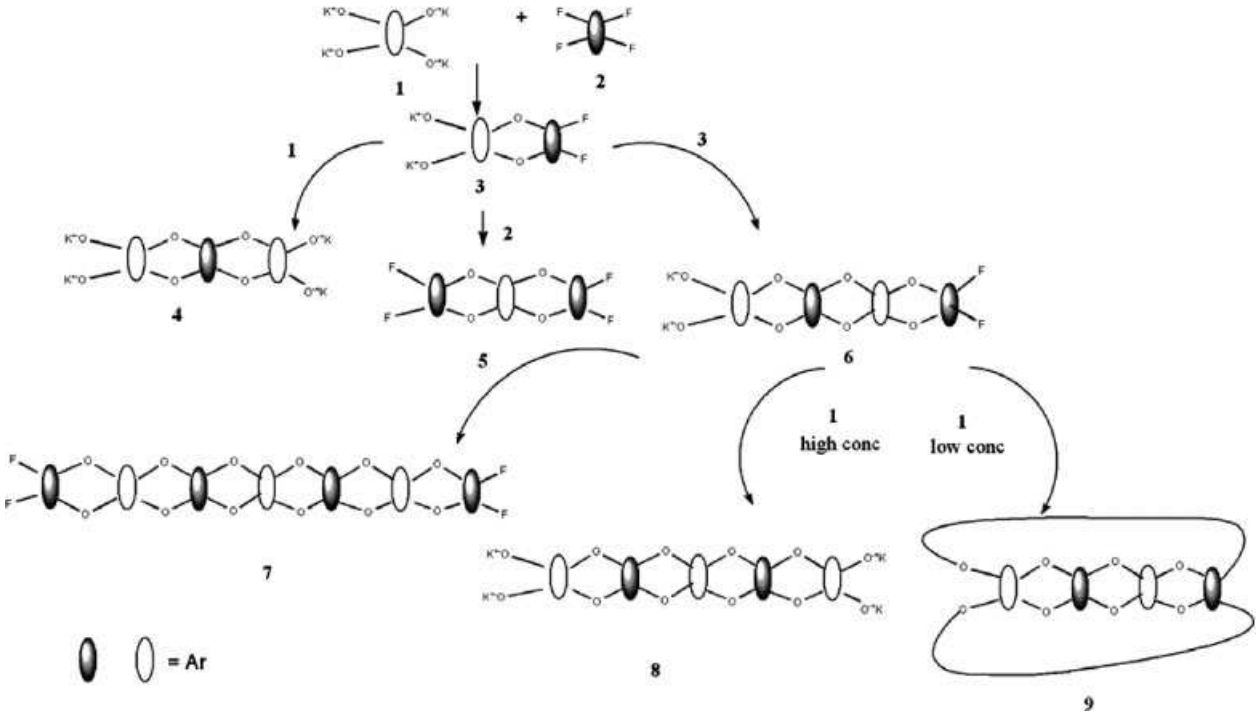
even in a low temperature reaction (50 °C) under dilute conditions ($w_{monomer}/w_{DMAc} = 5{:}100$),[10] crosslinking still occurred as long as this ladder polymer precipitated from the reaction mixture. According to the method reported by Budd et al.,[2] we obtained two polymers at different reaction times (48 and 72 h, respectively) and compared these materials to our polymer.

The ideal structure of this ladder polymer is a linear unbranched chain free of macrocyclic species and crosslinking. The formation of this ladder polymer is schematically presented in Scheme 2. Although the reaction is complicated due to the monomers' multiple reactive groups, the simple model can help to explain how the cyclic species are formed in the reaction system. As the reaction is irreversible, no equilibrium exists in this polymerization process. The first step reaction product is the intermediate 3, which is much more reactive, due to its higher solubility, than the monomer salt 1. Therefore, the intermediate 3 preferentially reacts with the very reactive tetrafluoro aromatic 2 to give 5 or with itself to yield 6. Under normal stirring conditions where 1 very slowly goes into solution, its concentration is low so that the intermediate 6 could react with 5 to give 7 and with itself to yield a cyclic 9. Higher analogs of 6 could also give cyclic products when the concentration of 1 in solution is low, thus contributing to a broad molecular weight distribution. Under high-intensity mixing conditions, the concentration of 1 is high so that it is not only able to react with 6 and its higher analogs to give the soluble intermediate 8, but also with intermediates 3, 5, and 7 to form linear oligomers, and subsequently high molecular weight polymers.

