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Spectroscopic analysis of poly(bisphenol A carbonate) using high resolution ^{13}C and ^{1}H NMR

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Abstract

Quantitative structural and end-group analysis of poly(bisphenol A carbonate) (BPA-PC) was carried out and number average molecular weights (M_n) were determined using 125.76 MHz ^{13}C and 500.13 MHz ^{1}H nuclear magnetic resonance (NMR) spectroscopy. BPA-PC with a wide range of end-group ratios (0.26–2.83) and number average molecular weights (1500–9000 g/mol) was synthesized using melt transesterification by changing the initial monomer (bisphenol A and diphenyl carbonate) ratios and reaction conditions. Results of the NMR analysis for the melt-polymerized samples were compared with those of a commercial BPA-PC with a M_n of 16,000 g/mol. It was demonstrated that NMR spectroscopy is a very selective and accurate method not only for quantification of both phenolic and phenyl chain end-groups but also in the structural analysis of main chain groups. Extremely small concentrations of end-groups ($\sim$0.02 per repeating unit) were analyzed. In addition, NMR spectroscopy was found to be an excellent tool for detecting residual monomer and the presence of the reaction byproduct (phenol). The molecular weights that were determined using NMR end-group quantification agreed well with the molecular weights measured by gel-permeation chromatography (GPC).

Keywords: poly(bisphenol A carbonate); End-group analysis; NMR spectroscopy

1. Introduction

Poly(bisphenol A carbonate) (BPA-PC) is one of the most widely used thermoplastic engineering materials. The unique electrical, optical and mechanical properties of BPA-PC make it attractive for use in a variety of areas, including optical recording, electronic and electrical applications, automotive, health and medical, leisure, and safety applications. Typically BPA-PC is synthesized either by interfacial polymerization of bisphenol A and phosgene, or by melt transesterification of bisphenol A (BPA) and diphenyl carbonate (DPC). The chain end-groups for BPA-PC polymerized via interfacial polymerization are either chloroformate or phenolic, and the chain end-groups for BPA-PC polymerized via melt transesterification are either phenolic or phenyl. The presence of chloroformate and phenolic end-groups is known to decrease the stability and performance of BPA-PC [1,2]. Thus commercial grade BPA-PC chains are typically end-capped with phenyl or substituted phenyl groups. During the melt polymerization, the concentrations of the two end-groups must be close to stoichiometric in order to achieve high molecular weight polymer. The stoichiometric balance of the end-groups and therefore the achievable molecular weight is typically controlled by adjusting the BPA/DPC ratio [3]. End-group quantification during polymerization is valuable

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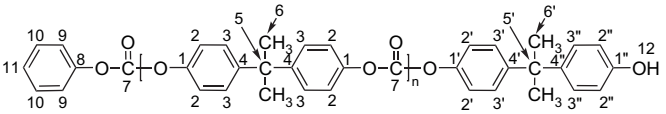
for monitoring the progress of the reaction, for characterizing the molecular weight, and for providing key information that can be used to develop a reaction model.

Development of a facile and reliable end-group analysis technique is critical for characterizing end-capping and for controlling the end-group ratio. End-group analysis techniques for BPA-PC that have been reported to date include titration [4,5], infrared (IR) [6], ultraviolet (UV) [7], gel-permeation chromatography (GPC) coupled with UV (GPC-UV) [8], reversed-phase high performance liquid chromatography (HPLC) [9–11], and nuclear magnetic resonance (NMR) spectroscopy [2,12–14]. The titration and IR methods have significant drawbacks that include an inability to differentiate phenolic end-groups from residual monomer. Although UV and GPC-UV based techniques are well-established for detecting phenolic end-groups and for quantifying uncapped chain ends, these techniques are not suitable for analysis of end-group ratios because they have no capability to quantify phenyl or chloroformate. The reversed-phase HPLC method has been used to detect residual monomers and end-capping molecules [11] in BPA-PC resin, phenyl or substituted phenyl group in BPA-PC hydrolysates [9], and chloroformate-containing BPA-PC oligomers [10]. ^{13}C NMR spectroscopy is a highly accurate and reliable technique for determining the degree of end-capping, the concentrations of end-groups, and the end-group ratios because of its high selectivity and its ability to detect both phenolic and phenyl end-groups [2,12]. The high selectivity of ^{13}C NMR enables accurate analysis of high molecular weight polymers that have low end-group concentrations. In addition, monomer removal is not required prior to polymer analysis because the ^{13}C nuclear resonance of the phenolic chain end is clearly separated from monomer resonances (bisphenol A) and the reaction byproduct (phenol). Since ^{13}C NMR spectroscopy is able to detect both of the end-groups, it is particularly well suited for quantifying end-group ratios. Knowledge of the ratio of end-groups is necessary in order to develop a kinetic model of the melt polymerization process or of solid-state polymerization for the synthesis of high molecular weight BPA-PC. However, it is not trivial to quantify and interpret ^{13}C NMR spectra. Issues that must be considered include gated proton-noise decoupling, the requirement for a long delay time between each pulse ($\tau > 5T_1$, where T_1 is the spin-lattice relaxation time), and the necessity to cancel Nuclear Overhauser Enhancement (NOE) effects during data acquisition.

^{1}H NMR is an effective technique to quantify phenolic end-groups. However, using only ^{1}H NMR is not effective in determining end-group ratios because *ortho* and *para* proton peaks for the phenyl chain end overlap with main chain proton peaks.

Even though NMR spectroscopy has clear advantages over other methods for the quantification of BPA-PC end-groups, only a few studies have been published [2,12–14] and they suffered from low resonance peak resolution, inappropriate choice of NMR solvent, and/or incorrect peak assignments. Urman et al. showed that ^{13}C and ^{1}H NMR could be used to quantify phenolic, chloroformate, phenyl, and *p-tert*-butylphenyl end-groups for BPA-PC synthesized via interfacial polymerization [2]. The end-group analysis results from NMR were compared with those from a chemical method. However, reasonably good agreements between NMR and chemical methods were only obtained when the number average molecular weight (M_n) of BPA-PC was in the range of 1100–2900 g/mol. The resolution of spectra was not good enough to quantify all of the end-group carbons because of the low resonance frequency (22.63 MHz ^{13}C). In addition, Urman et al. did not describe the detailed conditions for ^{13}C NMR spectra collection [2]. Schilling et al. used 25.16 MHz ^{13}C NMR to quantify BPA-PC hydrolysis products, including phenyl and phenolic chain ends [12]. However, they could not obtain the proper intensity ratio for the main chain carbons. In addition, not all of the end-group carbon peaks were found in their spectrum; quaternary ring carbons for the phenyl chain ends at 151 ppm were not present. Shi et al. and Hagenaars et al. estimated phenolic chain end concentration for BPA-PC using 400 MHz ^{1}H NMR with deuterated chloroform ($CDCl_3$) as a solvent [13,14]. The phenolic chain end concentrations were determined using the integration ratio of aromatic protons at the *ortho* position of the terminal hydroxyl group to the total absorbance of all aromatic protons on the main chain. However, this method was found to be deficient for two reasons. First, the resonance peak for $CDCl_3$ solvent at 7.25 ppm overlaps with the aromatic proton peaks at 7.02–7.50 ppm. When the BPA-PC solution concentration is low, the $CDCl_3$ peaks are larger than the aromatic proton peaks. This may cause inaccurate quantification of the phenolic end-groups. Second, the phenolic end-group concentration calculated using their method is one-fourth of the *number* of phenolic end-groups *per repeating unit* because the number of aromatic protons for the main chain is eight and the number of aromatic protons for the phenolic chain end is four, as shown below in the BPA-PC chemical structure.



