Use of GPC-UV to Determine the Location of Functional Groups in Styrenic Polymers

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SYNOPSIS

Gel permeation chromatography (GPC) is one of the most important characterization tools of the polymer chemist. The coupling of GPC with ultraviolet (UV) spectroscopy (GPC–UV) increases the power of the tool even further. This article describes the use of GPC–UV to determine the location of functional groups in polymers. This information is important for characterization of functionalized polymers being used as building blocks for making block and graft copolymers, and for the elucidation of polymer degradation mechanisms. The use of GPC–UV for quantitation of the level of functional groups is hampered by the inability to achieve complete conversion of some UV transparent functional groups (e.g., hydroxyl and carbonyl) to the uniquely absorbing derivative needed for the analysis. Attempts to quantitatively derivatize polymer-bound functional groups using conditions developed for model compounds failed. However, the use of GPC–UV to locate functional groups in polymers (pendant vs. chain-end) is clearly demonstrated.

INTRODUCTION

Polymers containing low levels of functional groups are important building blocks for the preparation of block and graft copolymers. Determination of the location (i.e., pendant or chain-end) and concentration of the functional groups is important information needed to characterize these materials. Also, when examining the thermal, photolytic, and biooxidative degradation of polymers, determination of the location and concentration of functional groups (i.e., carbonyl and/or hydroxyl) is necessary for the elucidation of the degradation mechanism. In the past, infrared analysis has been utilized to examine degraded polymer and has indicated the presence of carbonyl and/or hydroxyl functionality. However, this technique has failed to provide quantitative levels or give direct information indicating the location of the functional groups.[1,2] In an effort to overcome this problem, the tagging of functionalized groups on polymers to improve detection has been utilized. Most notable were attempts to derivatize carbonyl groups in natural rubber, oxidized natural rubber, oxidized polyethylene, and copolymers of styrene with acrolein, methyl vinyl ketone (MVK), acrylic acid, and glycidyl methacrylate with 2,4-dinitrophenylhydrazine[3–13] to form strongly ultraviolet (UV)-absorbing hydrazones. Subsequent UV analysis clearly showed the hydrazone chromophores at carbonyl levels as low as 0.01 mol %,[11,12] but the analyses gave no quantitative information because the derivatization reaction proceeded to low conversion. It would be of significant value to develop reaction conditions that would quantitatively convert the functional groups on polymers to a chromophoric derivative. Copolymers with accurately known levels of functional groups could then be prepared and derivatized for use as calibration standards. Also, previous derivatization techniques followed by UV analysis showed only that carbonyl moieties were present in the polymer and gave no indication of the location of the carbonyl on the polymer chain or the distribution of the functionality v. polymer molecular weight. It is our aim to couple the UV tag technique with gel permeation chromatography (GPC) to develop a facile method for

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determining the location of functional groups in polymers.

GPC was first developed by J. C. Moore of The Dow Chemical Company in 1964.[14] This powerful technique for molecular weight determination utilizes crosslinked polystyrene gel particles of carefully controlled pore size to separate polymer molecules according to size. GPC is especially useful since it gives both the weight average molecular weight (M_w) as well as the number of average molecular weight (M_n) of polymers. The original detector system for this technique was a differential refractometer.[14] Many types of detector systems have since been investigated[15] including the use of multiple detector systems.[16] Commonly used systems now include refractive index, UV, infrared, low-angle laser light scattering, photodiode array, and reaction detectors.

Polymers containing aromatic chromophores are strongly absorbing in the UV. UV detectors are therefore the most widely used for GPC analysis of aromatic polymers due to their relatively low cost, high sensitivity, linearity, and stability. In general, UV detectors are operated at a fixed wavelength, most commonly 254 nm because most aromatic compounds absorb strongly at this wavelength. In recent years, photo-diode array detectors (DAD) have become readily available and allow the practice of three-dimensional chromatography where time, wavelength, and absorbance are simultaneously monitored.[17] When performing GPC using a UV detector, functional groups on the polymer chain that are not UV absorbing, such as hydroxyl or carbonyl, are not detected and have very little effect upon the polymer response. By derivatizing the functional groups with a dye or tag reagent, a chromophore with a unique UV or visible response can be generated. If a tag is selected that absorbs at a wavelength distinct from the polymer backbone absorbance, the ratio of the backbone absorbance to the derivative absorbance should allow calculation of the functional group concentration provided that the derivatization goes to completion. If the derivative has little or no contribution to the polymer backbone response, the backbone absorbance can be used as an internal standard.