According to the mechanism described above and our previous experience, we note that the synthesis of a ladder polymer having an ideal structure could be carried out at elevated temperature and high concentration conditions, using a solvent that is substantially compatible with the monomer salts and the polymers dissolved in the reaction mixture. After a number of trials, we found improved reaction conditions that could achieve high molecular weight linear ladder polymers which are almost free of crosslinking and cyclic species. Compared to the 3-day reaction (Budd et al.) and the 1-day reaction (Kricheldorf et al.) reported in previous reports, the present reaction can be completed within a few minutes. A typical procedure can be carried out as follows: a flask was charged with 5.106 g (15 mmol) of TTSBI, 3.003 g (15 mmol) of DCTB, 6.2 g (45 mmol) K_2CO_3, and 25 mL DMAc. This gives a ratio of 1.5 mol equiv. available K^+ ions to 1.0 mol equiv. of –OH groups in the tetrahydroxy monomer. Under a flow of argon and a temperature of 155 °C, the mixture was vigorously stirred for 2 min and then 20 mL toluene was added into the reaction mixture. The reaction was continued for 2 min, when precipitate appeared and the reaction mixture became viscous. Another 20 mL toluene was added, otherwise stirring could not be continued



Scheme 2. Illustration of the hypothetical formation of the ladder polymer.

Table 1. Properties of the ladder polymers prepared under different conditions.

Polymer	$\overline{M}_n$	$\overline{M}_w$[1]	$\overline{M}_w/\overline{M}_n$	Yield[a)]	Tensile stress at break	Tensile strain at break
				%	MPa	%
a-72 h	54 000	473 000	8.7	80	/	/
a'-24 h	84 000	312 000	3.7	80	43.3	10.2
b-8 min	75 000	131 000	1.7	91	49.7	15.8
c-8 min	102 000	257 000	2.5	93	45.3	11.3

[a)]Isolated yield after purification.

easily. After another four more minutes the polymer was isolated by precipitation in methanol and filtered. After reprecipitation in a chloroform/methanol mixture, the polymer was boiled in hot water for several hours to remove the salt and solvent, then filtered off and dried overnight at 60 °C in vacuo to give 91% yield (polymer *b*). Different from previous polymerization protocols, toluene was introduced into this reaction system to increase the solubility of polymer and to remove water. Alternatively, the reaction was carried out using the same procedure as for polymer *b* without toluene. However, after 4 min, unrecoverable crosslinked polymer was formed.

Although the polymer dissolved in the reaction mixture when toluene was added, the solubility of the monomer salt decreased at the same time. Another reaction was carried out using the same procedure as for polymer *b* but, in this case, 0.2 mL water was added together with 2 mL toluene after 6 min to increase the solubility of the monomer salt. The reaction mixture became very viscous in just a few seconds, and 2 min later the polymer was isolated in 93% yield (polymer *c*). This indicates that an increase in the monomer salt solubility indeed leads to a much faster reaction rate. It is generally believed that the presence of a small amount of water in this system will result in detrimental side reactions, and almost all reported that nucleophilic polycondensation polymerization conditions rigorously exclude water because the hydration of phenoxide anions reduces the reactivity. However, in the present work, the reaction was completed within several seconds after adding a small amount of water. The structure of the polymer is the same as the one which was obtained by the Budd method as observed by FT-IR,[11] ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR.[12] No decomposition or other structures were observed. The mechanical properties of these samples were tested, with the exception of polymer a (72 h), which was too brittle to make the dumb-bell specimen. As shown in Table 1, tensile stress at break and tensile strain at break show that when the $\overline{M}_n$ is high enough, the polymer with linear ladder structure (lower polydispersity index) had better mechanical properties. Apparent surface areas were obtained from Brunauer–Emmett–Teller (BET) analysis (Powder, N_2 adsorption). BET of polymer *b* was around 830 $m^2 \cdot g^{-1}$, while polymer a'-24 h was in the range of 700–750 $m^2 \cdot g^{-1}$. Pure gas permeability data indicated that polymer *b* has a combination of very high permeability with reasonable selectivity (e.g., selectivity $\alpha O_2/N_2 > 3$) that exceeds the Robeson upper bound. Compared with the previously