BPA-PC

In order to calculate the number of phenolic end-groups *per repeating unit* properly, a factor of two should be used for the aromatic protons in the *ortho* and *para* positions of the terminal hydroxyl group (peak assignments 2″ and 3″, respectively) and it should be compared to the total aromatic protons (peak assignments 2 and 3). Shi et al. also used 80 MHz ^{13}C NMR to quantify the phenyl chain end concentration using an incorrect carbon peak assignment [13]. They assigned the peak at 115 ppm to three terminal unsubstituted aromatic carbons for the phenyl chain end-groups (peak assignments 9, 10, and 11). However, the 115 ppm peak is due to the *ortho* position carbons of the hydroxyl group for the phenolic chain end-group (peak assignment 2″) [12]. This is also confirmed in a heteronuclear multiple quantum coherence (HMQC) (2D ^{1}H–^{13}C one bond correlation) NMR spectrum of BPA-PC, as will be discussed later.

In this study, we report quantitative end-group analysis of melt-polymerized BPA-PC with a wide range of end-group ratios (0.26–2.83) and molecular weights (M_n of 1500–9000 g/mol) using 125.76 MHz ^{13}C and 500.13 MHz ^{1}H NMR spectroscopy. The results were compared with those of commercial BPA-PC with M_n of 16,000 g/mol. The high operating resonance frequencies and large digital resolution points of 64,000 in the spectra yield good end-group peak resolutions and sensitivity, such that the peaks are clearly separated from the main chain peaks and the monomer/byproduct peaks. In the sections that follow, it is demonstrated that by using a ^{13}C gated decoupling experiment with an ^{1}H decoupler during data acquisition, and by employing a sufficiently long time between each pulse ($\tau > 5T_1$), ^{13}C NMR is very accurate and selective for not only structural analysis of the main chain but also for quantifying both the phenolic and phenyl end-groups. The phenolic end-group quantification from ^{13}C NMR was compared to that from ^{1}H NMR and showed good agreement. The molecular weights determined by NMR agreed well with those determined by gel-permeation chromatography (GPC) using a light scattering detector.

2. Experimental section

2.1. Materials

Bisphenol A (BPA, >99% purity), diphenyl carbonate (DPC, >99% purity), and lithium hydroxide monohydrate ($LiOH \cdot H_2O$, >99.995% purity) were purchased from Sigma–Aldrich (St. Louis, MO). Commercial BPA-PC standard was purchased from Sigma–Aldrich. Methanol (HPLC grade), tetrahydrofuran (THF, HPLC grade), and deionized ultrafiltered (DIUF) water were purchased from Fisher Scientific (Pittsburgh, PA). BPA was recrystallized from a methanol and DIUF water mixture (2/1 by volume) and dried in a vacuum at 60 °C for at least 2 days. DPC was recrystallized from methanol and dried in a vacuum at 40 °C for at least 2 days. $LiOH \cdot H_2O$ was used as received. The carbon dioxide source was Coleman gas (99.99% purity) and the nitrogen source was Ultra High Purity (99.999% purity), obtained from National Welders (Charlotte, NC). The carbon dioxide was passed through three inline high-pressure oxygen traps (Alltech Associates, Inc, Deerfield, IL) and the nitrogen was passed through a gas purifier (Drierite, Xenia, OH) and an oxygen trap (Model 1000, Chromatography Research Supplies, Louisville, KY) before introduction into the reactor.

2.2. Polymer synthesis

BPA-PC was synthesized by the melt transesterification of BPA and DPC using an aqueous solution of $LiOH \cdot H_2O$ (0.001 g/ml) as a catalyst. The polymerization was carried out in a RC1e Reaction Calorimeter manufactured by Mettler Toledo (Schwerzenbach, Switzerland) and a 1200 cm^3 high-pressure reactor manufactured by Premex Reactor AG (Lengnau, Switzerland). The RC1e Reaction Calorimeter was equipped with an electronic control, a monitoring unit, a magnetic stirrer, a jacket heating and cooling unit (thermostat), and a cover heating unit. During polymerization, the reaction pressure, temperature, and stirring speed were controlled and monitored using WinRC^{NT} reactor control computer software (Schwerzenbach, Switzerland). Table 1 shows experimental conditions used for the synthesis of the samples that were analyzed. In a typical experiment, 182.63 g of BPA (0.8 mol) and 186.80–176.52 g of DPC (0.872–0.824 mol) were introduced into the reactor. After the reactor was purged with N_2 at 580 ml/min for 15 min, the temperature was increased to 160 °C with stirring under a N_2 atmosphere, but without N_2 flow (sample PCP2), or with an N_2 flow rate of 580 ml/min (samples PC2 and PCP5–PCP9). The reactor temperature was maintained at 160 °C for 10 min and then 18 ppm (based on the BPA weight) of $LiOH \cdot H_2O$ was introduced into the reactor through an injection port. The reactor temperature then was increased in multistage fashion, as described in Table 1. The reaction byproduct (phenol) was removed either by flowing nitrogen at atmospheric pressure or supercritical carbon dioxide ($scCO_2$), at the pressures shown in Table 1, through the reactor.

