Controlled Molecular Weight by the Precipitation Polymerization of 2,6-Dimethylphenol

Huub A. M. Van Aert[a]; Robert W. Venderbosch[a]; Marcel H. P. Van Genderen[b]; Piet J. Lemstra[a]; E. W. Meijer[c]

[a] Centre for Polymers and Composites, [b] Laboratory of Organic Chemistry, [c] Laboratory of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

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CONTROLLED MOLECULAR WEIGHT BY THE PRECIPITATION POLYMERIZATION OF 2,6-DIMETHYLPHENOL

HUUB A. M. VAN AERT

Centre for Polymers and Composites

ROBERT W. VENDERBOSCH

Centre for Polymers and Composites

MARCEL H. P. VAN GENDEREN

Laboratory of Organic Chemistry

PIET J. LEMSTRA

Centre for Polymers and Composites

E. W. MEIJER[*]

Laboratory of Organic Chemistry

Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Key Words: Poly(2,6-dimethyl-1,4-phenylene ether); 2,6-Dimethylphenol; Precipitation polymerization; Oxidative coupling

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ABSTRACT

Low molar mass poly(2,6-dimethyl-1,4-phenylene-ether)s (PPE) have been prepared by the precipitation polymerization of 2,6-dimethylphenol (DMP) under the action of a Cu(I)Cl/amine-catalyst and O_2. The polymers prepared possess a rather narrow molecular weight distribution (D = 1.7–2.2), and the molecular weight can easily be controlled by adjusting the solvent mixture of 2-propanol and toluene. Molecular weights were determined using ^{1}H-NMR spectroscopy, GPC, and FD-MS, and range from M_n = 2700 to 7500 g/mol. No Mannich-base-type endgroups and no incorporation of DPQ (3,5,3′,5′-tetramethyl-4,4′-diphenoquinone) has been detected.

INTRODUCTION

The oxidative coupling polymerization of 2,6-dimethylphenol (DMP), as discovered by Hay [1, 2], results in high molecular weight poly(2,6-dimethyl-1,4-phenylene ether) (PPE), which is of great commercial interest due to its outstanding physical and chemical properties. PPE is an amorphous high performance thermoplastic exhibiting a high T_g of approximately 220°C and excellent mechanical properties with respect to toughness, for example. However, high molecular weight polymers cannot be melt-processed without severe degradation due to the high processing temperature required (300–350°C). PPE is therefore often applied in blends.

Recently, low molecular weight PPE for use in block copolymers of well-defined architectures and low T_g has attracted considerable interest [3–8]. Several methods are available for the preparation of low molecular weight PPE (**1**). The polymerization of 4-bromo-2,6-dimethylphenolate in the presence of an oxidizing
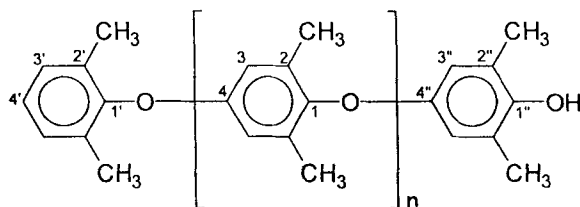
PPE (I)

agent is described by Price [9]. A more elegant approach is based on the phase-transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol in the presence of either 2,4,6-trimethylphenol or 4-*tert*-butyl-2,6-dimethylphenol [10]. However, a number of side reactions are detected; 2,4,6-trimethylphenol can undergo an oxidative dealkylation, which leads to 4,4′-dihydroxy-3,3′,5,5′-tetramethyldiphenyl-methane units. In the phase-transfer catalyzed depolymerization of PPE in the presence of either 2,4,6-trimethyl or 4-*tert*-butyl-2,6-dimethylphenol, no side reac-