By coupling the derivatization technique with GPC, any excess tag reagent that interferes with the UV analysis is separated from the polymer during the chromatography. Previous work,[10] which did not utilize GPC separation, required purification of the polymer to remove excess tag reagent. Using a GPC equipped with a DAD, the polymer backbone response can be monitored simultaneously with the derivatized functional group response. This technique would provide information regarding the concentration of the functional group and the location of the functional group (i.e., pendant v. chain-end).

Recently, coupled GPC and UV (GPC–UV) has been used to quantitatively measure the level of phenolic uncapped chain-ends in commercial polycarbonate samples.[18] In this case, derivatization of the hydroxyl end-groups was not necessary because phenolic hydroxyls have a unique absorbance spectrum compared to totally capped polycarbonate (Fig. 1).

By comparing the area under the GPC curves obtained at detection wavelengths of 264 and 288 nm, the phenolic end-group content of a PC sample can

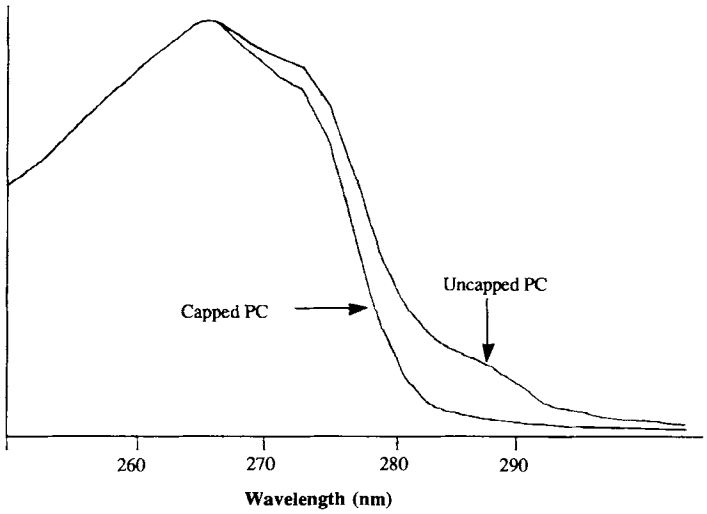


Figure 1 UV spectra of capped and uncapped PC samples (spectra are normalized at their maximum).

be measured quantitatively with excellent precision. Overlaying the 264- and 288-nm signals for a capped and an uncapped polycarbonate, the location of the phenolic hydroxyl on the chain end was demonstrated (Fig. 2).

The 288-nm response is due to end-group chromophores. Since the concentration of end-groups increases as the molecular weight decreases, the 288-nm signal peak appears at a longer retention time (lower molecular weight) than the 264-nm signal. The 264-nm signal results from backbone chromophores that are approximately equal in concentration in all polymer chains and therefore closely approximates the true polymer molecular weight. This offset of the two GPC signals represents the qualitative value of GPC–UV analysis for determining the location of functional groups in polymers.

EXPERIMENTAL

Materials

Anisole, 2-phenoxyethanol (PEA), dimethylaminoazobenzenesulfonyl chloride (DABSYL-Cl), 1,4-diazobicyclo[2.2.2]octane (DABCO), tetraglyme, trimethylsilyl chloride, and 4-nitrophenylhydrazine (NPH) were obtained from the Aldrich Chemical Company. Styrene and hydroxyethyl acrylate (HEA) were produced by The Dow Chemical Company. Toluene, tetrahydrofuran (THF) and methylene chloride were obtained from Fisher Scientific Inc. All materials were used as received without further purification.

Reaction Kinetics Study between PEA and DABSYL-Cl

A stock solution was prepared consisting of anisole (1.0136 g, 0.009373 mol) (internal standard), PEA (1.2928 g, 0.009357 mol), and 100 g methylene chloride [high-performance liquid chromatography (HPLC) grade].

To a 50-mL, round-bottom flask equipped with a septum and magnetic stirrer was charged 2.21 g stock solution, methylene chloride (5 g), and DABSYL-Cl (0.2682 g, 0.8283 mmol), followed by triethylamine (0.4191 g, 0.004141 mol). Aliquots of the reaction mixture were removed at various time intervals and the conversion of PEA followed using HPLC.

HPLC

Chromatograph: Hewlett-Packard 1090M equipped with a DAD. Column: A 150 × 4.6 mm Spherisorb CN (3 micron particle size) column (Keystone Scientific) was used. Mobile Phase: A linear gradient from 100% heptane to 50% heptane/50% THF over 5 min was used to achieve peak separation. Detection wavelength: The detection wavelength used to follow conversion of PEA was 260 nm.