2.3. Analytical methods

NMR: all of the pulsed-field NMR experiments were performed using a Bruker Avance 500 MHz Spectrometer equipped with an Oxford narrow bore magnet, RedHat Linux host workstation, and XwinNMR software (version; 3.6). The instrument is equipped with three frequency channels with wave form memory and an amplitude shaping unit, a three channel gradient control unit (GRASP III), a variable temperature unit, and a pre-cooling and temperature stabilization unit. A 5 mm ID inverse ^{1}H/BB (broad band) (^{109}Ag–^{31}P) triple-axis gradient probe (ID500-5EB, Nalorac Cryogenic Corp.) was used for all measurements. The NMR probe was tuned to ^{13}C frequency, which is 125.75 MHz for the 500 MHz spectrometer (^{1}H frequency of 500.13 MHz). The ^{13}C NMR samples were prepared by dissolving each polymer sample in deuterated chloroform ($CDCl_3$). High solution concentration samples were prepared at room temperature in the following concentrations: 23 wt% for low molecular weight polymers (PCP2–PCP9 in Table 1); 18 wt% for high molecular weight polymers (PC2 and commercial BPA-PC in Table 1) for ^{13}C NMR spectra quantification. Deuterated methylene chloride (CD_2Cl_2) was used to prepare samples for ^{1}H NMR measurements to overcome the main chain aromatic peak overlapping problem in the 7.02–7.50 ppm region with $CDCl_3$ peaks. Prior to the NMR measurements, commercial BPA-PC was purified by dissolving it in methylene chloride and then precipitating it using methanol. The polymer was then dried in a vacuum oven at 40 °C for at least 2 days. The polymer synthesized by melt esterification was not purified before the NMR measurement in order to observe the monomer and byproduct resonance peaks in the spectra. NMR measurements of purified PCP2 were also performed to help verify monomer and byproduct peaks in the unpurified NMR spectra and to assign peaks. For ^{1}H NMR

Table 1
Conditions for the synthesis of BPA-PC via melt transesterification

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
PC2 DPC/BPA = 1.09	25–160 °C, 45 min	160 °C, 1 h	180 °C, 1 h	200 °C, 1 h	220 °C, 1 h	240 °C, 1 h	260 °C, 1 h	280 °C, 3 h
				N_2, 580 ml/min				
PCP2 DPC/BPA = 1.09	25–160 °C, 45 min	160 °C, 1 h	180 °C, 1 h	200 °C, 1.5 h	220 °C, 1.5 h			
	no sweep flow	no sweep flow	no sweep flow	$scCO_2$, 136 bar, 120 ml/min	$scCO_2$, 138 bar, 120 ml/min			
PCP5 DPC/BPA = 1.09	25–160 °C, 45 min	160 °C, 1 h	180 °C, 1 h	200 °C, 1 h	220 °C, 1 h	220 °C, 1.5 h	240 °C, 2.5 h	
		N_2, 580 ml/min			$scCO_2$, 69 bar, 250 ml/min	$scCO_2$, 138 bar, 120 ml/min	$scCO_2$, 205 bar, 130 ml/min	
PCP6 DPC/BPA = 1.06	25–160 °C, 45 min	160 °C, 1 h	180 °C, 1 h	200 °C, 1 h	220 °C, 1 h	240 °C, 1 h	240 °C, 3.4 h	
		N_2, 580 ml/min			$scCO_2$, 69 bar, 250 ml/min	$scCO_2$, 138 bar, 120 ml/min	$scCO_2$, 205 bar, 130 ml/min	
PCP7 DPC/BPA = 1.03	25–160 °C, 45 min	160 °C, 1 h	180 °C, 1 h	200 °C, 1 h	220 °C, 1 h	240 °C, 1 h	240 °C, 3.4 h	
		N_2, 580 ml/min			$scCO_2$, 69 bar, 250 ml/min	$scCO_2$, 138 bar, 120 ml/min	$scCO_2$, 205 bar, 130 ml/min	
PCP9 DPC/BPA = 1.03	25–160 °C, 45 min	160 °C, 1 h	180 °C, 1 h	200 °C, 1 h	220 °C, 1 h			
			N_2, 580 ml/min					

The stirring rate for PCP2, PCP5, PCP6, PCP7 was 520 rpm. The stirring rate for PCP9 was 1000 rpm.

measurements, 1.0 wt% solution concentration samples were prepared. The solutions were transferred to a 5-mm NMR tube (Kontes, Vineland, NJ) for analysis. The tubes were carefully washed and dried for 24 h in an oven and bubbled with nitrogen before being capped for storage.

For one-dimensional (1D) ^{13}C NMR measurements, a 1D sequence with inverse gated ^{1}H decoupling spectrum was generated. Proton decoupling was employed for the duration of the acquisition time in order to avoid the NOE effect. All spectra were acquired at 25 °C. Tetramethylsilane (TMS) was used as internal standard. The instrumental parameters for acquisition of the 1D proton and carbon data are listed in Table 2. The NMR spectra were analyzed using the NUTS NMR data processing program (Acorn NMR Inc., Livermore, CA).

Two-dimensional homonuclear correlation spectroscopy (2D COSY) ($^{1}H-^{1}H$), two-dimensional heteronuclear multiple quantum coherence (HMQC) (2D $^{1}H-^{13}C$ one bond), and two-dimensional heteronuclear multiple bond correlation (HMBC) (2D $^{1}H-^{13}C$ long range) NMR experiments were carried out to assign peaks and to characterize polymer structure. The 2D COSY experiment shows the correlation between protons coupled through scalar coupling. The HMQC NMR experiment shows the correlation between carbons and protons directly bonded to each other ($^{1}J_{H-C}$ correlation). The HMBC NMR experiment shows the correlation between carbons and protons due to long range coupling ($^{n}J_{C-H}$). The 2D NMR data were processed using Bruker software XWINMR 3.5. For the 2D NMR measurements the polymer was dissolved in CD_2Cl_2. The solution concentration for 2D COSY NMR measurements was 1.0 wt% and the polymer concentration for the 2D HMQC and 2D HMBC NMR experiments was 9.6 wt%.

The spin-lattice relaxation times (T_1) of various ^{13}C nuclei were determined using the inversion recovery pulse sequence. The pulse sequence began with a recycle delay that was sufficiently long to ensure that all magnetization returned to equilibrium (i.e., pure z-magnetization). A 180° pulse was then applied, which inverted the magnetization. A recovery delay followed to allow varying degrees of spin-lattice relaxations (which were dependent upon the value of the recovery delay time). The final 90° pulse then converted any z-magnetization into observable transverse magnetization, which was detected during the acquisition period immediately following the final pulse. The resulting curve was an exponential correlation with a rate of $1/T_1$. T_1 values were in the range of 200 ms, 8 ms, 1.9 s, 2.7 s, with the longest value being 3.7 s. Our

Table 2
Experimental set-up for ^{13}C NMR and ^{1}H NMR measurements

Parameter	^{13}C value	^{1}H value
Spectrometer frequency (MHz)	125.76	500.13
Spectral width (Hz) and (ppm)	25.063 Hz or 200 ppm	6009.6 Hz or 12 ppm
Number of data points	64,000	32,000
Relaxation delay (s)	14	2
Acquisition time (s)	17	2.72
Pulse width (μs) and tip angle	11 at 90°	10.5 at 90°
Number of scans	3600–12,300	64
Number of dummy scans	16	0

relaxation delay time (17 s) is greater than five times the second longest value of T_1, so that the various carbons in the main chain can fully relax.

