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Suzuki Polycondensation: On Catalyst Derived Phosphorus Incorporation and Reproducibility of Molecular Weights

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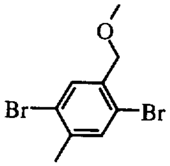
Abstract: This paper describes the quantification of the extent to which phosphorus is incorporated into polymer backbones during Suzuki polycondensation and gives details on how this step-growth polymerization is best performed to ensure reproducible results specifically regarding the achievable molecular weights. © 1997 Published by Elsevier Science Ltd.

The Suzuki polycondensation has been developed into an important tool for the synthesis of polyarylenes and related polymers.[1] It is now one of the few established step-growth polymerizations which proceed with formation of carbon-carbon bonds and, thus, complements the wealth of polyreactions which lead to bond formation between carbon and hetero atoms. The great attraction of this polymerization originates from its regiospecific course, its high functional group compatibility, and the high molecular weights which can be achieved. It uses aryl boronic acids and aryl halides as coupling partners and Pd(0) complexes which typically carry stabilizing phosphine ligands as catalyst precursors. The catalytic cycle is believed to involve Pd(II) species, though an alternative suggestion has been made.[2] Recently, reports appeared in the literature which shed light on potential side reactions of this cross-coupling. For example, Cheng reported on a facile aryl-aryl exchange reaction between Pd center and phosphine ligands in Pd(II) complexes[3] and Marcuccio used this exchange to explain that a certain boronic acid not only coupled with the aryl halide provided but also to some extent with an aryl group of the phosphine ligand.[4] Similar reactions have also been observed in the related Stille cross-coupling.[5] In low molecular weight chemistry scrambling of aryl groups is disadvantagous but may still be acceptable as long as the yields of side products are not too high and they can be separated off. In Suzuki polycondensations, however, aryl-aryl scrambling would be devastating. It was Novak who pointed out that phosphorus containing groups could not only by incorporated as terminator, but also as integral parts of the backbone.[6] He in fact found evidence for phosporous incorporation in a polycondensation. In the first case, the rigid-rod character of the polyarylene backbone would be retained. In the second, however, phosphorus acts as kink or even net-point. This would considerably decrease the value of this method for the synthesis of structurally perfect rod-like polymers, which it was believed to be. We, therefore, decided to investigate the issue of phosphorus incorporation in some depth and devised experiments (a) to see whether the P-incorporation was a general phenomenon, (b) to quantify the degree of incorporation, and (c) to possibly determine the way P is incorporated into the polymer structure. We also contribute to another matter of importance in Suzuki polycondensation which is its reproducibility regarding the achievable molecular weights.

RESULTS AND DISCUSSION

For the investigations the dibromides **1**[7] and **2**[8] and bisboronic acid **3**[9] were used, which gave the corresponding polymers **4**[7] and **5**[8]. The model compounds **6-8** were also employed. Polycondensations were done using the standard Suzuki protocol[10] and catalyst precursors $Pd(PPh_3)_4$ (A: as purchased; B: freshly prepared[11]) and $Pd[P(p\text{-}tol)_3]_3$[12] (C). All questions regarding P-incorporation were investigated by ${}^{31}P$ NMR spectroscopy. The molecular weights were determined by gel permeation chromatography (GPC) versus polystyrene (PS) standard. Details regarding monomer purification, polycondensation, molecular weight determination and determination of the P-content are outlined in the Experimental Section. The results regarding molecular weights (21 runs) and P-incorporation (8 runs) are summarized in Table 1.



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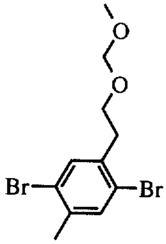

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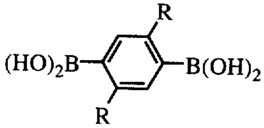

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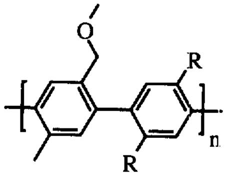

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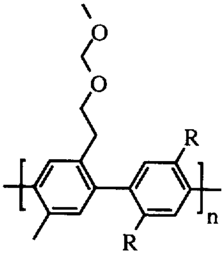