Preparation of the DABSYL Derivative of PEA

To a 100-mL, round-bottom flask equipped with a magnetic stirrer was charged DABSYL-Cl (0.6484 g, 0.002002 mol), PEA (0.1446 g, 0.001046 mol), triethylamine (2.0340 g, 0.02010 mol), and 20 g anhydrous methylene chloride (dried over 3A molec-

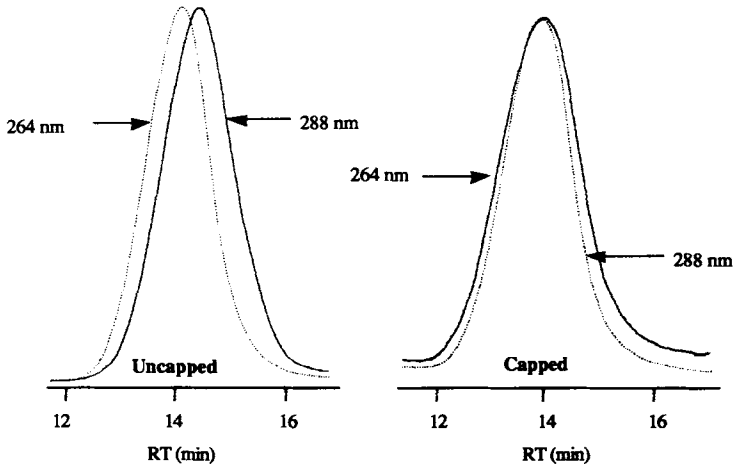


Figure 2 Overlay of 264- and 288-nm GPC signals (normalized) of capped and uncapped PC.

ular sieves). The flask was stoppered and the mixture stirred for 4 h.

The reaction product mixture was transferred to a separatory funnel and washed with cold 0.1 *M* aqueous HCl (5 × 150 mL), followed by cold 0.1 *M* aqueous $NaHCO_3$ (5 × 150 mL). The organic phase was dried overnight with anhydrous sodium sulfate. The organic phase was decanted and the methylene chloride evaporated to yield a deep red/purple residue. The residue was recrystallized from a methylene chloride/isopropanol mixture to give 0.0595 g (0.1398 mmol) (13% yield) of deep red crystals of 2-phenoxyethyl dimethylaminoazobenzenesulfonate (PEA-DABSYL MP = 159–160°C).

GPC Analysis

Chromatograph: Hewlett-Packard 1090M equipped with a DAD. Column: Polymer Laboratories (PL) gel 5 μm trimodal mixed-bed GPC. Mobile phase: THF at a flow rate of 0.5 mL/min.

GPC Response Factor Determination for PEA-DABSYL

A solution (10 μL) of the PEA-DABSYL (0.0116 g, 0.0273 mmol) in THF (12.8250 g) was analyzed by GPC. The ultraviolet response at 260 and 440 nm was determined.

Polymer Synthesis

Styrene-co-hydroxyethyl acrylate (SHEA) was prepared by spontaneous thermal polymerization of a mixture of styrene (98 mol %) and hydroxyethyl acrylate (2 mol %) in an evacuated glass ampoule at 140°C for 24 h. The resulting polymer was precipitated three times from methylene chloride-methanol and the polymer powder air dried overnight. ^{13}C nuclear magnetic resonance (NMR) analysis of the polymer showed that it contained 2 mol % HEA.

Styrene-co-methyl vinyl ketone (SMVK) was prepared by polymerization of a mixture of 99 wt % styrene and 1 wt % MVK in a continuous stirred tank reactor (CSTR) as described elsewhere.[19] The polymer syrup exiting the polymerizer contained 38% by polymer and was continuously devolatilized *in vacuo* at 230°C. The polymer exiting the devolatilizer was extruded into a strand and cut into granules. Infrared analysis of the polymer[20] showed that it contained 1.8 mol % MVK.

Derivatization of SHEA Copolymer with DABSYL-Cl Using Triethylamine as Base

A 100-mL, round-bottom flask equipped with a septum and magnetic stirrer was charged with SHEA copolymer (0.20635 g) and triethylamine (0.07548 g, 0.746 mmol) dissolved in 80 g methylene chloride. The mixture was stirred until the polymer dissolved. DABSYL-Cl (0.04625 g, 0.143 mmol) was added. The mixture was stirred at ambient temperature. Samples were taken at various time intervals and analyzed by GPC. After 20 h, very little reaction had taken place as evidenced by extremely low absorbance at a detector wavelength of 440 nm. A large excess of triethylamine (0.7 mL) was added and stirring continued for another h. GPC analysis showed that <1% conversion of the hydroxyl groups had taken place.