GPC: the molecular weight of BPA-PC was measured using gel-permeation chromatography (GPC) with tetrahydrofuran (THF) as a mobile phase. The GPC system was equipped with three THF Styragel® 4.6 × 300 mm columns (models HR3, HR4, and HR4E, Waters Corporation, Milford, MA) for separation. An Optilab® rEX (refractometer with EXtended range, Wyatt Technology, Santa Barbara, CA) was used as the concentration detector and a miniDAWN Tristar was used as the light scattering detector (Model WTR-02, Wyatt Technology, Santa Barbara, CA). With the intensity of light scattered and the absolute concentration measured, the molar mass was obtained. Polymer solutions with a concentration of 2 mg/ml were prepared. The solutions were filtered into GPC sampling vials using 0.2 μm PTFE syringe filters. The GPC data was processed using ASTRA software (version 5.1.9.1, Wyatt Technology, Santa Barbara, CA) and number average molecular weight (M_n) and weight average molecular weight (M_w) were determined. A dn/dc value of 0.177 was used for the molecular weight calculation.

3. Results and discussion

Fig. 1 shows the ^{13}C NMR spectrum of commercial, high molecular weight BPA-PC (M_n and M_w as determined by GPC are 16,000 and 21,000 g/mol, respectively) and the resonance peak assignments. Using the results of Williams et al. [15] and Schilling et al. [12] for their analysis of the ^{13}C NMR spectrum of BPA-PC and using ^{13}C NMR spectra of model compounds (BPA, DPC, and phenol), the main chain carbon peaks and chain end carbon peaks were assigned with the results shown in Fig. 1 and Table 3. The structural analysis and molecular weight estimation from interpretation of the ^{13}C NMR spectrum are listed in Table 4. The molecular weight estimated from NMR is compared with the molecular weight determined by GPC in Table 4. The main chain carbon resonance intensity ratio for 1:2:3:4:5:6 was 1.99:4.01:3.97:1.99:1.00:1.98. This intensity ratio value is very close to the theoretical main peak ratio of 2:4:4:2:1:2. In addition, the ratio of main chain aromatic carbon (1, 2, 3, and 4) to carbonyl carbon (7) at 152 ppm is 11.7:1, which is very close to the theoretical value of 12:1. This compatibility between the NMR determined carbon intensity ratios and the theoretical values indicates that, in contrast to the work of Schilling et al. [12], our gated decoupling sequence leads to negligible NOE build-up and that the delay time of 17 s is sufficient for the various types of carbons in the main chain to fully relax. Schilling et al. [12] were not able to obtain the proper intensity ratio for the main chain carbons. As shown in Fig. 1, a close examination of the aromatic region of the spectra reveals the presence of phenyl end-groups (peak assignments 8, 9, 10, and 11) and shows that the aromatic carbons in the phenyl end-groups are clearly isolated from other peaks. Phenolic end-groups were not found in the spectrum, indicating that the commercial BPA-PC was end-capped with phenyl end-groups. The intensity ratio of the four different types of carbons in the phenyl end-groups (8:9:10:11) is 0.89:2.02:1.99:1.00. This ratio is also very close to the theoretical ratio of 1:2:2:1. The slightly small intensities for carbonyl carbon (7) at 152 ppm and quaternary ring carbon (8) at 151 ppm are possibly due to general relaxation phenomena.

The number average molecular weight (M_n) of commercial BPA-PC can be calculated using the peak area of the main chain aromatic carbons and the phenyl chain end carbons by

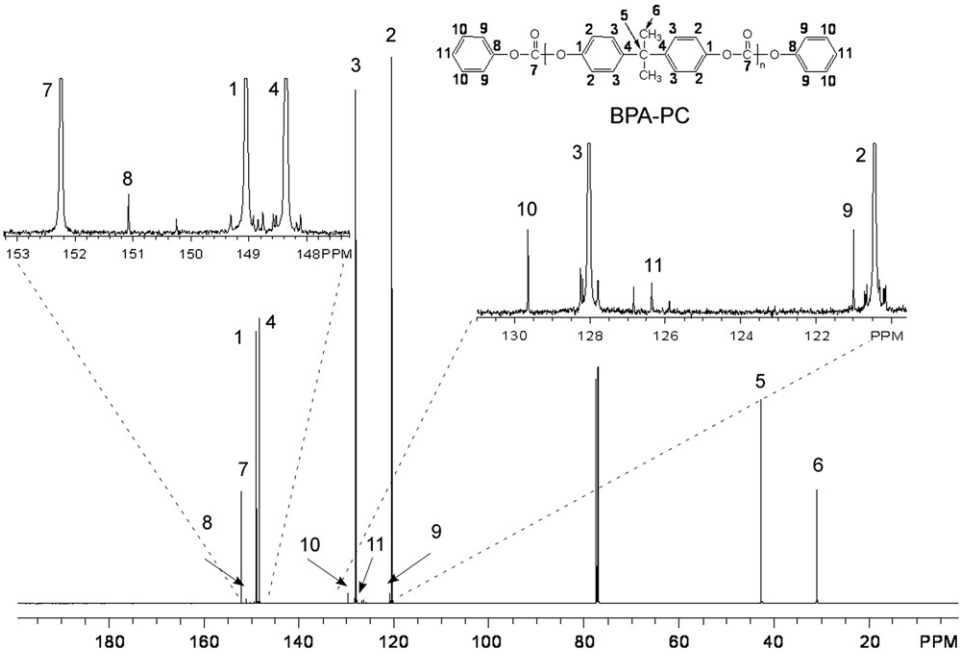


Fig. 1. ^{13}C NMR spectrum of commercial BPA-PC at a frequency of 125.76 MHz. The polymer concentration in $CDCl_3$ was 18 wt%. M_n as determined by GPC is 16,000 g/mol.