tions occur [11], but the polydispersity is large (D = 3-7). White describes the separation of low molecular weight PPE during the redistribution reaction of PPE oligomers [12]. This method is very laborious because the trimer, 4-[4-(2,6-dimethylphenoxy)2,6-dimethylphenoxy]-2,6-dimethylphenol, has to be prepared first. Finally, low molecular weight polymers are prepared if the polymerization is stopped at low conversion [13]. However, several side reactions can occur as well by using this method. One side reaction is due to copper–amine complexes which are well-known catalysts in the oxidative coupling polymerization of DMP; secondary amines, which are used as a ligand for copper, are often incorporated into the polymer by means of a Mannich-base-type endgroup [14]. Another side reaction yields the colored DPQ (3,5,3′,5′-tetramethyl-4,4′-diphenoquinone), which can also be incorporated into the polymer by the quinone-coupling reaction between PPE and DPQ. This reaction leads to a bifunctional polymer with two OH functionalities [15]. Both Mannich-base- and DPQ-incorporation are regarded as side reactions in the PPE synthesis that lead to materials with undesired properties.

In this paper we use precipitation polymerization in order to prepare low molecular weight polymers without impurities. An additional advantage of this technique is that the molecular weight distribution will be narrow due to the precipitation method. In the past a number of papers, mainly patents, concerning the polymerization of 2,6-dimethylphenol in a poor solvent or in a solvent/nonsolvent mixture have been published; however, no details on the polymers prepared are given [16–19].

EXPERIMENTAL

Materials and Methods

2,6-Dimethylphenol (DMP) was supplied by General Electric Plastics and recrystallized from n-hexane. N,N'-Di-t-butylethylene diamine (DBEDA) and di-n-butylamine (DBA) were used as obtained from General Electric Plastics. N,N, N',N'-Tetra-ethylethylene diamine (TEED), 99+%, pure was obtained from Janssen Chimica. Cu(I)Cl, chloroform, toluene, and 2-propanol were obtained p.a. from Merck. Methanol was used extra pure from Lamers & Pleuger.

Techniques

The polymers were characterized using ^{1}H-NMR, ^{13}C-NMR, GPC, and field-desorption mass spectrometry (FD-MS).

The molecular weights were determined using 400 MHz ^{1}H-NMR on a Bruker AM-400 spectrometer by comparing the aromatic C—H peaks of the endgroups with those of the repeating unit. A reproducible number-average molecular weight could be calculated within an accuracy of 5%. The peak assignments were taken from Percec et al. [20]. ^{13}C-NMR spectra were measured at 100.6 MHz on a Bruker AM-400 spectrometer. All NMR spectra were referenced to TMS (δ = 0 ppm).

The molecular weights were also determined with GPC in chloroform at 25°C using the universal calibration method with a set of standard polystyrene specimens. From GPC, using the Mark–Houwink equation with K_{PPE} = 48.3 × 10^{-3} mL/g and a_{PPE} = 0.64 [21], the M_n, M_w, and D = M_w/M_n were calculated.

Field desorption mass spectrometry was performed at the Max-Planck-Institut für Polymerforschung in Mainz, Germany.

Precipitation Polymerization of DMP

A 1-L jacketed flask was thermostated at 40°C. A gas mixture of 80% N_2 and 20% O_2 was let through with a gas flow of 2 mL/s. Two grams (0.016 mol) DMP, 1.39 g (0.008 mol) DBEDA, and 10.44 g (0.08 mol) DBA were dissolved in 416 mL solvent/nonsolvent mixture (vide infra). When the reaction mixture was heated to 35°C, the reaction was started by the addition of 0.4 g (0.004 mol) CuCl to the reaction mixture. Then 48 g (0.39 mol) DMP in 250 mL solvent/nonsolvent mixture was added slowly in 1 hour. After a reaction time of 5 hours, the precipitated polymer was filtered, washed with methanol, and dried in vacuum at 60°C. The polymer was reprecipitated twice from 250 mL chloroform in 3 L methanol.

Other polymers are prepared in a similar way. Solvent/nonsolvent mixtures of 2-propanol with 0–20% v/v toluene were used in order to prepare different molecular weights. If methanol is used as solvent, an even lower molecular weight polymer can be prepared. Also, the tertiary amine TEED is used as ligand in polymerizations with the same solvent compositions. Here 8.7 g (0.051 mol) TEED is used instead of the DBEDA/BDA–ligand system as described above. All polymer yields are between 85 and 95%.

