Facile Measurement of Phenolic End-Groups in Bisphenol-A Polycarbonate Using GPC-UV Analysis

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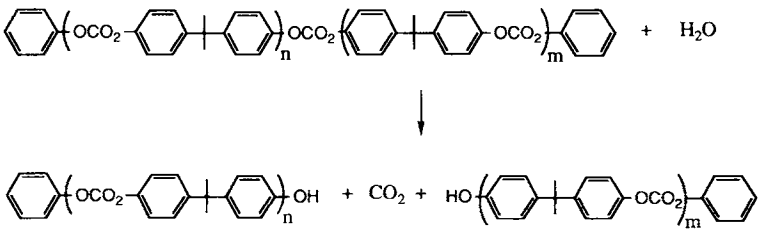
SYNOPSIS

To maximize polycarbonate (PC) stability, it is extremely important that the polycarbonate manufacturing process be operated in such a way as to minimize uncapped polymer chain-ends. Insurance of complete end-capping during manufacture would require constant process monitoring using a fast and accurate phenolic end-group analysis technique for samples typically having < 5% uncapped chain-ends. Published end-group analysis techniques are inaccurate if the polymer samples are contaminated with monomer or other small phenolic molecules. Accuracy can be improved by purifying the polymer before analysis, but this procedure is sometimes tedious. This article describes the development of a facile gel permeation chromatography–ultraviolet (GPC–UV) technique for quantitative determination of low levels of phenolic uncapped chain-ends in PC. This technique improves accuracy because monomers and other small molecule impurities are separated and excluded from the PC during the analysis.

INTRODUCTION

Polycarbonates (PC) derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A) were first synthesized over 30 years ago. Molecular weight control was achieved by having one of the reactants in excess. However, this technique was inadequate because the PC end-groups were either chloroformate or phenolic. These end-groups made the polymer extremely unstable. The technical breakthrough that allowed PC to become a leading engineering thermoplastic was the use of a calculated amount of a monofunctional chain stopper to regulate chain growth and stabilize the polymer. However, even with the use of a chain stopper, most commercial PC has a small fraction of chains that are not capped. The amount of uncapped chains has been shown to have a strong influence upon the hydrolytic stability of PC.[1] In fact, the overall rate of hydrolysis of solid PC has been shown to exhibit a pronounced autocatalytic effect. This likely occurs because polymer hydrolysis results in the formation of increasing phenolic end-groups, subsequently increasing the polymer's hydrophilicity.

The general equation of PC (phenyl capped) hydrolysis is shown below:



To maximize PC stability, it is extremely important that the PC manufacturing process be operated in such a way as to minimize uncapped polymer chains.

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To ensure complete end-capping during manufacture would require constant process monitoring using a fast and accurate end-group analysis technique. However, published techniques suffer from the lack of differentiation between polymer bound phenolic end-groups and residual monomer, chain stopper, or stabilizers. Pryde and Hellman[1] (using IR) found that small molecules (acetone extraction) present in the commercial PC used in their study contributed ~ 40% to the total phenolic end-group content, thus making direct phenolic end-group analyses, without prior purification, highly inaccurate.

Most of the literature describing end-group analysis of PC deals with uncapped oligomers. Techniques used to characterize uncapped PC oligomers include: gel permeation chromatography (GPC),[2,3] high-performance liquid chromatography (HPLC),[3-5] potentiometric titration,[6] nuclear magnetic resonance (NMR),[7] infrared (IR),[1] and ultraviolet (UV).[8]

The fastest hydroxyl end-group analysis method reported to date is the UV technique developed by Shchori and McGrath.[8] The technique is based on the observation that completely capped PC has a different UV absorbance spectrum than completely uncapped chains (Fig. 1).