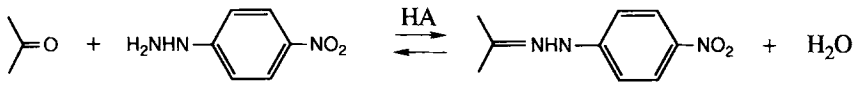
Derivatization of SHEA Copolymer with DABSYL-Cl Using DABCO as Base

A 50-mL, round-bottom flask equipped with a septum and magnetic stirrer was charged with SHEA copolymer (0.1 g), DABCO (0.046 g, 0.41 mmol), and methylene chloride (40 g). The mixture was stirred until the polymer dissolved. DABSYL-Cl (0.05 g, 0.154 mmol) was added. The mixture was stirred for 24 h at ambient temperature.

GPC–UV analysis was performed to determine the incorporation of the DABSYL group into the polymer. The response factor obtained from PEA-DABSYL was used to calculate the conversion of available hydroxyl groups.

Attempts to Drive SMVK Completely to Its NPH Derivative

To a 1-L, three-necked, round-bottom flask equipped with a Dean Stark trap, a mechanical stirrer, and heating mantle was charged toluene (200 mL) and NPH (2.04 g, 0.0133 mol). The mixture was refluxed with stirring for 2 h to remove moisture (0.2 mL water was collected). A 10% by wt solution of SMVK in toluene (330 g) was added, followed by chlorotrimethylsilane (0.1 mL, 0.0008 mol). The mixture was heated at reflux temperature for 3 h. An aliquot of the solution was removed, cooled, and the polymer triple precipitated using methanol/methylene chloride. The polymer sample was light yellow. An infrared spectrum showed some loss of the MVK carbonyl.



NPH

Scheme 1 Reversibility of hydrazone formation.

The reaction vessel was charged with additional chlorotrimethylsilane (0.5 mL, 0.005 mol) and the resulting mixture stirred at solvent reflux for 3 h. An aliquot of the solution was removed, cooled, and the polymer precipitated using methanol. Further loss of the carbonyl band was seen, although it was still present. The reaction vessel was cooled and 30 drops of concentrated aqueous hydrochloric acid solution was added. The solution was heated to reflux for 1 h. Again, analysis of the solution indicated that incomplete reaction had taken place.

The reaction vessel was cooled and tetraglyme (2.64 mL, 0.0120 mol) was charged. The mixture was heated to reflux conditions for 8.5 h. Samples were taken at 2.0, 4.0, 6.0, and 8.5 h, cooled, and polymer precipitated using methanol. Infrared analysis of the four samples showed successive decreases in the intensity of the carbonyl band.

The reaction vessel was charged with additional tetraglyme (2.64 mL, 0.012 mol), and the mixture refluxed for 4 h, and then cooled. Infrared analysis showed a loss of ~ 90% of the carbonyl band (1710 cm^{-1}) found in the starting SMVK. The reaction mixture was cooled and the polymer triple precipitated using methanol/methylene chloride. The final polymer sample was bright yellow.

Infrared Spectroscopy

The reaction between SMVK copolymer and NPH was monitored using a Perkin-Elmer 1750 [Fourier transform infrared (FTIR) (polymer films cast from methylene chloride). The intensity of the carbonyl band (1710 cm^{-1}) was used to follow the conversion of the ketone moieties to the hydrazone.

Three-Dimensional GPC–UV

The Hewlett-Packard 1090M liquid chromatograph with a DAD was used to collect ultraviolet spectra (240–500 nm) every 2 s during the elution of the polymer peak from the GPC column. The purified SMVK hydrazone was dissolved in THF at 0.25% by wt and injected onto the GPC column. After the analysis was completed, the data was plotted in a 3D format (absorbance vs. spectrum vs. time). A polystyrene having terminal carbonyl groups, which was prepared by fragmentation chain transfer[21] and converted to the 2,4-dinitrophenylhydrazone, was also analyzed under the same conditions to show the effect of having the hydrazone attached to the chain end.

RESULTS AND DISCUSSION

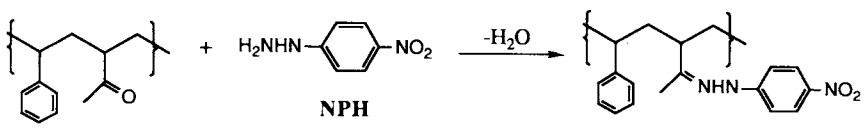
Derivatization of Carbonyl-Functional Polystyrene

The reaction of ketone with nitrophenyl hydrazine is reversible, as shown in Scheme 1.

