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Functional Oligomers, Telechelics, and Graft and Star-Shaped Poly(2,6-dimethyl-1,4-phenylene ether)s Prepared by Redistribution

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The conventional synthesis of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is based on the oxidative coupling polymerization of 2,6-dimethylphenol as discovered by Hay.¹ Mechanistic studies have revealed that this polymerization is catalyzed by a copper–amine complex via either radicals or ionic species.² Concurrently with the polymer-forming C–O coupling, a redistribution takes place, which can be regarded as a transesterification of phenols and phenolic ethers. In contrast to the oxidative coupling, only a few reports deal with the mechanism of redistribution. Recently, Heitz showed that the competition of polymerization and redistribution is operative under normal conditions in the copolymerization of tetramethyl-Bisphenol acetone and 2,6-dimethylphenol.³ Earlier, Bolon and Cooper reported on the redistribution of phenol dimers under the influence of free-radical initiators or a copper catalyst.⁴ Based on this free-radical redistribution reaction, low molecular weight hydroxyarylene ethers are prepared when phenols are brought into reaction with PPE in the presence of a suitable initiator.⁵ Compounds such as 3,3',5,5'-tetramethyl-4,4'-diphenylquinone (TMDPQ), *tert*-butyl perbenzoate, and benzoyl peroxide are active initiators. Via this technique, several PPE/epoxy laminates could be prepared.⁶ A phase-transfer-catalyzed (PTC) depolymerization by a radical-anion mechanism in the presence of either 2,4,6-trimethylphenol or 4-*tert*-butyl-2,6-dimethylphenol is described by Percec⁷ using commercially available PPE. However, the polymers thus obtained show a bimodal molecular weight distribution, possibly due to the presence of Manich bases.^{5a,8} In this paper we present the depolymerization of PPE by the redistribution with functional phenols or multifunctional phenols without the use of radical initiators. The polymers prepared via this transesterification are well-defined and have a monomodal molecular weight distribution. Employing different phenols, a wide variety of functional polymer systems can be synthesized, including telechelics and graft and star-shaped polymers.

The experiments presented here were triggered by the observation that upon the addition of 4-*tert*-butyl-2,6-dimethylphenol (TBDMP) (4.55 g, 25.5 mmol) to PPE (10.0 g, $M_n = 3500$, 83.17 mmol of dimethylphenol repeating units, made by precipitation polymerization⁹) at room temperature in toluene (100 mL) using a Pyrex glass vessel, the latter is depolymerized to low molecular weight oligomers ($M_n = 650$). TBDMP is consumed and is incorporated as the tail unit in the oligomeric product as observed by ¹H-NMR spectroscopy.

Table 1. Monitoring Reaction by ¹H-NMR Spectroscopy

reacn time (h)	TBDMP conv (%)	(\overline{DP}) ^a
0	0	29.1
1	28	9.1
24	35	5.4
144	60	4.3
192	66	3.8
336	70	4.2

^a \overline{DP} (PPE) corresponds to the degree of polymerization as determined from the ratio of the peak integrals of the repeating units and end group.

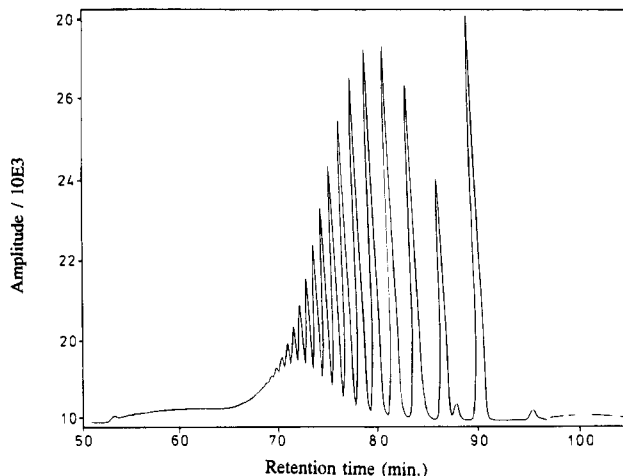


Figure 1. GPC oligomers from PPE redistribution with TBDMP.