The purpose of the UV analysis developed by Shchori and McGrath was to monitor polymerizations aimed at making uncapped PC. The end-group analysis technique allowed them to quickly calculate the M_n of the PC using eq. 1, where R is the 288/264 nm absorbance ratio:

$$M_n = 3450/[4.29R/(1 - 0.17R) - 0.03]. \quad (1)$$

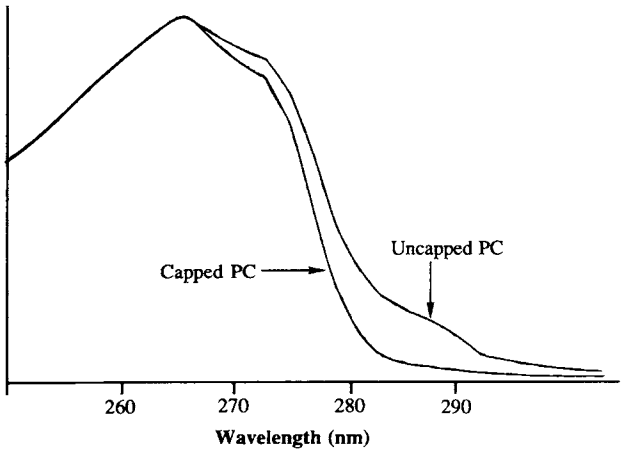

Figure 1 UV spectra of capped and uncapped PC samples (spectra are normalized at their maximum).

Shchori and McGrath only used the technique to analyze totally uncapped PC samples having low molecular weight; therefore, interference by low levels of phenolic impurities was negligible. However, our intent is to use the technique to analyze highly capped PC samples in the commercial molecular weight range. Thus, the analysis becomes very sensitive to impurities because of the extremely low absorbance ratios being measured.

Equation (1) only applies for totally uncapped PC samples. Our interest is in the weight fraction (ppm) of OH end-groups (ppmOH) in a partially capped PC sample. This is expressed as eq. 2, where 34 is the molecular weight of the two OH end-groups:

$$\text{ppmOH} = 34 \times 10^6/M_n. \quad (2)$$

Therefore, to calculate the weight fraction of uncapped chain-ends in a PC sample requires that both the M_n and R be known. It would be especially convenient if both could be determined by one analysis.

In a recent study, a method was described to analyze for functional groups in polymers.[9] The method involved the use of GPC coupled with ultraviolet spectroscopy (GPC–UV). Since the functional groups being analyzed in the polymers were non-UV absorbing, they were tagged with highly absorbing reagents. Subsequent GPC–UV analysis clearly showed whether the functional group was located on the chain-ends or randomly pendant to the polymer backbone. A major advantage of this technique is that any excess tagging reagent present in the polymer sample does not interfere with the analysis because it is separated from the polymer during the chromatography. Application of this technique to phenolic end-group analysis in PC, however, does not require derivatization because of the unique UV absorptivity of the phenolic moiety. The same advantage would result from application of GPC–UV analysis to PC because small molecules that contribute to the absorptivity of the PC sample are separated and excluded during the analysis.

EXPERIMENTAL

Preparation of Phenolic-Terminated PC

Methylene chloride (1 L), triethylamine (2 mL), bisphenol-A (272.4 g), and deionized water (1 L) were placed in a 3-L round bottom flask equipped with a nitrogen inlet, condenser, mechanical stirrer, pH controller, sodium hydroxide pump, and phosgene inlet tube. Sodium hydroxide solution (50%)