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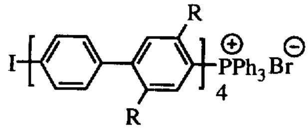
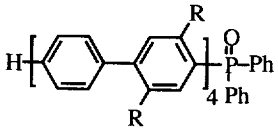


8a



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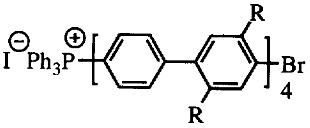
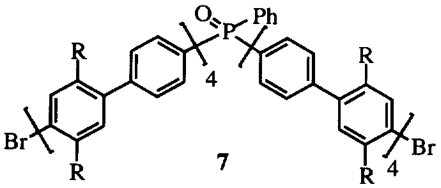


8b



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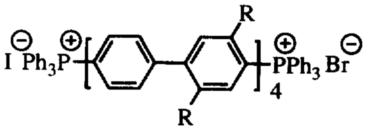

8c

P-incorporation was studied for eight different preparations of **4** and **5** using the different catalyst precursors A, B, and C (Table 1, entries 2,7,10,11,13,15,17,21). The purified polymers were dissolved in $CDCl_3$ and the ^{31}P NMR spectra were taken (Fig. 1). The signals downfield 40 ppm stem from the internal integration standard (δ = 46.6 ppm) and impurities associated with it. All up-field signals stem from phosphorus compounds which cannot be removed by extraction (except for the signal at approximately δ = 27 ppm which belongs to residual triarylphosphine oxide). Thus, both kinds of polymers regardless of the catalyst used and the molecular weight obtained actually contain phosphorus. This finding, together with that of Novak,[6] makes it reasonable to assume that incorporation of phosporus during Suzuki polycondensation is a general phenomenon. The degree of incorporation was determined quantitatively by NMR integration (see Experimental). As can be seen from the data in Table 1, the values vary considerably but lie between 1 phosphorus per 3-7 polymer chains for the higher molecular weight polymers (entries 7,10,11,13,21). This extent of incorporation is low and establishes the negligible importance of this side reaction. Most chains are in fact free of any phosphorus. For the low molecular weight polymers the incorporation is even less pronounced. Expressing the degree of P-incorporation in number of chains implies that the molecular weight is accurate, which presumably is incorrect. For a comment on this matter see the Experimental Section.

Table 1. Molecular weights (M_n, M_w), degrees of polymerization (P_n, P_w) and phosphorus incorporation of polymers prepared.

Entry	polymer	catalyst pre-cursor$^{\alpha}$	M_n (g/mol)	Mw (g/mol)	P_n	P_w	D^{β}	yield (%)	weighed polymer mass (mg)	P-content (10^{-4} mmol)	r.u's/ P-atom
1	4	A	5,400	9,300	14	25	1.7	77			
2	4	A	6,100	12,300	16	33	1.3	94	52.8	0.5	2562
3	4	A	7,900	17,400	21	46	2.2	96			
4	4	A	8,900	21,100	23	56	2.4	94			
5	4	B	15,300	43,300	41	114	2.8	96			
6	4	B	16,700	60,600	44	160	3.6	97			
7	4	B	17,900	53,000	47	140	3.0	99	41.6	3.9	282
8	4	B	18,200	55,400	48	146	3.0	98			
9	4	B	18,300	56,800	49	150	3.1	96			
10	4	C	27,200	87,700	72	232	3.2	99	68.0	7.5	239
11	4	C	28,000	91,500	74	242	3.3	99	68.3	4.0	453
12	4	C	29,800	115,900	78	306	3.9	99			
13	4	C	31,300	100,000	83	264	3.2	96	68.5	3.0	605
14	5	A	3,800	7,300	9	19	1.9	70			
15	5	A	4,500	7,000	11	17	1.6	94	59.6	2.0	714
16	5	A	5,100	8,500	12	20	1.7	83			
17	5	B	6,400	7,800	15	27	1.8	94	55.8	4.9	268
18	5	B	9,700	23,300	23	55	2.4	92			
19	5	C	21,000	66,700	50	158	3.2	97			
20	5	C	22,100	85,700	52	203	3.9	99			
21	5	C	23,500	58,800	56	139	2.5	99	55.8	8.1	163

$^{\alpha}$A = purchased $Pd[PPh_3]_4$; B = freshly prepared $Pd[PPh_3]_4$; C = freshly prepared $Pd[P(p\text{-tol})_3]_3$. $^{\beta}$ M_w/M_n.