Due to the extremely high polarity of 2,4-dinitrophenyl hydrazine (DNPH), a polar solvent is necessary (usually ethanol or dimethylformamide) for its use. Typically, no attempt is made to remove the water formed during the reaction.

Use of this reaction to derivatize low-molecular-weight ketones usually proceeds to high conversion due to the precipitous formation of the hydrazone. This precipitative driving force is not operative when derivatizing polymers and equilibrium is achieved at low carbonyl conversion.

We chose a random SMVK prepared by free rad-



SMVK NPH SMVK Hydrazone

Scheme 2 Hydrazone formation of polymer-bound carbonyl.

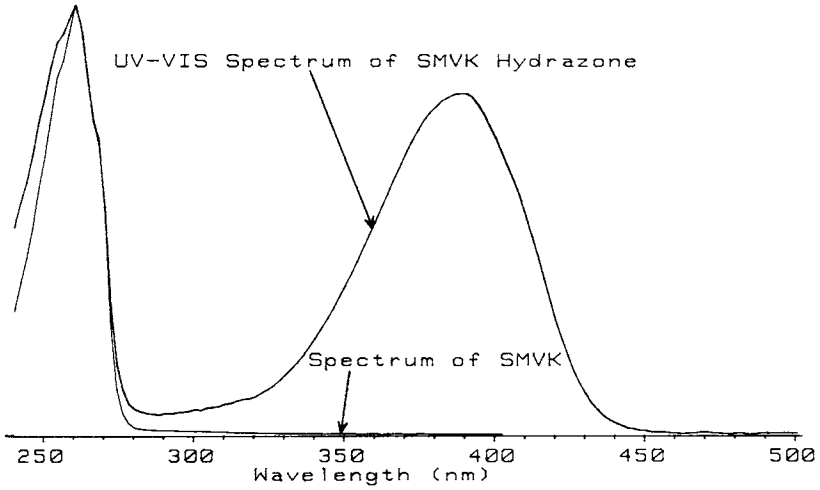


Figure 3 UV spectrum of SMVK and its hydrazone derivative.

ical polymerization in a CSTR[19] to investigate techniques to improve conversion of carbonyl groups attached to polymers. NPH was used to derivatize the carbonyl groups (Scheme 2) instead of DNPH. This allowed the use of hydrophobic solvents (e.g., toluene) as a natural driving force for the reaction by removal of water by azeotropic distillation.

The addition of a small amount of polyether (e.g., tetraglyme) was found to facilitate the reaction of NPH with the carbonyl groups in SMVK so that high conversion (~ 90%) to the hydrazone was achieved (estimated by FTIR analysis of polymer films). The highest conversion of polymer-bound carbonyl to hydrazone reported to date is < 50%.[9]