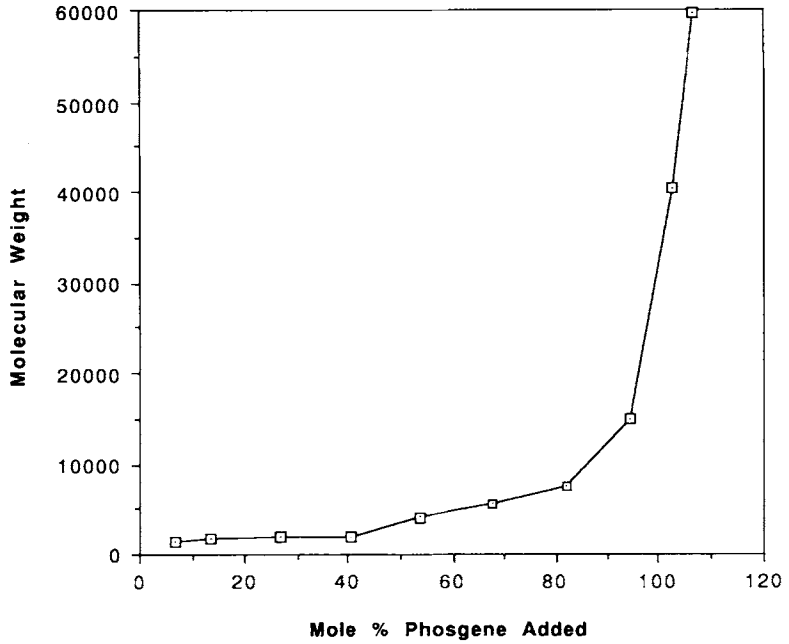

Figure 2 Molecular weight (GPC) of PC produced during phosgenation of bisphenol-A in the presence of triethylamine at pH = 8.5.

was added to adjust the pH to 8.5. The sodium hydroxide pumping rate was then set to be controlled so that a pH of 8.5 would be maintained in the reactor during addition of phosgene. Phosgene (120 g) was added at a rate of 3 g/min. Samples were withdrawn periodically from the reactor and the molecular weight measured using GPC. Figure 2 shows the molecular weight of the PC produced at various stages of phosgenation.

GPC–UV Analysis

GPC–UV analyses were performed using a Hewlett-Packard 1090 liquid chromatograph equipped with a diode-array detector and a set of DuPont ZORBAX PSM Trimodal columns. The instrument was calibrated using LEXAN 101 broad calibration standard having a M_n = 12,000 and a M_w = 25,000. Chromatograms were collected at 264 and 288 nm (4 nm bandwidth). The absorbance ratio (R) was determined by integrating the area under the polymer peak of the two signals and calculating the area ratio.

RESULTS AND DISCUSSION

To develop the GPC–UV method for quantitative phenolic end-group analysis in PC requires good calibration standards. Also, the precise contribution of the PC backbone to the absorbance at 288 nm must be known.

Determination of the PC backbone absorptivity at 288 nm requires a completely capped PC. To obtain this material, a commercial PC sample (LEXAN 101) was dissolved in methylene chloride and exhaustively treated with excess phenyl chloroformate and triethylamine. The reaction mixture was sampled at 15-min intervals and the polymer analyzed by GPC. The GPC was equipped with a diode-array detector so that chromatograms could be simultaneously generated at a variety of wavelengths. Overlaying the GPC signal curves collected at 264 and 288 nm before exhaustive capping clearly shows an offset (Fig. 3) indicative of an end-group effect.[9] The offset disappears when overlaying the 288- and 264-nm GPC curves collected after exhaustive end-capping, indicating the high conversion of the capping reaction. The absorbance ratio of each of these samples was determined by dividing the area of the 288-nm GPC curve by the area of the 264-nm curve. Since the solvent for the GPC analysis was tetrahydrofuran (THF), the data should correspond closely to that of Shchori and McGrath. The results are shown in Figure 4.

The absorbance ratio (R) diminished during the end-capping reaction and reached a minimum value of 0.00533. This is slightly lower than the value determined by Shchori and McGrath (0.007).