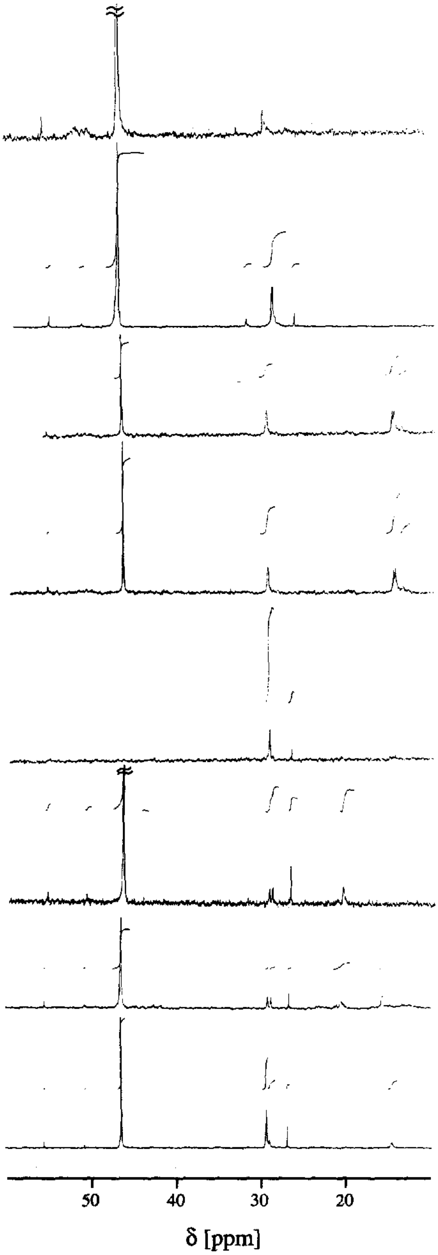

Fig. 1: ^{31}P NMR spectra (203 MHz, $CDCl_3$) of polymers **4** and **5** ordered from top to bottom like the corresponding entries in Table 1 (**4**: entries 2,7,10,11,13 and **5**: 15,17,21). For a description see text.

In the next step, the question of the nature of incorporated phosphorus was approached by chemical shift considerations using data from literature[13] and those of the model compounds **6-8**. It should be mentioned that during work-up all phosphines were automatically oxidized to the corresponding oxides. Two shift regions in the spectra are of obvious importance namely $\delta = 29 - 30$ and $\delta = 14 - 16$ ppm. They were assigned as triaryl phosphine oxides and as tetraarylphosphonium bromides, respectively. The former typically absorb in the range of $\delta = 25 - 35$ ppm and the latter in that of $\delta = 10 - 22$ ppm. The signals of the model compounds also lie in these ranges supporting the assignment [**6**: $\delta = 28.85$, **7**: $\delta = 28.88$, **8**: $\delta = 18.60$ (Br^- counter ion) and 10.30 (I^- counter ion) ppm]. Based on it the lower field signals reflect aryl/aryl scrambling, thus, a polymer chain bound to Pd and a phenyl group of a phosphine ligand at the same Pd were exchanged. The higher field ones are due to formation of phosphonium ions by the known Pd-mediated coupling of excess triaryl phosphine and aryl bromides.[6,14] Since all spectra contain the first category of signals it can be concluded that all polymerizations are accompanied by aryl/aryl scrambling whereas phosphonium ion formation obviously takes place only during some of them.

Aryl/aryl scrambling leads in the first step to termination through the incorporation of diphenylphosphino end groups. If, in a subsequent step, a phosphine carrying two phenyl groups and a polymer chain is again involved in a scrambling process, phosphorus becomes an integral part of the backbone. The question of where the phosphorus is incorporated was addressed with model compounds **6** and **7** which resemble the different possibilities. Not completely unexpected, the shift differences were too small for an interpretation (see above). Nevertheless, it is assumed that at least part of the phosphorus incorporated by aryl/aryl scrambling is positioned at chain ends, because (a) this is the necessary first step, and (b) the GPC elution curves are monomodal. Two successive scrambling steps would provide polymers with one kink at phosphorus and doubled molecular weight. This argument should, however, not be overemphasized because the concentration of these defects is very small anyhow and detection in GPC has its limits.