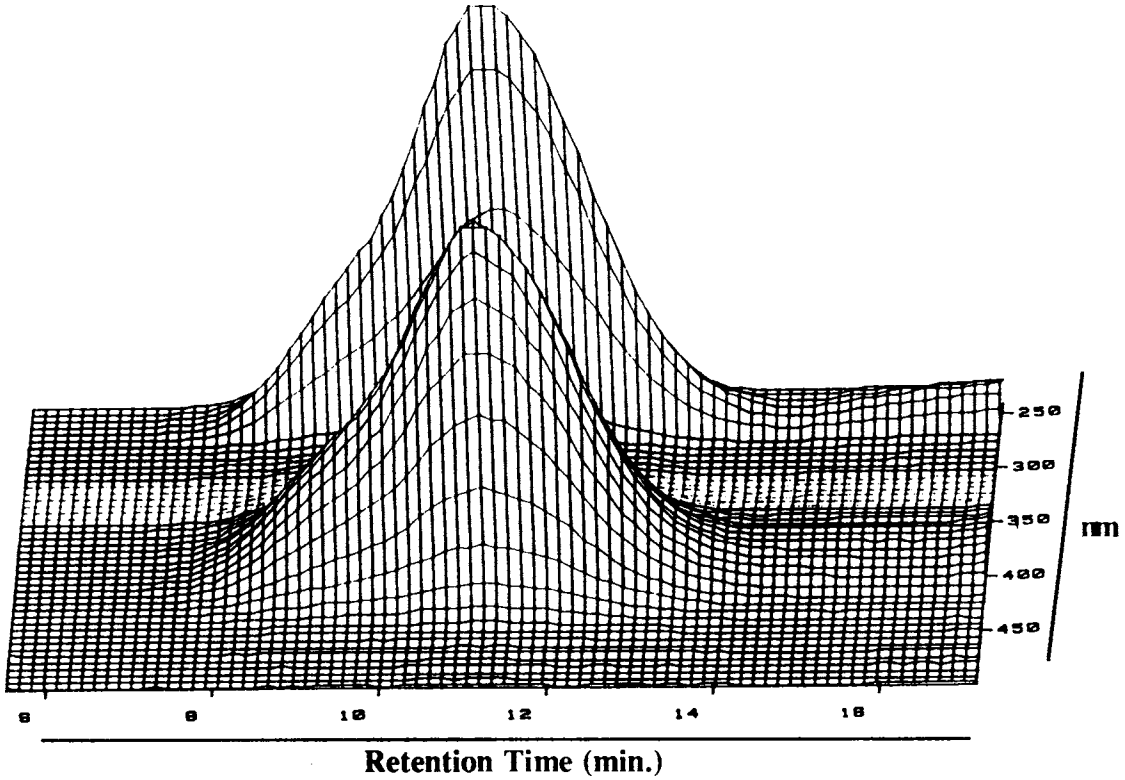


Figure 4 Three-dimensional GPC–UV of SMVK hydrazone.

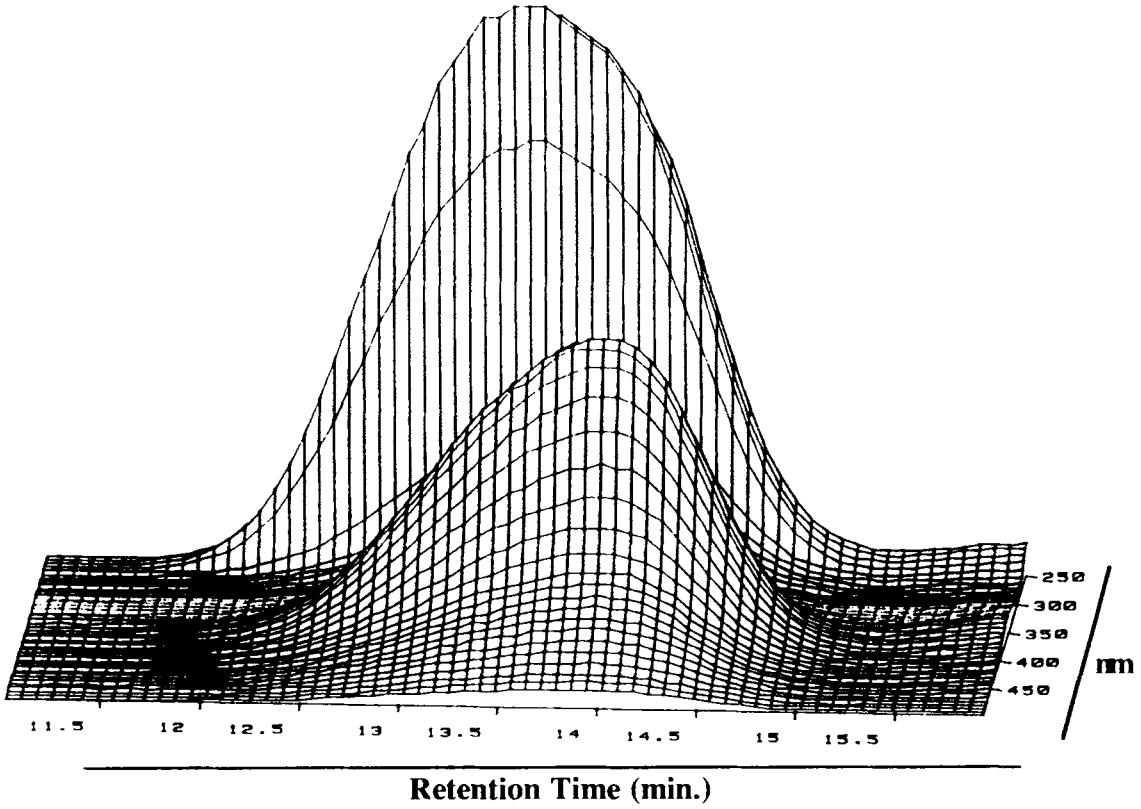
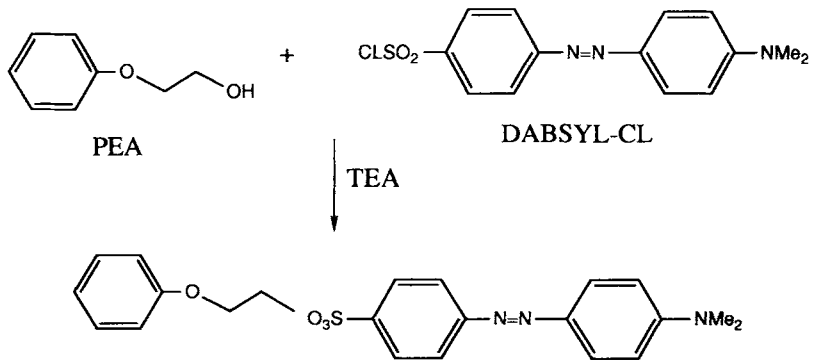