Table 3
^{13}C NMR chemical shifts for a commercial BPA-PC (denoted PC1) with $M_n = 16{,}000$ g/mol, PCP2 with $M_n = 1500$ g/mol, and model compounds

Atom index	PC1	PCP2	Correspondence with model compound
	Chemical shift (ppm)		
1P	—	155.87	155.00, 1P
1″	—	153.80	
1B	—	153.55	154.88, 1B
7	152.24	152.56	152.31, 5D
8	151.08	150.96	151.13, 1D
1′	—	149.25	
1	149.05	148.94	
4′	—	148.75	
4	148.36	148.42	
4B	—	142.86	142.29, 4B
4″	—	142.01	
10	129.65	129.65	129.67, 3D
3P	—	129.53	129.60, 3P
3	128.03	128.03	
3′	—	127.99	
3″	—	127.81	
3B		127.77	127.82, 3B
11	126.36	126.40	126.41, 4D
9	120.99	120.91	121.07, 2D; 120.84, 4P
2	120.44	120.42	
2′	—	120.22	
2P		115.39	115.23, 2P
2″	—	114.96	
2B		114.81	114.81, 2B
5	42.64	42.55	
5″	—	42.08	
5B		41.59	41.36, 5B
6B	—	31.18	30.92, 6B
6″	—	31.03	
6	31.07	30.89	

$$M_n = 254 \times \frac{\text{sum of aromatic carbons 1, 2, 3, 4 peak area}}{\text{sum of aromatic carbons 8, 9, 10, 11 peak area}} + 2 \times 121 \quad (1)$$

where 254 is molecular weight of the repeat unit and 121 is molecular weight of the phenyl end-group. Only the number average molecular weight (M_n) can be determined from the end-group analysis. From Eq. (1), M_n for commercial BPA-PC is 17,500 g/mol. The M_n from GPC is 16,000 g/mol. The larger molecular weight determined by NMR relative to that from GPC is possibly a result of a low signal-to-noise ratio for the small end-group peaks for the high molecular weight BPA-PC, resulting in underestimation of the end-group concentration. As will be discussed in the next section, better agreement between molecular weights determined from NMR and GPC was obtained with low to medium molecular weight BPA-PC.

Fig. 2 shows the ^{13}C NMR spectrum of oligomeric BPA-PC (PCP2, M_n and M_w as determined by GPC are 1500 and 1900 g/mol, respectively) and peak assignments. The spectrum was divided into six spectral regions. The peak assignments of the spectrum are listed in Table 3. Peaks labeled 1″–4″ are assigned to phenolic chain end carbons and peaks labeled 1′–6′

Table 4
Structural analysis and M_n for commercial BPA-PC, PC2, and PCP2–PCP9 measured using ^{13}C, ^{1}H NMR, and GPC

	DPC/BPA ratio	Main chain peak ratio (1:2:3:4:5:6)	Phenyl end-group peak ratio (8:9:10:11)	Phenolic end-group peak ratio (1″:2″:3″:4″)	Phenyl/phenolic end-group ratio			M_n (g/mol)		M_w (g/mol
					Eqs. (2) and (3)	Eqs. (2) and (4)	Eqs. (2) and (5)	Eqs. (2) and (6)	NMR	GPC	GPC
Commercial BPA-PC (4800 scan)	—	1.99:4.01:3.97: 1.99:1.00:1.98	0.89:1.02:1.99:1.00	—	—	—	—	—	17,500	16,000	21,000
PCP2 (6140 scan)	1.09	2.13:3.98:3.87: 2.10:1.00:2.01	0.98:2.18:2.12:1.00	1.01:2.02:1.93:1.00	0.26	0.26	0.24	0.25	1100	1500	1900
PCP5 (3610 scan)	1.09	2.04:4.00:4.04: 2.02:1.00:1.99	0.98:2.11:2.07:1.00	0.91:1.97:2.08:1.00	1.59	1.56	1.57	1.56	2900	3600	5400
PCP6 (3580 scan)	1.06	2.04:3.93:3.94: 2.04:1.00:2.01	0.92:1.96:1.93:1.00	1.00:2.05:2.10:1.00	0.76	0.77	0.77	0.75	3400	3800	5500
PCP7 (3600 scan)	1.03	2.03:3.99:3.99: 1.98:1.00:2.02	0.97:2.12:2.04:1.00	1.00:1.96:1.97:1.00	0.67	0.68	0.66	0.67	3200	3400	5400
PCP9 (4800 scan)	1.03	2.00:3.95:3.92: 1.99:1.00:1.89	1.04:2.02:2.06:1.00	0.97:1.99:1.98:1.00	1.01	1.02	1.09	0.99	1900	2400	3200
PC2 (5120 scan)	1.09	2.14:4.03:4.08: 2.17:1.00:1.92	1.04:2.08:1.99:1.00	0.97:2.21:2.13:1.00	2.55	5.46	2.35	2.43	8800	9000	19,000
PC2 (12,300 scan)	1.09	2.01:4.01:3.98: 2.05:1.00:2.02	0.94:2.13:2.08:1.00	0.84:2.00:2.03:1.00	2.83	2.43	2.77	2.88	8000	9000	19,000