RESULTS AND DISCUSSION

The traditional Cu(I)Cl–amine catalytic system was employed in the precipitation polymerization of 2,6-dimethylphenol (DMP). The polarity of the reaction mixture was adjusted with a solvent mixture of toluene (solvent for PPE) and 2-propanol (nonsolvent for PPE). The systems studied consisted of solvent compositions between 100% 2-propanol and 80% 2-propanol/20% toluene. Two different Cu(I)Cl–amine catalysts were used; Cu(I)Cl with a combination of N,N'-di-t-butylethylene diamine (DBEDA) and di-n-butylamine (DBA), being secondary amines, and N,N,N',N'-tetra-ethylethylene diamine (TEED) as an example of a tertiary amine. In order to prevent the formation of DPQ, a high amine/Cu(I)Cl ratio was used and DMP was added slowly. The polymers precipitated from the reaction mixture and were purified by reprecipitation from chloroform in methanol. Characterization of the polymers prepared was performed with ^{1}H- and ^{13}C-NMR spectroscopy, GPC, and field desorption mass spectrometry.

The results of two series of polymerization using the two different catalyst systems are presented in Table 1. For both ligand systems a similar molecular weight is obtained for a particular solvent/nonsolvent mixture as indicated in Fig. 1. The polydispersity index D determined from the GPC measurements is smaller when a solvent is used with a higher polarity, which is caused by a earlier precipitation in more polar solvents. From Fig. 1 it is concluded that the molecular weight can be regulated easily by adjustment of the solvent composition. The results obtained from ^{1}H-NMR spectroscopy and GPC are similar, so the Mark–Houwink equation remains useful even with the low molecular weight polymers. The results from NMR are probably slightly more accurate because here the determination of molecular

TABLE 1.   Molecular Weight as a Function of Solvent Composition

Toluene, % v/v	Amine	M_n, g/mol		D
		^{1}H-NMR	GPC	
0	DBA/DBEDA	2750	2800	1.66
	TEED	2700	3300	1.95
5	DBA/DBEDA	3300	3000	1.75
	TEED	3400	3400	2.05
10	DBA/DBEDA	4500	4500	1.71
	TEED	4550	4500	1.96
15	DBA/DBEDA	5500	6000	2.04
	TEED	5750	5100	2.09
20	DBA/DBEDA	7500	6900	2.22
	TEED	7400	6500	2.22
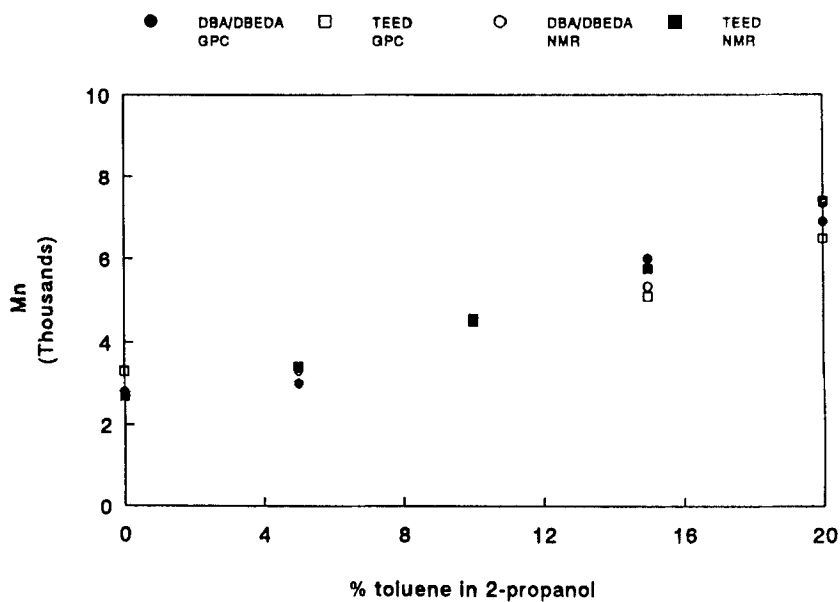
FIG. 1.   Molecular weight as determined by ^{1}H-NMR and GPC.