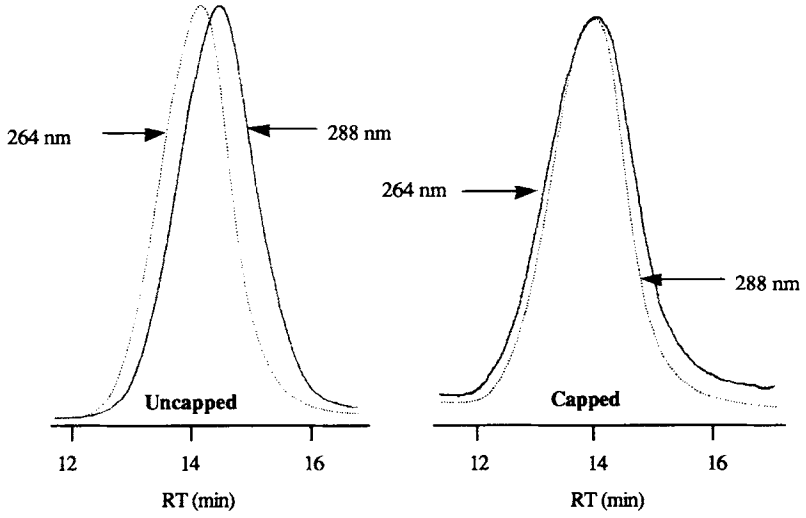

Figure 3 Overlay of 264- and 288-nm GPC signals of capped and uncapped PC.

In previous studies,[1,8] bisphenol-A was chosen as the model for a pair of uncapped ends. We felt that it would be better to use uncapped PC oligomers of known length because they contain carbonate moieties. The synthesis of phenolic terminal PC oligomers of controlled molecular weight has been described by using the pyridine solution process[8] or, alternately, a hydrolytically labile chain stopper can be used that can be removed after the polymerization reaction.[10] We chose to attempt to make uncapped PC samples of controlled M_n using the interfacial process without a chain stopper.

Typically, the interfacial process to make PC is performed in two steps. The phosgenation step is accomplished at high pH (usually > 12) to produce a mixture of low-molecular-weight PC oligomers having mostly chloroformate end-groups. The second step involves the addition of an amine catalyst to couple the oligomers to form high polymer. The coupling step occurs very rapidly and is usually complete within a few seconds. The resulting PC is free of chlorine containing end-groups but does typically contain a trace of phenolic end-groups. If a chain stopper is not added before the coupling reaction is performed, ultrahigh-molecular-weight PC is made, resulting in reactor stalling.

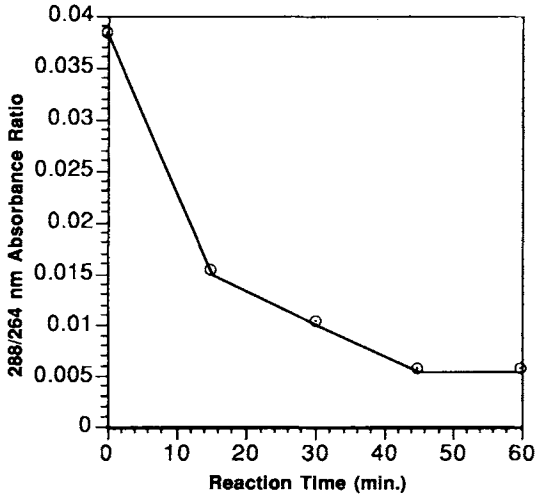

Figure 4 288/264 nm absorbance ratio change during exhaustive end-capping.

To prepare PC samples having no chlorine containing end-groups and having low molecular weight, we chose to add the amine catalyst before phosgenation. We also found that maintaining a low pH (8.5) during phosgene addition allowed smooth and controllable molecular weight growth until the stoicheometric amount of phosgene was approached (Fig. 2), which is typical of step growth polymerizations run in homogeneous solution. This indicates that at low pH the propagation step is taking place mainly in the organic phase rather than at the interface.

Collection of samples at various times during the phosgenation resulted in a variety of phenolic terminal PC samples of differing molecular weights. HPLC analysis of these samples, using previously described conditions,[4] allowed resolution of each oligomer with degrees of polymerization (DP) ranging from 1–16 (Fig. 5).

Since the HPLC was equipped with a diode-array detector, chromatograms were recorded at signal wavelengths of 264 and 288 nm (4 nm bandwidth).