An explanation for the phosphonium ion formation may be the following. As described in the Experimental the catalyst sometimes stayed in solution until the polymerization was quenched. In other cases it precipitated as a black amorphous powder. Interestingly whenever the catalyst stayed homogenous, the higher field signals appeared in the spectra (entries 10,11,17). Obviously an increased lifetime of the catalyst is required for phosphonium ion formation to take place. There is no significant difference in the molecular weights achieved for the higher molecular weight samples whether or not there is phosphonium ion formation (compare entries 10,11 with entry 13). This side reaction therefore does not seem to be an inherent phenomenon of the cross-coupling but rather a subsequent step which presumably takes place between liberated triphenyl phosphine and bromine end groups of the polymer chains.[15] It can be suppressed by quenching the polycondensation once the maximum molecular weight is reached. For this purpose the molecular weight dependence on polycondensation time has to be monitored (by GPC) for each set of monomers and reaction conditions.

Finally the reproducibility of the molecular weights achieved in Suzuki polycondensations should be commented upon. The yields of isolated and lyophilized polymer are almost throughout very high (Table 1). The GPC measurements were done using representative material which had not been fractionated. For a given catalyst precursor and a given monomer the molecular weights obtained are very similar specifically in the (most interesting) higher molecular weight cases (entries 5-9, 10-13, and 19-21). Thus, Suzuki polycondensation gives reproducible results. It should be emphasized at this point, however, that this holds true only if the Pd complexes are freshly prepared or recrystallized. Storage in a dry box (< 1 ppm oxygen, < 1 ppm water) can only be recommended for a few days. It is also necessary to freshly distill the dibromides **1** and **2**. In contrast, the diboronic acid **3** can be easily stored at room temperature, under nitrogen and in the dark for several months without any decrease in quality. The data also show that the commercially available Pd catalyst (regardless of the company it was purchased from) should not be used as obtained.

Model compounds **6-8** were prepared only to measure their ^{31}P NMR chemical shifts. Except for **6** no detailed procedures were therefore developed. Compounds **7**[16] and **8a-c** were obtained as product mixtures which were not separated into the individual components since the structure/shift correlation could be done with certainty. For example, compound **7** was accompanied by a phosphine oxide with two aryl groups (phenyl and oligophenylene) and one butyl group (from the use of butyl lithium). The two ^{31}P-NMR signals of this mixture appeared at $\delta = 31.08$ and $\delta = 28.88$ and were easily differentiated by taking into consideration that replacement of aryl by alkyl groups in phosphine oxides results in a high field shift. Additionally, the $^{31}P/^{1}H$ 2D NMR spectrum showed for the higher field ^{31}P-signal a cross peak with α-CH_2 in the ^{1}H NMR. All synthetic procedures involved standard phosphine chemistry. Compound mixture **8a-c** showed two ^{31}P NMR signals at $\delta = 18.60$ (Br^- as counter ion)and $\delta = 10.30$ (I^- as counter ion) which were assigned to phosphonium bromides and iodides respectively. Because of the large distance between the phosphonium ions in **8c** no extra signal for this compound was detected. Its existence however was proven by mass spectroscopy.

First experiments with the Beller type catalyst precursor show that it is very reactive in Suzuki cross couplings but leads to an unacceptably high degree of deboronification (for a polycondensation).[17] Further work will be needed to show whether conditions can be found for its usage in polycondensation reactions.

CONCLUSION

The Suzuki cross coupling reaction of bifunctional monomers is a truly powerful method for step-growth polymerizations leading to high molecular weight polyarylenes and related polymers. Results are fully reproducible if freshly prepared catalyst precursors are used and stoichometry is strictly balanced. The incorporation of ligand derived phosphorus is virtually negligible.