weight is direct and no calibration is required. Molecular weights are determined directly from ^{1}H-NMR by comparing of the peaks of the endgroups with those of the repeating unit [20]. The accuracy of the determination of the molecular weights and polydispersity index with GPC depends predominantly on the analysis of the chromatograms, determination of the base line and detection of the beginning and end of the peak, and the calibration curve determined with standard polystyrene specimens.

Field desorption mass spectrometry (FD-MS), as developed in 1969 by Becky [22] and rapidly developed since, has proved to be a powerful tool in polymer characterization [23–25]. In Fig. 2 the FD-MS spectrum is shown for a polymer with $M_n = 1500$ g/mol (according to ^{1}H-NMR). This polymer is prepared by precipitation polymerization in methanol. When methanol is used as solvent, a lower molecular weight distribution is obtained in comparison with the polymerization in 2-propanol ($D = 1.46$ as determined from GPC). All oligomeric species are separately detectable and differ by the mass of one repeating unit (120.15). In the low molecular weight region, smaller peaks are also present due to double-charged ions. No peaks that can be assigned to side products are detected. From the FD-MS spectrum it can be calculated that $M_n = 1620$ g/mol, $M_w = 2046$ g/mol, and $D = 1.26$. The polydispersity index obtained from FD-MS is lower than the one obtained with GPC, possibly because high molecular weight PPE is more difficult to ionize. For polymers with $M_n > 1500$, the polydispersity index is even smaller than 1.26. Therefore, FD-MS seems only applicable for very low molecular weight samples of PPE.
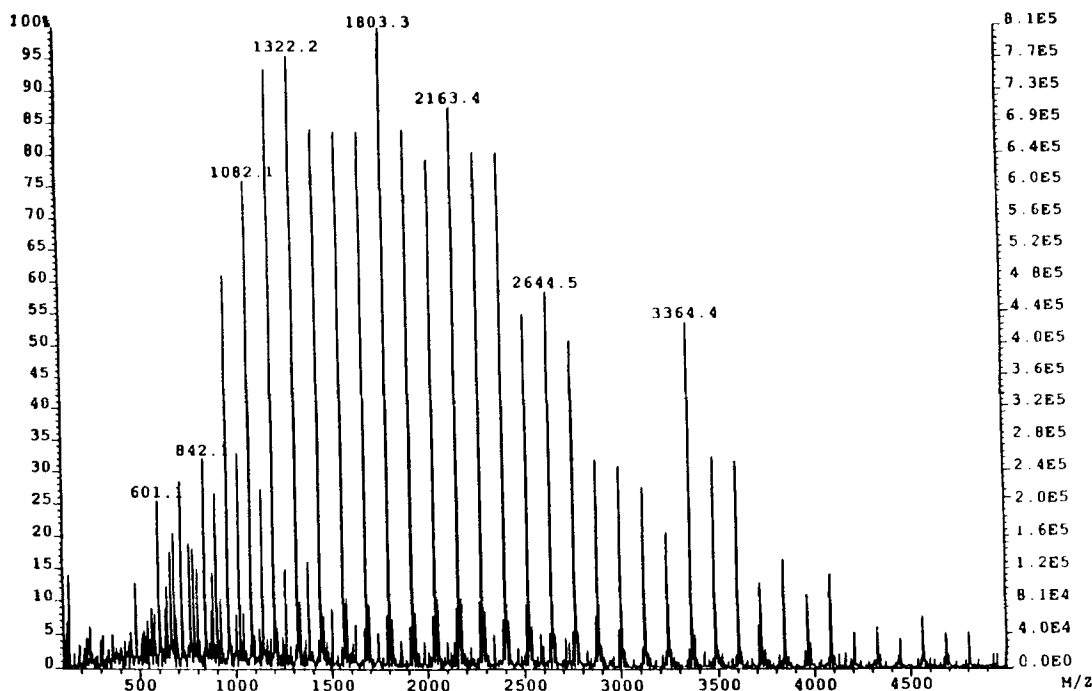

FIG. 2.   FD-MS spectrum of PPE, $M_n = 1500$ g/mol; the resonances are as assigned in structural formula (1).