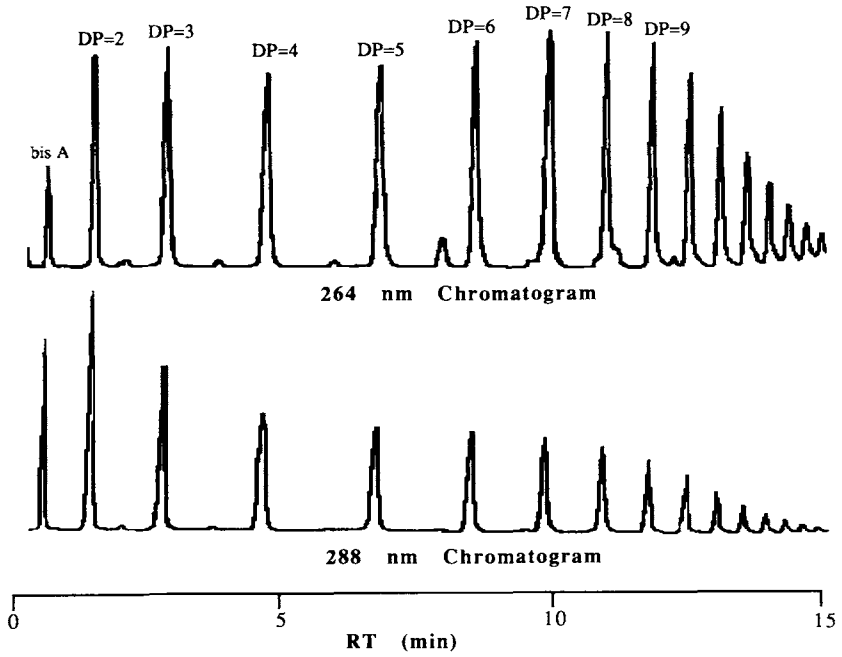

Figure 5 HPLC of uncapped PC oligomers at 264 and 288 nm.

This data was used to calculate R for each oligomer. Since the M_n of each oligomer is known, the ppmOH in each oligomer can be calculated. We know from Figure 4 that the absorbance ratio at infinite M_n is 0.00533. The results are shown in Figure 6.

The 288/264 nm absorbance ratio of commercial capped PC samples is expected to be < 0.1. The oligomers have absorbance ratios > 0.2. To obtain calibration standards having OH contents closer to the range of interest, we decided to make several

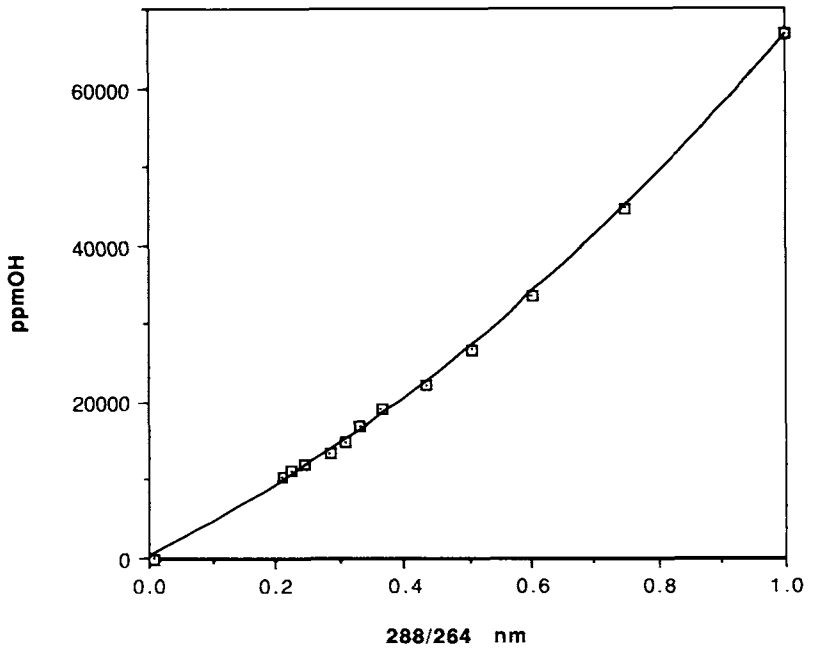

Figure 6 288/264 nm absorbance ratio of uncapped PC oligomers (DP = 2 – 13) by HPLC–UV.