Figure 5 Three-dimensional GPC–UV of carbonyl terminal polystyrene hydrazone.

Previously, this same phenomenon had been observed with small molecules. Crown ethers form 1 : 1 complexes with phenyl hydrazines allowing hydrazone formation in lipophilic solvents.[22] The UV spectra of the SMVK copolymer and its hydrazone derivative are shown in Figure 3.

GPC–UV analysis of the SMVK hydrazone (Fig. 4) clearly shows the polystyrene backbone (λ_{max} = 260 nm) and the NPH hydrazone chromophore (λ_{max} = 390 nm) eluting in concerted concentration distribution. This vividly shows that the carbonyl groups in this copolymer are indeed randomly and uniformly placed along the polymer backbone.

A polystyrene having terminal carbonyl groups (prepared by fragmentation chain transfer)[21] was converted to the 2,4-dinitrophenyl hydrazone. Three-dimensional GPC analysis of the corresponding hydrazone derivative (Fig. 5) showed that the polymer backbone and the hydrazone chromophore do not elute in concert. Instead, the chro-



Scheme 3 Model compound experiment.

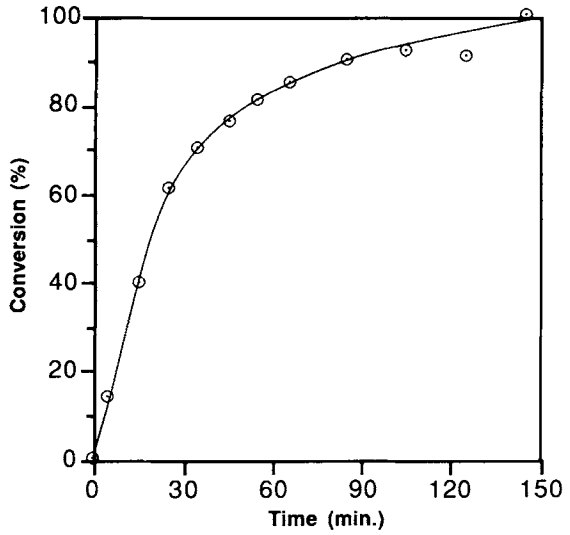


Figure 6 Kinetics of the reaction of PEA (1 mol) with DABSYL-Cl (4 mol) in the presence of TEA (20 mol).

mophore is at a higher concentration in the lower-molecular-weight chains. This occurs since the ends of the polymer chains are where the chromophores reside, and the concentration of end-groups increases as the molecular weight decreases. This phenomenon was first demonstrated in bisphenol-A polycarbonate made without the addition of an end-capping group.[18]

Hydroxyl-Functional Polystyrene

SHEAs have been utilized as substrates to make polystyrene-*g*-polycarbonates[23] useful as compatibilizers for blends of polystyrene and polycarbonate.

Several possible colored derivatization reagents were considered for tagging hydroxyl-functional polystyrene. DABSYL-Cl was selected for this investigation. To gain information regarding the kinetics of the reaction between an alcohol and DABSYL-Cl, a model compound experiment was conducted.

To mimic the hydroxy function in SHEA, PEA was chosen as the model alcohol. Since HCl is a by-product of the reaction, triethylamine (TEA) was added as an acid scavenger to enhance product formation (Scheme 3).