The mixture of DBEDA and DBA frequently used by General Electric Plastics is a well-known ligand system [26] and can lead to Mannich-base-type endgroups [14]. TEED is a tertiary amine and therefore cannot lead to a Mannich-base-type endgroup. For example, when DBA is used, the phenolic endgroup can contain a dibutylamine group bonded to the ortho-methyl group. According to White, amine incorporation can be detected by ^{13}C-NMR spectroscopy [14]. In order to investigate the occurrence of these side reactions in our precipitation polymerization, we have compared the ^{13}C-NMR spectrum of a commercial polymer, PPO-803 M_n = 11,000 g/mol (Fig. 3), as a reference with a polymer with M_n = 2750 g/mol prepared by precipitation polymerization (Fig. 4). The commercial polymer is prepared with the DBA/DBEDA ligand system. In the ^{13}C-NMR spectrum some peaks of Mannich-base-type endgroups are detected (δ = 53.1, 28.3, 20.5, and 13.9 ppm). The ^{13}C-NMR spectrum also shows some DPQ incorporation (δ = 154.3, 137.4, 127.7, and 127.3 ppm). The peaks from amine and DPQ incorporation are higher or equal in size in comparison with the peaks of the unmodified endgroups (δ = 154.7, 151.4, 146.4, 131.4, 128.9, 124.9, 124.5, and 114.1 ppm) as assigned in the structural formula (1). Figure 4 shows the ^{13}C-NMR spectrum of a polymer with M_n = 2750 g/mol, made with the DBA/DBEDA ligand system by precipitation polymerization. The ^{13}C-NMR spectra of the polymers made with the DBEDA/DBA ligand system show no peaks of amine or DPQ incorporation within the limit of detection. The signal-to-noise ratio is higher in comparison with the spectrum of the commercial polymer, PPO-803, because endgroup peaks are much higher due to the low molecular weight. Also, no additional peaks have been determined in the
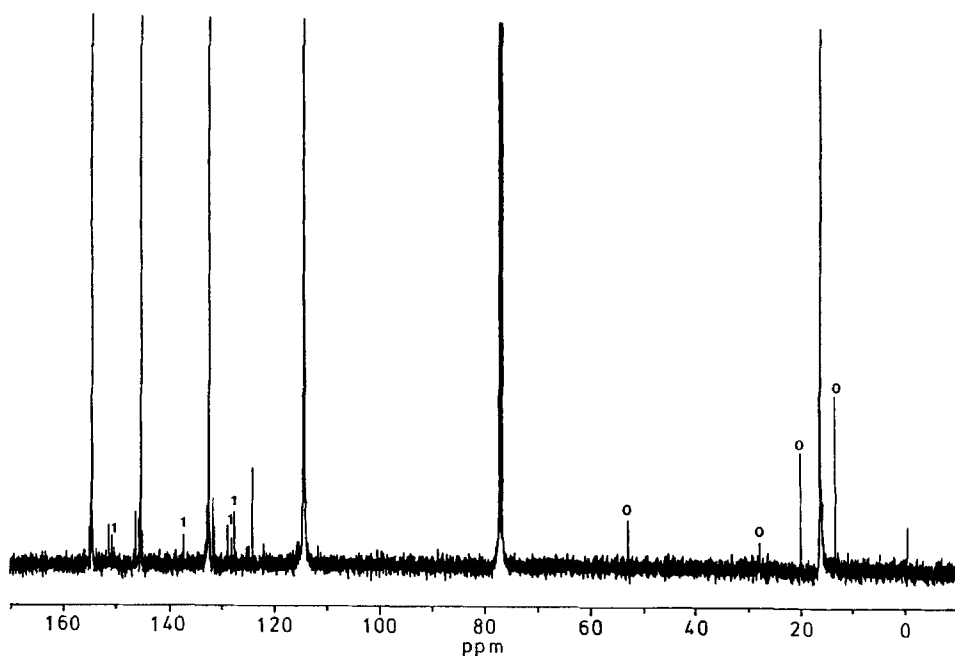