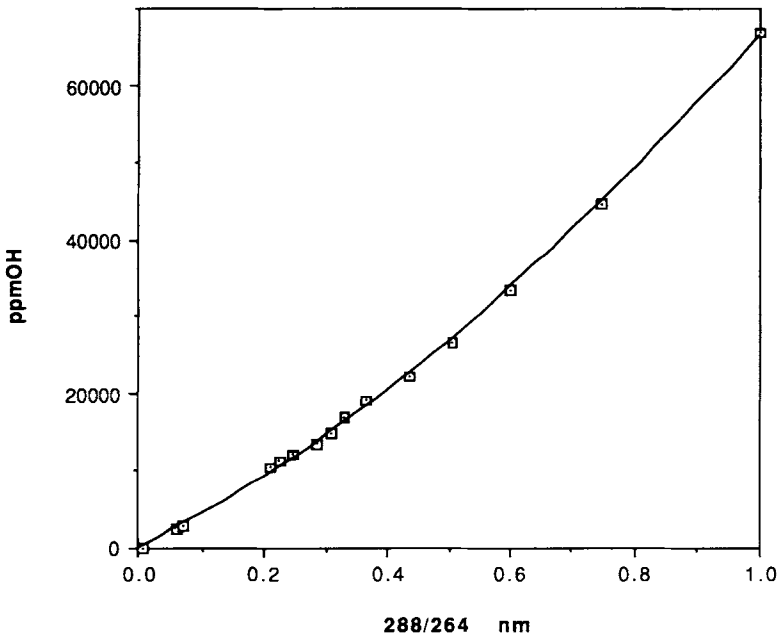

Figure 7 288/264 nm absorbance ratios of 12 uncapped oligomers, and 6 uncapped and 1 totally capped polymer by combined GPC–UV and HPLC–UV data.

uncapped PC samples having M_n values close to the typical M_n range of commercial capped PC products (i.e., ~ 12,000). We also wanted to demonstrate our ability to reproducibly make uncapped PC samples of ~ 12,000 M_n using interfacial polymerization. The M_n values (GPC) for products from six runs were between 11,600 and 13,700. The weight fraction of OH pairs in the six samples was calculated from the M_n values obtained during the GPC–UV analysis. The R value for each sample was determined

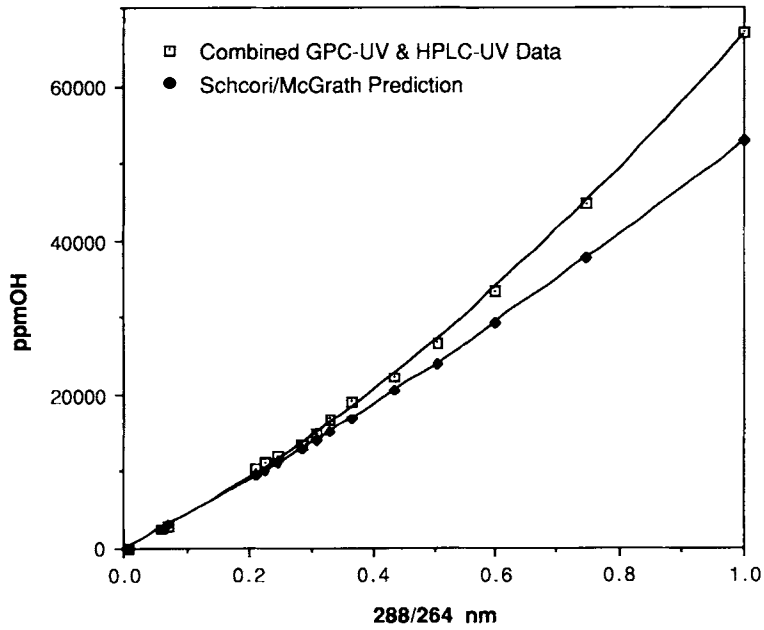

Figure 8 Comparison of the combined GPC–UV and HPLC–UV data with Shchori–McGrath prediction.