EXPERIMENTAL SECTION

Monomer purification

The water content of the diboronic acid **3** was determined NMR-spectroscopically as described elsewhere.[8,18] Typically monomer **3** contained between 2.5 and 5.0% water. Since these determinations were found to have an uncertainty of approximately 0.5% an additional measure to ensure correct stoichiometry was taken. Monomer **3** was subjected to test polycondensations with monomer **1** taking this water content to calculate the amount of comonomer, but also assuming both a slightly larger and a slightly lower water content. For example, if NMR integration of a sample of **3** gave a water content of 2.7% three polycondensations were performed, the required amount of **1** was calculated using water contents not only of 2.7% but also 2.1% and 3.3%. The water content which led to the polymer with the highest degree of polymerization was then considered correct and was further used for all experiments with this batch. It should be mentioned that the boronic acid used does not contain self-condensation products. The degree to which such products are formed can be controlled by the precise mode of recrystallization. Generally, the faster the monomer is cooled after it had completely dissolved in refluxing acetone containing 1% HCl the less condensation takes place. Monomer **3** should, of course, also not be exceedingly dried. Best results are usually obtained if a batch of 50 g is dried in high vacuum at room temperature for 45 min. The dibromides **1** and **2** were freshly distilled through a Vigreaux column in high vacuum before each use. Both monomers were stored in Schlenk tubes in the dark under nitrogen.

Polycondensations

All polycondensations were performed with one and the same batch of monomer **3**. This could not be done with monomers **1** and **2** which had to be distilled prior to use. Here series of three to four polycondensations were done with each batch. All polycondensations were performed in refluxing 2N Na_2CO_3/toluene for 3 d using 1.00 mmol of each monomer and 1 mol-% of catalyst precursor A, B, or C [A: commercial tetrakis(triphenylphosphine)Pd(0); B: freshly prepared tetrakis(triphenylphosphine)Pd(0);[11] C: trikis[(tri-para-tolyl)phosphine]Pd(0)]. After 3 d most of the reactions had turned black in some, however, the organic phase stayed yellow. The reaction can be stopped once the catalyst has precipitated. Monitoring of a polycondensation of **1** and **3** for 22 h after the mixture has turned black (after 16 h) neither revealed any change in molecular weight (and dispersity) nor in phosphorus incorporation. The polymers were recovered by precipitating them twice into MeOH followed by lyophilization with benzene. During this procedure all phosphines were oxidized into the corresponding phosphine oxides (^{31}P NMR). To remove possible P-containing impurities not bound to the polymer, the material was hot extracted with MeOH. This way, only one compound was removed which was identified as either triphenylphosphine oxide [$\delta(^{31}P) = 27.12$ ppm] if catalysts A or B were used or tri(p-tolyl)phosphine oxide [$\delta(^{31}P) = 27.52$ ppm] if catalyst C was used. It should be mentioned that the structures for polymers **4** and **5** are simplified in that the regio isomers formed due the lack of symmetry of both dibromides are disregarded.

Molecular weight determination

The molecular weights given in Table 1 were determined by gel permeation chromatography (GPC) in THF at 20° C calibrated with polystyrene (PS) standards. Since it is not reasonable to assume that PS is a good reference for the rod-like polymers reported here the data should be considered with care. This calibration may lead to an over- as well as underestimation of the actual molecular weight by a factor of up to two as was shown for a PPP derivative with sulfonate groups[19] and one with iodomethyl substituents,[20] respectively. All GPC curves are monomodal except for those of entries 10-13, where the respective main peak is accompanied by a small one at significantly shorter retention time. This latter peak is due to reversible aggregates, which was proven by injecting more highly diluted and pre-warmed solutions in which no such additional peak was observed.