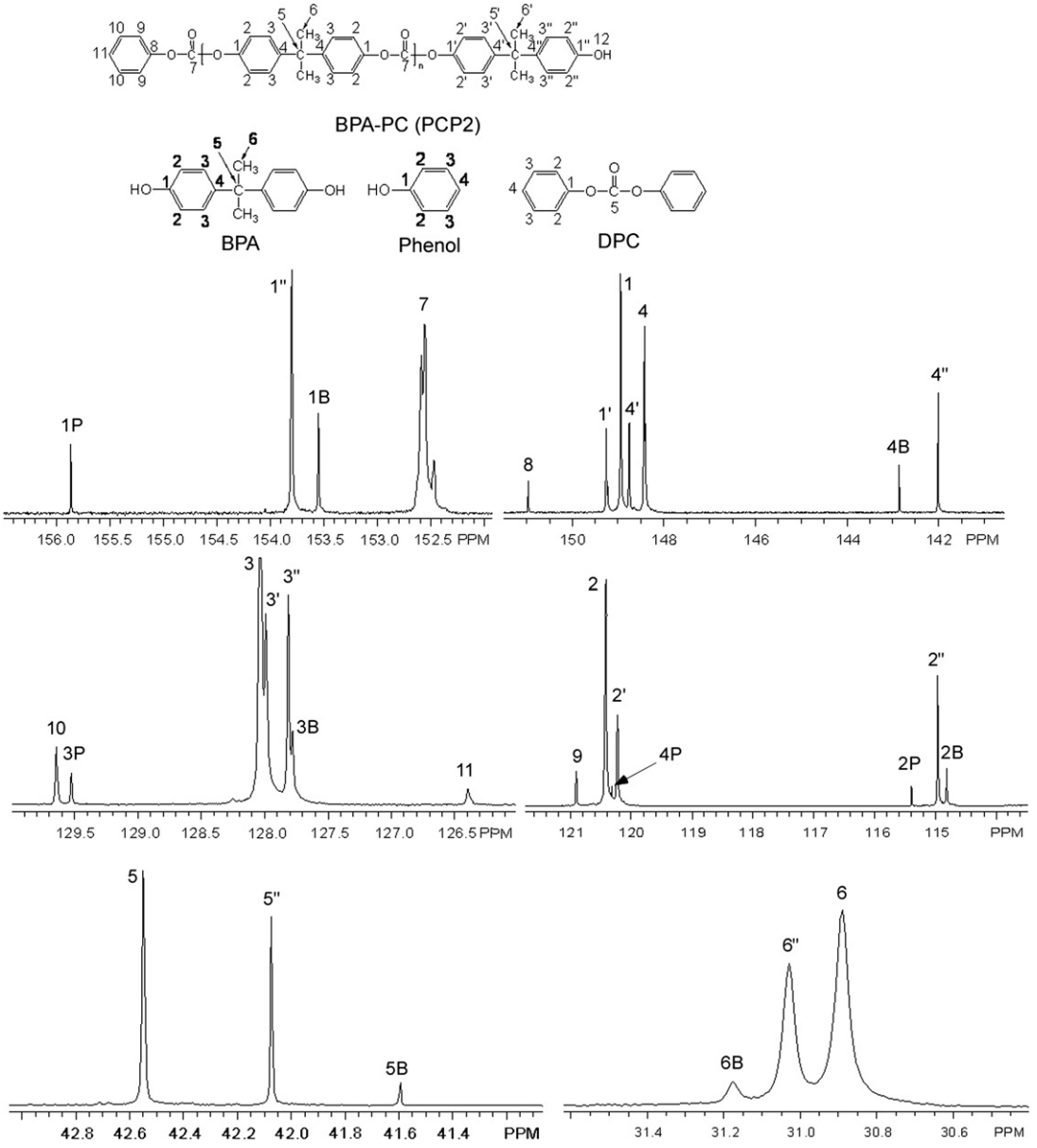


Fig. 2. ^{13}C NMR spectrum of the oligomeric BPA-PC at a frequency of 125.76 MHz. The polymer concentration in $CDCl_3$ was 23 wt%. M_n as determined by GPC is 1500 g/mol.

are assigned to aromatic, methyl, and quaternary carbons connected to the phenolic chain end. Peaks labeled 1P–4P are assigned to phenol and peaks labeled 1B–6B are assigned to BPA. These peaks were assigned using the ^{13}C NMR spectra of BPA, DPC and phenol, the ^{13}C NMR spectra of PCP2 + BPA, PCP2 + DPC and PCP2 + phenol, the ^{13}C NMR spectrum of purified PCP2, and 2D HMQC (^1H–^{13}C one bond) NMR spectra. These peak assignments agree well with Schilling et al. [12] except for the protonated aromatic carbon region around 128 ppm (peak assignment 3, 3′, 3″, and 3B). The 3, 3′, 3″, and 3B peaks of the ^{13}C NMR spectrum in Schilling et al. [12] were not resolved sufficiently to be assigned to each of the four peaks; only two highly overlapped peaks were shown in their spectrum. They assigned the large peak at the downfield to 3, 3′, and 3B and the small peak at the upfield to 3″, based on the shifts of similar carbons in BPA and the internal BPA-PC repeat unit. In contrast, we assigned the peak at 127.77 ppm to 3B because the 3B peak and other corresponding BPA peaks disappeared in the purified PCP2 ^{13}C NMR spectra. The 3′ and 3″ peaks in our spectra were assigned using 2D HMQC (^1H–^{13}C one bond) NMR (see Fig. 3). It is noted that incorrect peak assignments were done in the Shi et al. paper; the peak at 115 ppm was assigned to three terminal unsubstituted aromatic carbons in the phenyl end-group (peak assignments 9, 10 and 11 in Fig. 2) [13]. However, the peak at 115 ppm is due to *ortho* carbons in the phenolic end-group (peak assignment 2″ in Fig. 2), as was confirmed by 2D HMQC (^1H–^{13}C one bond) NMR spectrum of PCP2 (see Fig. 3). As shown in Fig. 2, aromatic carbons (1″, 2″, 3″, and 4″) for the phenolic chain ends are clearly isolated from other peaks. In addition, the quaternary carbon in the phenolic chain end (5′) is also separated from the quaternary

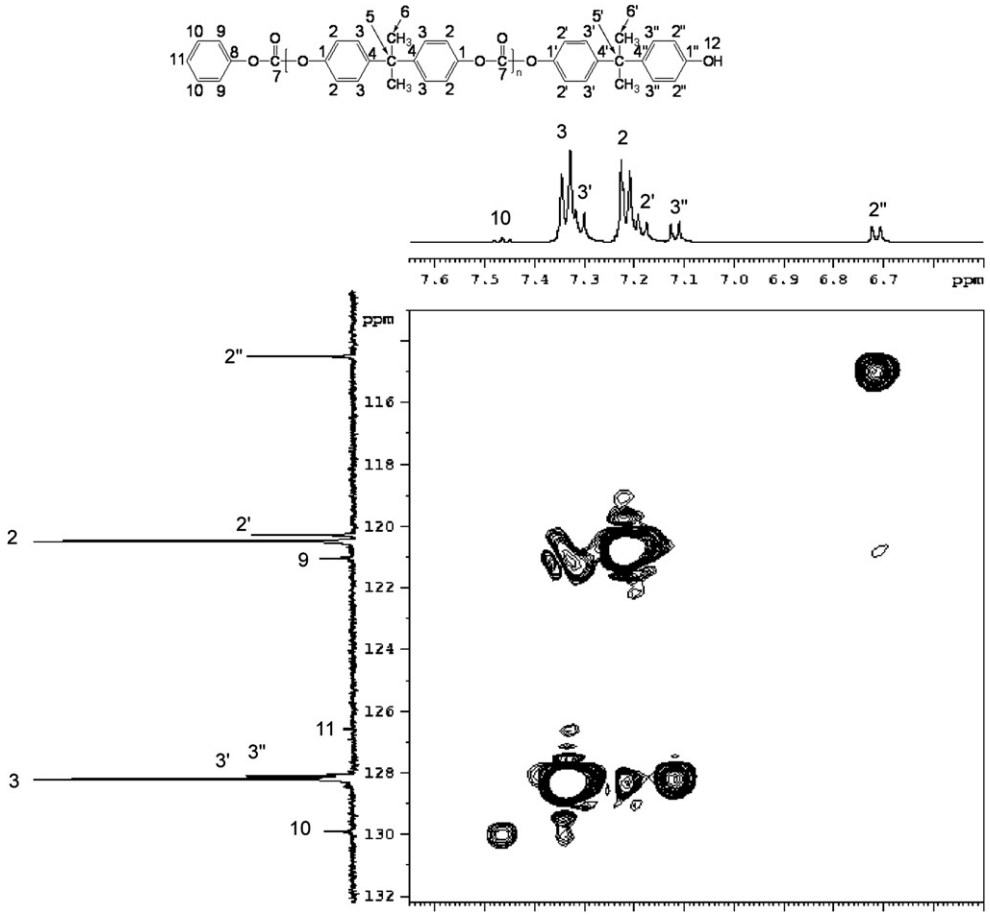


Fig. 3. Expanded aromatic region of two-dimensional (2D) heteronuclear multiple quantum coherence (HMQC) (2D $^{1}H-^{13}C$ one bond) spectrum of PCP2. The polymer concentration in CD_2Cl_2 was 9.6 wt%. M_n as determined by GPC is 1500 g/mol.

carbon in the main chain (5). Therefore, either the aromatic carbons or the quaternary carbons of the phenolic chain end can be used in quantification of this end-group. The peak intensity ratios of the main chain carbon, phenyl end-group, and phenolic end-groups are listed in Table 4. It can be seen that the peak intensity ratios agree well with the theoretical values.