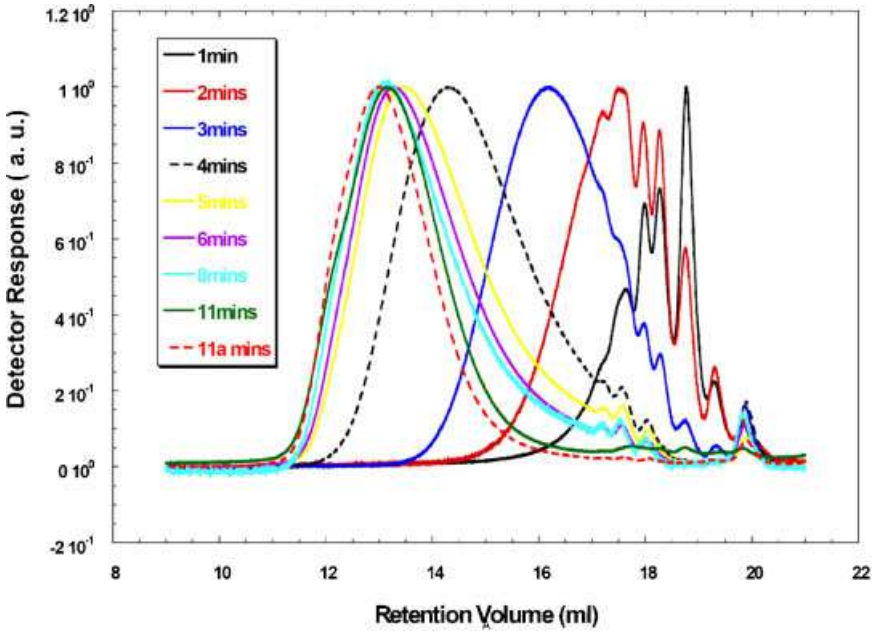


Figure 1. GPC curves for the Ladder polymer *d* 1–11 min.

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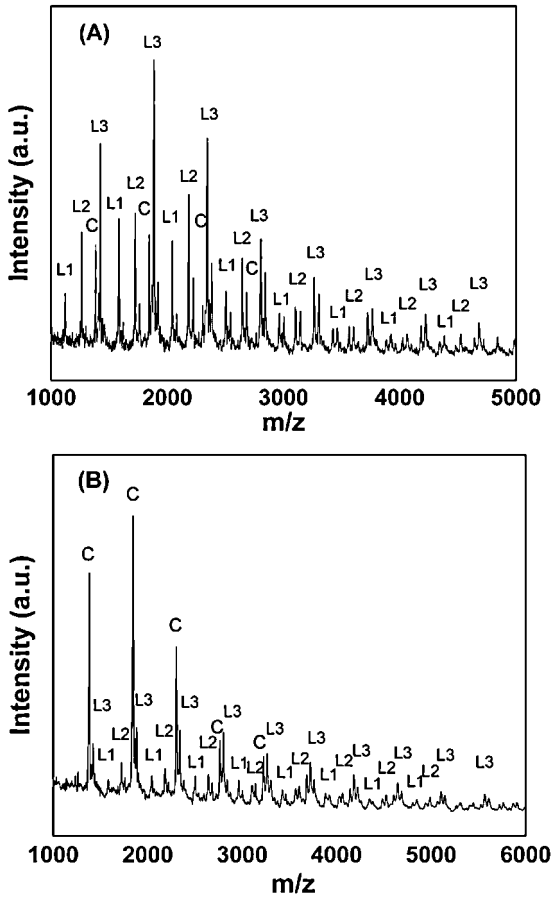

Figure 2. MALDI-TOF mass spectrum of the ladder polymer *d* (A) sample 3, made in 3 min; and (B) sample 4, made in 4 min.

reported PIM-1, the permeability of polymer *b* was 1500–1800 Barrer at 50 psig and 25 °C, which is significantly higher than previously reported gas permeability data for PIM-1.[4] More detailed comparative studies on gas separation properties on PIM-1 prepared by different methods are underway.