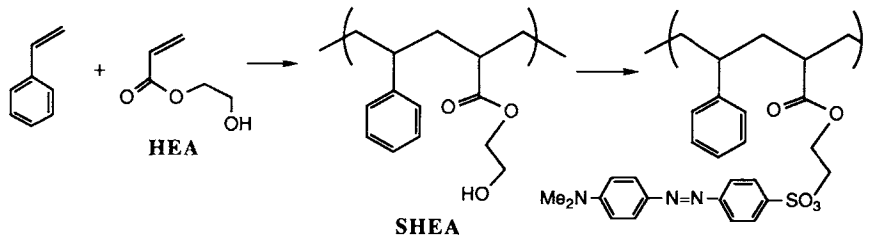
The conversion of the PEA to the sulfonate ester was followed by analyzing the reaction mixture v. time by HPLC. It could be demonstrated that a 4- and 20-mol excess of DABSYL-Cl and TEA, respectively, were required to achieve complete conversion of the alcohol at ambient temperature and within a 3-h time period. The kinetics of the reaction are shown in Figure 6.

Next, these reaction conditions were utilized for the derivatization of SHEA copolymer containing 2% by wt HEA units. After reaction under the same conditions that gave complete conversion of the model compound to the DABSYL derivative, only slight reaction could be detected. This result prompted the use of a more powerful acid scavenger DABCO. Indeed, in the presence of this powerful amine the rate of the model reaction was increased by more than an order of magnitude. The presence of this amine also increased the conversion of the SHEA functionality to the DABSYL derivative (Scheme 4), but high conversion still was not achieved.

The inability to push this reaction to completion removes its utility for quantitative analysis but it will, nonetheless, be very useful as a method to determine the location of the hydroxyl functionality in polymers providing the tagging reaction is kinetically indiscriminant with regard to polymer molecular weight and end vs. pendant placement.

CONCLUSIONS

The complete conversion of functional groups of polymers to highly UV-absorbing derivatives is difficult to achieve. However, GPC–UV analysis of even



Scheme 4 Preparation and derivatization of SHEA copolymer.

partially tagged polymer samples reveals information regarding the location of the functional group in the polymer (i.e., pendant vs. chain end). This information is very useful for characterizing polymers that will subsequently be used as building blocks for making block or graft copolymers. The location of functional groups is also useful as an aid in the elucidation of polymer degradation mechanisms.

REFERENCES

1. N. L. Maecker and D. B. Priddy, *J. Appl. Polym. Sci.*, **42,** 21 (1991).
2. R. A. Nyquist, *Appl. Spectroscopy,* **41,** 797 (1987).
3. K. Kato, *J. Appl. Polym. Sci.,* **19,** 951 (1975).
4. K. Kato, *J. Appl. Polym. Sci.,* **18,** 2449 (1974).
5. K. Kato, *J. Appl. Polym. Sci.,* **18,** 3087 (1974).
6. M. Johnson and M. E. Williams. *Eur. Polym. J.,* **12,** 843 (1976).
7. A. J. Boon, *Polym. Commun.,* **29,** 45 (1988).
8. D. Barnard, M. E. Cain, J. I. Cunneen, and T. H. Houseman, *Rubb. Chem. Tech.,* **45,** 381 (1972).
9. D. R. Burfield, *Polymer,* **23,** 1259 (1982).
10. D. R. Burfield and K. S. Law, *Polymer,* **20,** 620 (1979).
11. A. Subramaniam, *Proc. Int. Rubb. Conf.,* **IV,** 3 (1975).
12. A. Subramaniam, *J. Rubb. Res. Inst. Malaysia,* **25,** 61 (1977).
13. G. Ayrey, D. Barnard, and T. H. Houseman, *Chem. Rev.,* **71,** 371 (1971).
14. J. C. Moore, *J. Polym. Sci.,* **A2,** 835 (1964).
15. R. L. Bartosiewicz, *J. Appl. Polym. Sci.,* **C21,** 329 (1968).
16. J. R. Runyon, D. E. Barnes, J. F. Rudd, and I. H. Tung, *J. Appl. Polym. Sci.,* **13,** 2359 (1969).
17. S. L. Warner, B. A. Howell, and D. B. Priddy, *Polym. Prepr.,* **30**(2), 211 (1989).
18. C. O. Mork and D. B. Priddy, *J. Appl. Polym. Sci.,* to appear.
19. K. Sikkema, D. Brennan, M. Hanner, P. B. Smith, and D. B. Priddy, *Polym. Degr. & Stabil.,* to appear.
20. M. Hanner, M. A. McKelvy, K. D. Sikkema, and D. B. Priddy, *Polym. Degr. & Stabil.,* to appear.
21. G. F. Meijs and E. Rizzardo, *Makromol. Chem., Rapid Commun.,* **9,** 547 (1988).
22. F. Voegtle and W. M. Mueller, *Chem. Berlin,* **113,** 2081 (1980).
23. J. Cantrill, U. S. Patent 3,461,187 (1969).

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