Fig. 4 shows the ^{1}H NMR spectrum of purified PCP2 with its peak assignments. The peak assignments were carried out by comparing the spectrum with the ^{1}H NMR spectrum of commercial BPA-PC, the monomers and phenol, and 2D $^{1}H-^{13}C$ NMR spectra. It can be seen that the aromatic protons at the *ortho* (peak assignment 2″ at around 6.65 ppm) and *meta* (peak assignment 3″ at around 7.05 ppm) positions of the

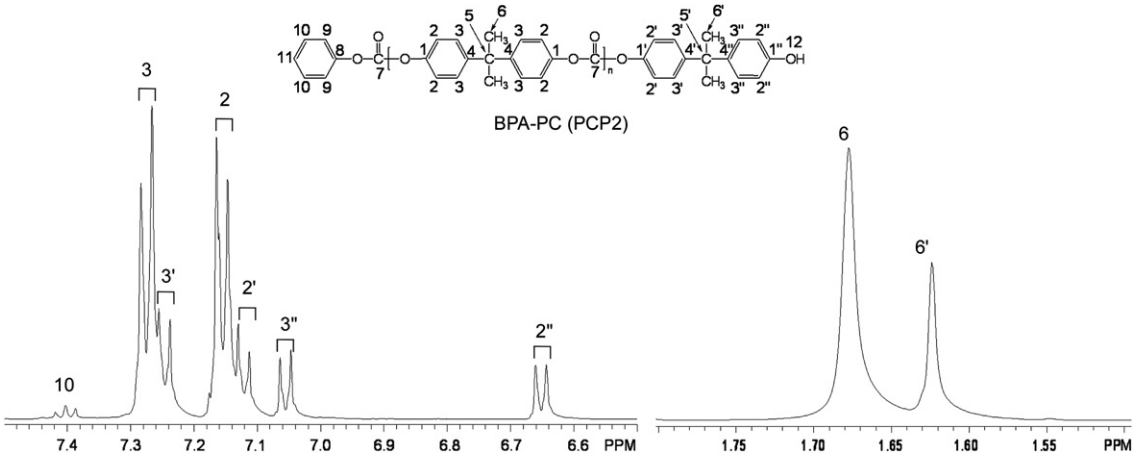


Fig. 4. ^{13}H NMR spectrum of PCP2 at a frequency of 500.13 MHz. The polymer concentration in CD_2Cl_2 was 1.0 wt%. M_n as determined by GPC is 1500 g/mol.

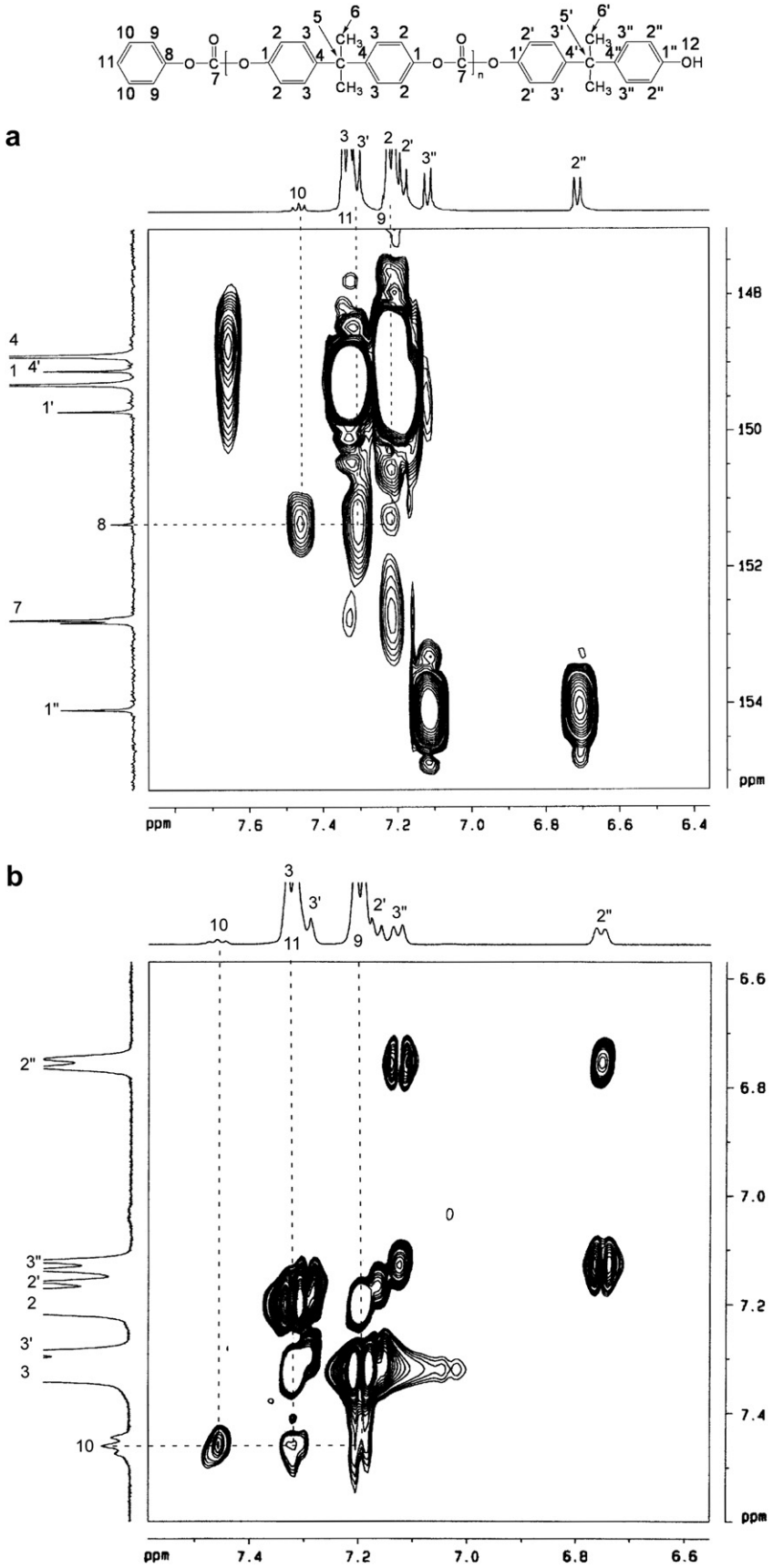


Fig. 5. (a) Expanded region of two-dimensional (2D) heteronuclear multiple bond correlation (HMBC) coherence (2D $^{1}H-^{13}C$ long range) spectrum of PCP2. (b) Expanded aromatic region of two-dimensional homonuclear correlation spectroscopy (2D COSY) ($^{1}H-^{1}H$) of PCP2. The polymer concentration in CD_2Cl_2 was 9.6 wt%. M_n as determined by GPC is 1500 g/mol.