Because the reaction rate was too fast for detailed analysis when 1.5 mol equiv. available K^+ ions to 1.0 mol equiv. of –OH groups in the tetrahydroxy monomer was used, a model reaction was performed using less K_2CO_3 and samples of polymer *d* at reaction times of 1 min increments were extracted for evaluation. The procedure used was also the same as above (polymer *b*), but with reduced K_2CO_3 (4.18 g, 30.3 mmol), corresponding to a slightly greater than 1:1 ratio of K^+: –OH. Figure 1 shows the GPC curves for the samples 1–9 of polymer *d* made at different reaction times. From the GPC curves of samples 1 and 2, which are the products of the reaction during the first and second minute, respectively, the main peaks are almost low molecular weight oligomers. The molecular weight increased rapidly in the next 6 min. Figure 2A shows the MALDI-TOF MS[13] of sample 3 made at the third minute. There are three series of linear ladder polymers, having four –F end groups (L1), four –OH end groups (L2), two –OH/two –F groups (L3), and a series of cyclics (C). This is consistent with the hypothesis illustrated in Scheme 2. After 3 min, the low molecular weight linear chain increased rapidly. From GPC data in Table 2, we see that 1 min later (the fourth minute) the $\overline{M}_w$ of sample 4 is about 19 400 Da and only 10% of the polymers have $\overline{M}_w$ (including cyclics and oligomers) below 2 600 Da. In Figure 2, it is seen that in the low molecular weight region, the intensity of the main peaks corresponding to cyclic species decreases quickly after 2 300 Da and almost disappears around 4 000 Da. There are also few low molecular weights L1, L2, and L3 species, but most linear oligomers polymerize and move to the high molecular weight region. From the GPC data of sample 8 (11 min reaction time), we observe that 90% of polymers have $\overline{M}_w$

Table 2. Properties of the samples of polymer *d* made at different reaction times.

	Time	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$ 10.0	$\overline{M}_w$ 10.0
	min	Da	Da		% Low	% High
1	1	1 100	1 600	1.4	530	4 200
2	2	1 700	2 700	1.6	630	7 400
3	3	3 600	6 300	1.7	1 300	16 400
4	4	9 100	19 400	2.1	2 600	55 900
5	5	12 000	33 300	2.2	3 100	104 900
6	6	21 900	41 200	2.2	3 900	123 900
7	8	24 500	46 200	2.3	4 100	134 300
8	11	28 000	52 700	2.1	6 700	137 700
9	11[a)]	34 100	58 700	1.7	12 700	168 000

[a)]Isolated product after purification.

higher than 6 700 Da. At this reaction time, the amount of cyclics present as identified by MALDI-TOF MS is negligible as compared with that of polymer *a*. After purification, sample 9 (11 min reaction time) with a number-average molecular weight of 34 000 Da and a molecular weight distribution of 1.7 was obtained in a yield of 87.5%.

Conclusion

5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane was reacted by nucleophilic polycondensation with 4-dicyanotetrafluorobenzene, using a high-speed homogenizer at 155 °C to provide high molecular weight PIM-1 ladder polymer. It was shown that the presence of toluene and a small amount of water allowed a more complete reaction. The resulting ladder polymer was obtained in high yield within a few minutes. The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR spectra indicated that the polymer appears to have the same structure as the one which was previously reported by Budd et al. However, the present PIM-1 polymer has much better mechanical properties than that made by the previous methods. GPC and MALDI-TOF MS indicate that the polymers contained few macrocyclic oligomers and crosslinked fractions. The present work suggests that cyclic oligomers were formed because of slow dissolution of the salt. The application of high-intensity mixing conditions in irreversible polycondensations can be generally applied; thus, it can also be used for the synthesis of other ladder polymers based on tetraphenols with activated tetrafluoro aromatics.

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Keywords: cyclic-free; homogenizer; ladder polymer; molecular weight distribution; polycondensation

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[10] 3.040 g (10 mmol) of TTSBI, 2.001 g (10 mmol) of DCTB, only 2.79 g (20.2 mmol) of K_2CO_3, 115 mL DMAc were charged into a flask. Under Ar environment and 55 °C, the mixture was stirred for 72 h, then polymer a was isolated by precipitation in methanol.
[11] FT-IR spectra were measured on a Nicolet 520 Fourier transform spectrometer. Thin films of polymer samples were used.
[12] NMR analyses were recorded on a Varian Unity Inova 400 spectrometer at a resonance frequency of 399.961 MHz for ^{1}H and 376.0276 MHz for ^{13}C. ^{1}H NMR spectra a 2–5 wt.-% polymer solution was prepared in chloroform-d_6 and tetramethylsilane (TMS) was used as the internal standard.
[13] MALDI-TOF mass spectra were recorded on a Voyager DE-Pro MALDI-TOF (Applied Biosystems, Foster City, CA) with the instrument set in the reflection positive-ion mode. 1,8,9-Anthracenetriol (dithranol) was used as the matrix and KCl as dopant.

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