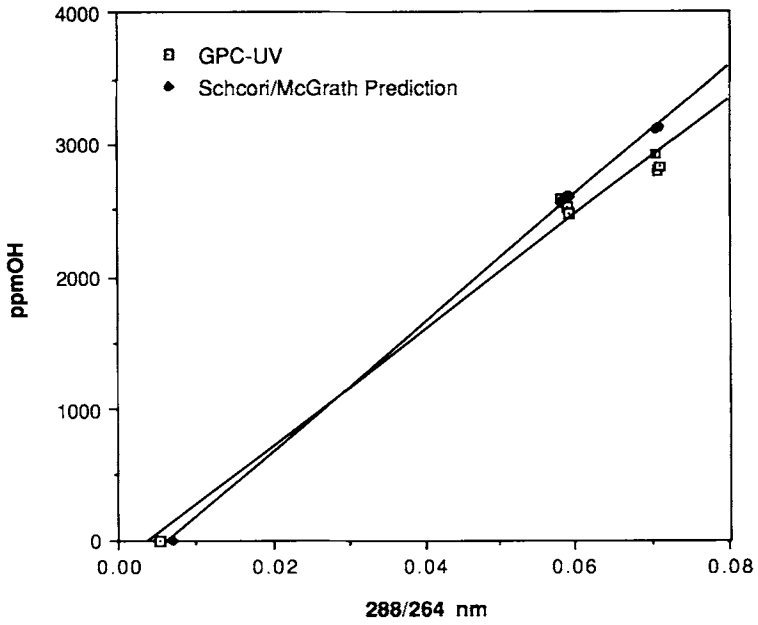

Figure 9 Comparison of GPC–UV data with Shchori–McGrath prediction.

using GPC–UV as previously described. This data was combined with the uncapped oligomer data obtained by HPLC–UV and the data from the totally capped PC sample obtained by GPC–UV. The results are shown in Figure 7.

The binomial best-fit line through this data is shown in eq. (3). Comparison of the data obtained from this study with the Shchori–McGrath prediction is shown in Figure 8.

$$y = 25519x^2 + 41054x + 37. \quad (3)$$

The deviation of our data from the Shchori–McGrath prediction at high OH content could be caused by the use of HPLC–UV to obtain the R values for the uncapped PC oligomers (high weight fraction of OH pair standards) since the solvent system was a THF/water gradient. During the HPLC analysis, as the oligomer DP increases the wt % THF in the gradient also increases and the closer the two curves approach. The beauty of the HPLC–UV method was the ability to completely resolve the uncapped PC oligomers, which are the perfect standards because the M_n is known.

Since the absorbance range of interest for our work is < 0.1, we chose to focus on this region. Figure 9 shows the GPC–UV data we obtained for samples falling within this region compared with the Shchori–McGrath prediction. The absorbance ratio data was determined during GPC–UV using 100% THF as the mobile phase, thus eliminating the possible data skewing observed by the HPLC–UV analysis. Equation (4) best fits this GPC–UV data set:

$$y = 43930x - 170. \quad (4)$$

Good agreement is found between the GPC–UV analysis method and the Shchori–McGrath prediction when analyzing PC samples having $R < 0.1$. The precision of this technique was determined to be 5% (2σ) (relative) by multiple (10×) analysis of a commercial PC sample.

CONCLUSIONS

GPC–UV analysis of PC provides a fast and convenient way to determine the molecular weight and extent of end-capping in commercial grades of PC in one analysis. The results from the GPC–UV method give good agreement with the UV technique of Shchori and McGrath. However, improved accuracy over normal UV analysis is obtained for highly end-capped PC samples because monomers and other impurities are excluded from the analysis.

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