The TBDMP conversion and average degree of polymerization (\overline{DP}) of the PPE are monitored during the redistribution by means of ¹H-NMR spectroscopy, and the results are presented in Table 1. Figure 1 shows the GPC chromatogram (THF, 40 °C, columns 3 × 100 Å and 5 × 500 Å type PL Gel 5, 210 nm UV–vis detector) of oligomers prepared after a reaction time of 14 days. HPLC and ¹H-NMR spectroscopy show the presence of mainly oligomers with a TBDMP tail unit and almost no oligomers (< 5%) with a 2,6-dimethylphenoxy tail unit. These results can be explained by a slow redistribution reaction without polymerization. By adding the polymerization catalyst CuCl/4-(dimethylamino)pyridine (DMAP), we could increase the reaction rate of the redistribution reaction significantly, especially when oxygen is present. However, in that case the well-known oxidative polymerization and some ill-defined oxidative side reactions¹⁰ occur as well. However, using oxygen-free conditions, we were able to obtain clean redistribution reactions with a reasonable rate, but without oxidation. If these oxygen-free conditions cannot be met, then less basic ligands with the catalyst (Cu(NO₃)₂·3H₂O/*N*-methylimidazole (NMI) or crown ethers) should be used to suppress/avoid the oxidative polymerization during the redistribution. This is in agreement with the mechanistic studies of Challa, Reedijk, and co-workers, reporting on the requirement of a phenolate as an intermediate in the copper-catalyzed oxidative polymerization.¹¹ Besides the type of ligand, also the ligand/copper (L/Cu) ratio is of interest.¹² Most appropriate reaction conditions are performed with the catalyst system CuCl/DMAP, L/Cu ratio ~1.6 with exclusion of oxygen, or Cu(NO₃)₂·3H₂O/NMI, L/Cu ratio ~10 under ambient conditions.

In order to study the scope and limitations of this redistribution reaction without oxidation, several mono-

Table 2. Examples of PPE Depolymerization

added phenol	$M_n(\text{PPE})$ begin	PPE repeating units/phenol ratio	M_n precipitated product ^a
2,6-dimethyl-4- <i>tert</i> -butylphenol	3500	9.5	1400
4- <i>tert</i> -butylphenol	11200	10	1910
4- <i>tert</i> -butylphenol	11200	15	2400
2,6-dimethylphenol	11200	1.8	2810

^a Molecular weights belonging to the polymer fraction insoluble in methanol; the low molecular weight fraction is soluble in methanol. Molecular weights are determined using ¹H-NMR spectroscopy.

functional phenols were brought into reaction with PPE in a good solvent. Some examples of PPE depolymerization are summarized in Table 2. Reaction time depends on reaction conditions and the phenol employed. The reaction rate is strongly influenced by the nature of the substituent of the phenol: generally phenols with electron-donating substituents show high reaction rates, whereas phenols with electron-withdrawing groups, like cyano, or steric bulky *ortho* substituents, like *tert*-butyl, are unreactive. The following *para*-substituted monofunctional phenols are simply introduced as a polymer tail unit: 4-*tert*-butyl-2,6-dimethylphenol, 4-*tert*-butylphenol, 4-methoxyphenol, 4-phenylphenol, 4-chlorophenol, 4-acetamidophenol, 4-(hydroxypropyl)-2,6-dimethylphenol, 4-allyl-2,6-dimethylphenol. *Para*-unsubstituted phenols employed in the redistribution are 2,6-dimethylphenol and the dimer 4-(2,6'-dimethylphenoxy)-2,6-dimethylphenol. The redistribution is monitored by ¹H-NMR spectroscopy. The protons in the tail or head units differ from those of the repeating unit, which is reflected by different chemical shifts, especially in the aromatic region. Moreover, not only the first and last repeating units are detected separately, but in the case of redistribution with *ortho*-unsubstituted phenols also the penultimate tail repeating unit is usually observed. These spectra show sharp peaks and the aromatic C-H peaks of the polymer head unit are clearly detectable, contrary to similar polymers synthesized by a PTC method.⁷ Therefore, the polymer seems to be extremely pure without any *ortho*-methyl group oxidation. This is confirmed by ¹³C-NMR spectroscopy (no peaks at 114.5 and 132.5 ppm) and FTIR spectroscopy (no absorption at 1645 cm⁻¹). Although the disproportionation in the redistribution mechanism should give rise to two types of oligomers, oligomers with a substituted tail unit and oligomers with an unsubstituted 2,6-dimethylphenoxy tail unit, almost no oligomers are present with an unsubstituted tail unit as observed by HPLC and ¹H-NMR spectroscopy. This suggests that some C-O coupling must occur.