FIG. 3. ^{13}C-NMR spectrum of PPE-803 made with the DBA/DBEDA ligand system; M_n = 11000 g/mol. The resonances marked with 0 and 1 are assigned to Mannich base type endgroups and DPQ incorporation, respectively.
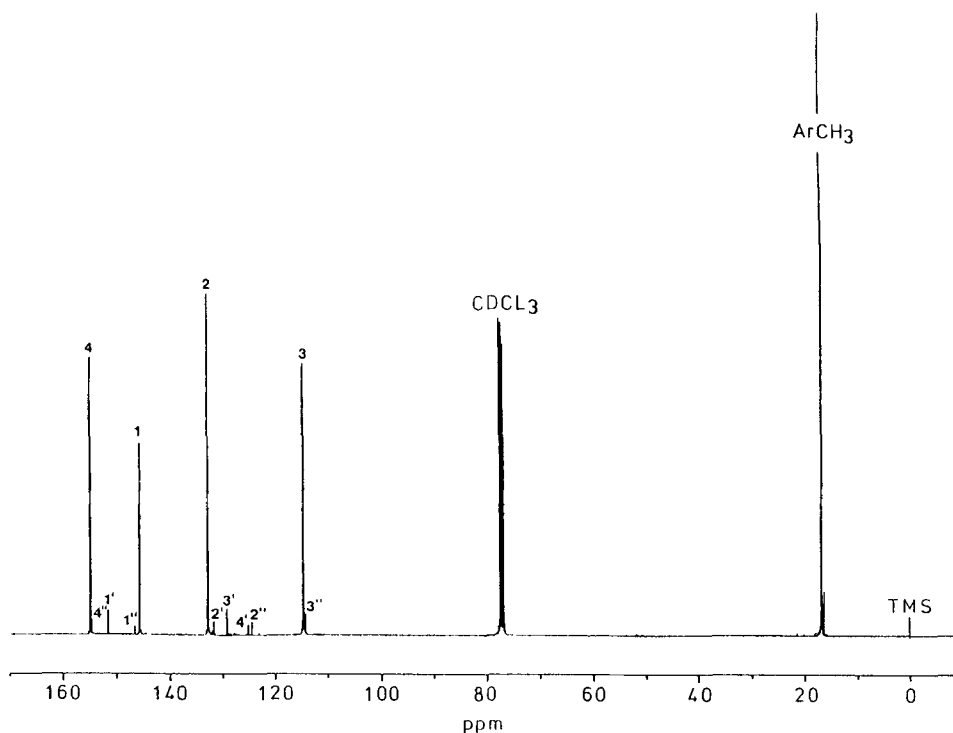
FIG. 4. ^{13}C-NMR spectrum of PPE made with the DBA/DBEDA ligand system; M_n = 2750 g/mol. The resonances marked are assigned as in structural formula (1).

polymer prepared with TEED. Explanations of why the side reactions are absent in the case of precipitation polymerization are purely speculative and are the subject of further research.

CONCLUSIONS

Precipitation polymerization in the oxidative coupling polymerization of 2,6-dimethylphenol gives well-defined monofunctional polymers in high yields. Products can be well characterized with a combination of NMR and GPC techniques. Molecular weight characterization by FD-MS is applicable for very low molecular weight PPE. No side reactions, like incorporation of secondary amines and DPQ, are observed. The molecular weights can easily be adjusted by using a particular solvent composition. The molecular weights are independent of the ligand system used.

ACKNOWLEDGMENTS

The authors are indebted to Mr. A. Landa for the GPC measurements performed at General Electric Plastics, Bergen op Zoom, The Netherlands, and Dr. H.

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