phenolic chain end are clearly separated from the aromatic protons in the main chain at 7.16 ppm (peak assignment 2) and 7.26 ppm (peak assignment 3), and the aromatic protons connected to phenolic chain ends at 7.12 ppm (peak assignment 2′) and 7.27 ppm (peak assignment 3′). The methyl protons in the main chain at 1.68 ppm (peak assignment 6) are also separated from the methyl protons in the chain end at 1.62 ppm (peak assignment 6′). Therefore, the phenolic chain end concentration can be determined using either aromatic protons or methyl protons. Fig. 5a shows 2D HMBC (2D $^{1}H-^{13}C$ long range) and Fig. 5b shows 2D COSY ($^{1}H-^{13}H$ one bond) spectra of PCP2. The 2D HMBC spectrum indicates long range correlation between quaternary carbon (peak assignment 8) and aromatic protons (peak assignments 9, 10, and 11) in the phenyl chain end. The 2D COSY spectrum indicates that the aromatic proton at the *meta* position of phenyl chain end at 7.4 ppm correlates with the aromatic proton at the *ortho* position of the phenyl chain end at 7.21 ppm (peak assignment 9) and with the aromatic proton at the *para* position of the phenyl chain end at 7.32 ppm (peak assignment 11). Thus the aromatic proton at the *ortho* position of the phenyl chain end (peak assignment 9) overlaps with the aromatic protons in the main chain (peak assignment 2) and the aromatic proton at the *para* position of the phenyl chain end (peak assignment 11) overlaps with the aromatic protons in the main chain (peak assignment 3). Therefore, the ^{1}H NMR spectrum cannot be used in the quantification of the phenyl end-group.

As discussed above, phenolic chain ends can be quantified using either ^{13}C NMR or ^{1}H NMR while phenyl chain ends can only be quantified using ^{13}C NMR. The number of phenyl and phenolic end-groups *per repeating unit* can be calculated by

$$\text{Number of phenyl end-groups per repeating unit} = \frac{2 \times \text{sum of aromatic carbons 8, 9, 10, 11 peak area}}{\text{sum of aromatic carbons 1, 2, 3, 4 peak area}} \quad (2)$$

$$\text{Number of phenolic end-groups per repeating unit} = \frac{2 \times \text{sum of aromatic carbons 1″, 2″, 3″, 4″ peak area}}{\text{sum of aromatic carbons 1, 2, 3, 4 peak area}} \quad (3)$$

$$\text{Number of phenolic end-groups per repeating unit} = \frac{\text{alkyl quaternary carbon 5″ peak area}}{\text{alkyl quaternary carbon 5 peak area}} \quad (4)$$

$$\text{Number of phenolic end-groups per repeating unit} = \frac{2 \times \text{sum of aromatic protons 2″, 3″ peak area}}{\text{sum of aromatic protons 2, 3 peak area}} \quad (5)$$

$$\text{Number of phenolic end-groups per repeating unit} = \frac{\text{methyl proton 6′ peak area}}{\text{methyl proton 6 peak area}} \quad (6)$$

Once both of the end-group concentrations are known, M_n can be estimated by

$$M_n = 254 \times \frac{\text{main chain concentration}}{\text{total end-group concentration}} + 2 \times \left[\frac{\text{phenyl end-group concentration}}{\text{total end-group concentration}} \times 121 + \frac{\text{phenolic end-group concentration}}{\text{total end-group concentration}} \times 227 \right] \quad (7)$$

where the main chain concentration is the sum of the peak area of the aromatic carbons 1, 2, 3, 4 in the main chain, the total end-group concentration is the sum of the peak area of the aromatic carbons 8, 9, 10, 11 in the phenyl chain end + sum of the peak area of the aromatic carbons 1″, 2″, 3″, 4″ in the phenolic chain end, 254 is molecular weight of the repeat unit, 121 is molecular weight of the phenyl end-group, and 227 is the molecular weight of the phenolic chain end. The phenyl to phenolic end-group ratio and the molecular weights estimated using Eqs. (2)–(7) are listed in Table 4. The end-group ratios estimated using the four different methods (Eqs. (2)–(6)) are all very similar and the main chain/end-group carbon peak ratios are very close to the theoretical carbon ratios. In addition, the molecular weights calculated using Eq. (7) agree well with the molecular weights measured using GPC. Therefore, structural analysis, end-group analysis and molecular weight estimation using ^{13}C and ^{1}H NMR appear to be quite good for characterizing BPA-PC with molecular weights in the range 2400–3800 g/mol.

When the molecular weight is high and the end-group concentration is low (~0.02 per repeating unit), it is necessary to perform a large number of scans in order to obtain reasonable end-group ratio values. As shown in the last two rows of Table 4, 5100 scans of high molecular weight PC (PC2, M_n and M_w determined by GPC are 9000 and 19,000 g/mol, respectively) did not resolve the quaternary carbon in the chain end properly. This may be because of relaxation phenomena. When the number of scans was increased to 12,300, the signal-to-noise ratio of the quaternary carbon for the chain end was enhanced and the end-group ratio was comparable to the ratios determined using other aromatic carbons or protons.

4. Conclusions

Quantitative analyses of BPA-PC for a wide molecular weight range of 1500–16,000 g/mol was carried out using 125.76 MHz ^{13}C and 500.13 MHz ^{1}H NMR spectroscopy. NMR spectroscopy was found to be reliable and accurate not only in quantification of both phenolic chain end and phenyl chain end-groups but also in the structural analysis of the main chain groups. The high selectivity of NMR enables the analysis of end-groups of high molecular weight polymers with low end-group concentrations. A variety of different methods using aromatic carbons, quaternary carbons, aromatic protons, and methyl protons were successfully used in the quantification of the phenolic end-group. However, when the concentration of the phenolic end-group is low (<0.02 per repeating unit), a large number of scans (>10,000) are necessary to obtain reasonable end-group ratios using quaternary

chain end carbons. The molecular weights determined by NMR analysis agreed well with the molecular weights determined using GPC.

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