The use of multifunctional phenols in this clean and convenient redistribution opens the pathway to the synthesis of numerous multifunctional PPE's. Bifunctional phenols are introduced into the polymer, resulting in telechelic polymers with two hydroxyl chain end functionalities, polymers that are of interest as precursors for block copolymers or polymer networks. The following bisphenols are employed: 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl-Bisphenol acetone) (TMBPA), 4,4'-isopropylidenediphenol (Bisphenol acetone) (BPA), bis(4-hydroxy-3,5-dimethylphenyl)-methane (tetramethyl-Bisphenol formaldehyde) (TMBPF), bis(4-hydroxyphenyl)methane (Bisphenol formaldehyde) (BPF). As an example the 400 MHz ¹H-NMR spectrum of a telechelic polymer with a TMBPA core is

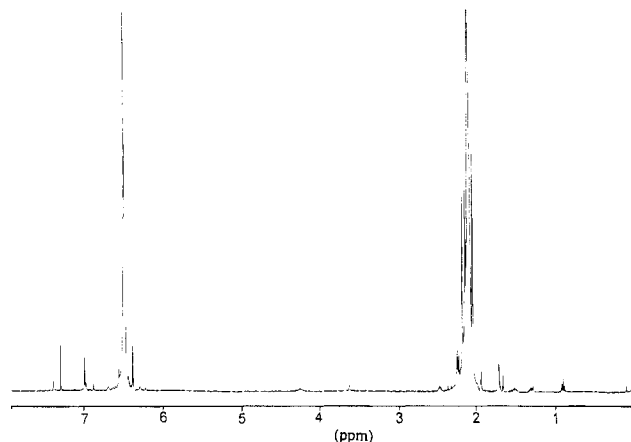
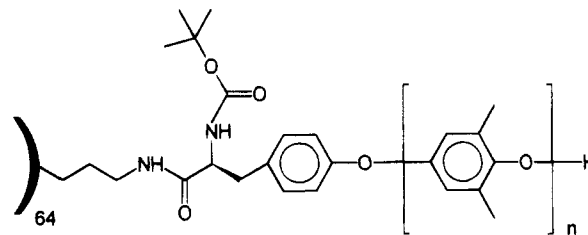


Figure 2. ¹H-NMR spectrum of telechelic polymers with a TMBPA core; preparation by reacting 0.16 g of TMBPA, 3.41 g of PPE ($M_n = 11200$), 0.14 g of DMAP, and 0.07 g of CuCl in 30 mL of chloroform under argon. After 9 h of reaction time, extraction with EDTA(aq. (10%)), HCl(aq. (10%)), NaOH(aq. (10%)), and evaporation of the chloroform, a telechelic polymer was isolated. Peak assignments are described by Risse^{13b} and Nava.^{13d}

Chart 1. PPE Star-Shaped Polymer with a 64-Functional Dendritic Core



shown in Figure 2. Although GPC shows a complete conversion of PPE into bifunctional telechelics, NMR spectroscopy indicates that the bisphenolic distributing agent is not built-in statistically. A significant portion of the bisphenol is found at the tail end, leading to a telechelic with two different end groups. Any explanations for this behavior are speculative at this time. Telechelic polymers have been prepared by the copolymerization of DMP with, e.g., TMBPA as well;¹³ however, besides the copolymerization, also substantial DMP homopolymerization takes place. Pure telechelic polymers are only obtained after redistribution.³