Determination of P-Content

The amount of phosporous contained in the polymer samples which had not been removed during the extraction was determined with ^{31}P NMR spectroscopy (Bruker AC, 203 MHz) externally referenced to 80% H_3PO_4 (Fig. 1). The spectra do not contain any signals outside the range shown. To ensure reliable inegrations, a pulse delay of 4 sec was applied. Tributyl phosphine oxide (95%) was used as internal integration standard. The determination was done as follows: The amount of polymer given in Table 1 was weighed into an NMR tube and 10 µL of a 0.0012 mM stock solution of the standard in $CDCl_3$ were added with an Eppendorff pipette whose calibration had been checked. Then approximately 1 mL of $CDCl_3$ was added and the ^{31}P-NMR spectrum recorded. All signals were integrated except for those from impurities contained in the commercial standard. The total integral of all signals was compared with the standard's integral yielding the mmols of P incorporated assuming that there are no magnetically equivalent P-atoms in the sample. Comparison of these figures for each run with those for the mmols r.u.'s led to the figures in the last row of Table 1.

Tetra-p-(2,5-di-n-hexyl-biphenylen)diphenylphosphine oxide (6). To a mixture of 4-bromo-4$^{(7)'}$-iodo-tetra-p-(2,5-dihexyl-biphenylene)[21] (95 mg, 0.07 mmol) and TMEDA (0.025 mL) in dry toluene (5 mL) a solution of butyllithium (1.6 M, 0.3 mL) in hexane is added at 20° C. The initially green solution is stirred for 2 h in which period it turns orange (after about 30 min). Then chlorodiphenyl phosphine (120 mg, 0.55 mmol) is dropped slowly into the solution which leads to formation of a white precipitate. The mixture is stirred overnight at room temperature, then water is added and the phases are separated. The aqueous layer is extracted twice with toluene, and the combined organic layer is dried over $MgSO_4$. After removal of the solvant, a white precipitate is obtained. The product is purified by using column chromatography (silica; eluent: toluene/acidic acid ethylester (4:1)). Yield: 50 mg (53%). ^1H NMR (500 MHz, $CDCl_3$):δ = 7.74 (4 H, dd, J = 7.7 Hz, J = 11.6 Hz, o-HC_{ar}-PO, P-decoupling leads to one doublet with J = 7.2 Hz), 7.56 (2 H, dt, J = 0.8 Hz, J = 7.4 Hz, p-HC_{ar}-PO, P-decoupling leads to one doublet with J = 7.4 Hz), 7.49 (4 H, dt, J = 2.0 Hz, J = 7.5 Hz, m-HC_{ar}-PO, P-decoupling leads to one doublet with J = 7.5 Hz), 7.43, 7.37, 7.26 (1 H, d, J = 4.3 Hz, 3-C_{ar}-H, P-decoupling leads to a singlet, 7.24, 7.21 , 7.16, 7.04 (1 H, d, J = 3.9 Hz, 6-C_{ar}-H, P-decoupling leads to a singlet), 2.82 (2 H, t, α-CH_2-2-$C_{ar\text{-}PO}$), 2.65 (10 H, m, α-CH_2), 2.59 (2 H, t, α-CH_2), 2.50 (2 H, t, α-CH_2-5-C_{ar}-PO), 1.53, 1.35, 1.22, 1.06, 0.82. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 145.29, 145.09, 141.93, 140.84, 140.71, 140.52, 140.26, 140.20, 139.39, 137.68, 137.63, 137.57, 137.50, 137.00, 134.69, 134.58, 133.85, 133.03, 132.43, 132.34, 132.01, 131.94, 131.65, 131.01, 130.95, 129.31, 129.04, 128.92, 128.60, 128.49, 128.39, 127.98, 126.66, 37.08, 33.94, 32.74, 32.63, 32.28, 31.94, 31.551, 31.38, 30.60, 29.69, 29.35, 29.27, 28.67, 27.24, 22.51, 22.44, 14.06. ^{31}P NMR (203 MHz, $CDCl_3$) δ = 28.85 ppm. Mass spectrum (FAB^+, Xenon, CH_5DF, $CHCl_3$/m-nitrobenzyl alcohol) m/z = 1484.

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15. An attempt to deliberately generate phosphonium ions at the bromo termini of polymer **4** (P_n = 67, P_w = 194) failed. Suzuki treatment of **4** with 10 mole-% of catalyst C for 36 h (no boronic acid present) led to an increase of the phosphine oxide NMR signal by a factor of approximately 1.8 but no detectable phosphonium ion signal or any other change. The percentage of the catalyst refers to number of r. u.s and was, thus, used in an enormous excess to bromine end groups.
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