The versatility of the redistribution is shown by synthesizing graft copolymers or star-shaped polymers. In a first approach, we used *tert*-butyl calix[*n*]arenes as a core with *n* = 4 and 8. Due to intramolecular hydrogen bonding in *n* = 4 we were not able to obtain well-defined structures from calix[4]arene. The redistribution in the case of calix[8]arene yields an eight-armed star polymer. All spectroscopic data indicate that here all phenols of the calix[8]arene have reacted. When poly(*p*-hydroxystyrene) is used for redistribution with PPE in THF, a graft copolymer is prepared with a polystyrene backbone and poly(2,6-dimethyl-1,4-phenylene ether) side chains. Star-shaped polymers with a dendritic core are of great interest and are prepared from PPE redistribution with *N*-*tert*-Boc-protected tyrosine modified poly(propylene imine) dendrimers (Chart 1).¹⁴ The arm length of the star-shaped polymers is determined by the molar ratio of PPE repeating units and tyrosine end groups. The number of arms is determined by the generation of dendrimer (i.e., 4, 8, 16, 32, or 64 end groups) or by a 64 end group dendrimer

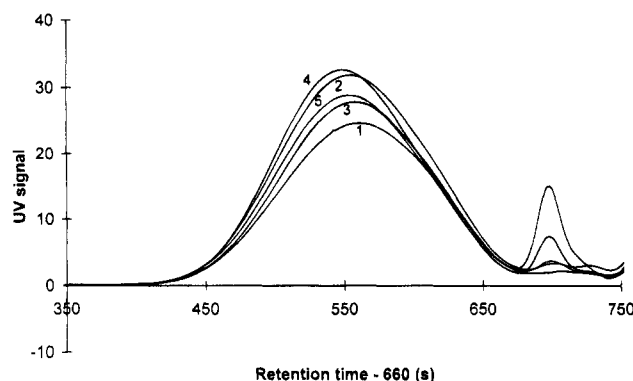


Figure 3. SEC star-shaped polymers prepared from different generations of dendrimer with the same estimated average arm length (22.5 units) using THF as eluents. The numbers 1–5 are indicative for the dendrimer generation (4–64 end groups).

Table 3. Dynamic Light Scattering Data

dendrimer generation	estd no. of PPE arms	\overline{DP}	R_H (nm)
5 ^a	0	0	2.1
5 ^b	12.8	22.5	2.4
5 ^b	32	22.5	3.4
5 ^b	51.2	22.5	4.0
5 ^c	64	22.5	5.7
4 ^c	32	22.5	4.2
2 ^c	8	22.5	3.7

^a Dendrimer 100% modified with phenylalanine end groups.

^b Dendrimer core modified with phenylalanine/tyrosine mixture.

^c Dendrimer core modified with tyrosine.

which is modified with a statistical mixture of tyrosine and phenylalanine. All star-shaped polymers show divergent physical properties in comparison with the linear analogues as observed by dynamic light scattering and size exclusion chromatography by implementing an on-line viscometer.¹⁵ Figure 3 shows the SEC chromatograms using a UV detector (THF, 40 °C, columns 2 × Shodex KF 80-M, 254 nm UV detector) and polymers with the same estimated average arm length but with a different number of arms show the same hydrodynamic volume. However, dynamic light scattering (DLS) measurements in THF (Table 3) (ALV/SP-86 goniometer, Spectra Physics series 2000 Ar⁺ laser (514.5 nm, 300 mW)) show that the hydrodynamic radius increases with the number of arms. This increase is proposed to be caused by a restricted mobility of the arms at high number of arms and/or generation, which is expressed in the hydrodynamic radius as measured with DLS but not in the hydrodynamic volume as measured by SEC.

In conclusion, a general synthetic technique for multifunctional poly(phenylene ether)s has been described. Oxidative polymerization and redistribution are disconnected by tuning the reaction conditions. Chain length and end group functionality can be varied easily.

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- (15) Star polymers with the same dendritic core but an increasing number of PPE arms of the same estimated length show a lower refractive index increment (dn/dc), while star polymers with same arm length prepared from different dendrimer generations show a constant dn/dc. The dn/dc is higher for the dendritic core than for the PPE arms. Therefore, only qualitative data could be obtained using SEC implementing a viscometer and refractive index (RI) detector; further studies are under way.

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