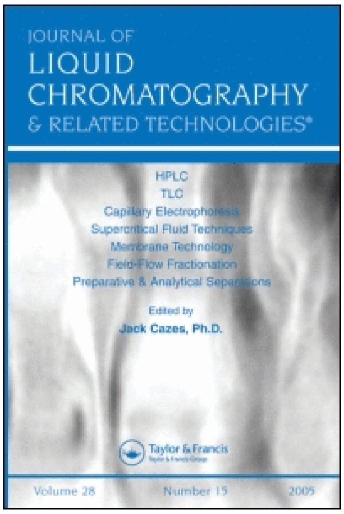

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SIZE EXCLUSION CHROMATOGRAPHY OF POLY(ETHYLENE TEREPHTHALATE) USING o-CHLOROPHENOL

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ABSTRACT

Ortho-chlorophenol (OCP) has previously been reported as one component in mixed solvent systems for the size exclusion chromatography of poly(ethylene terephthalate) (PET) [1,2]. In order to avoid the problems involved in maintaining mixed solvents, a technique has been developed to analyze PET in OCP alone. The system has been calibrated using narrow polystyrene and broad PET standards. Problems addressed include the high viscosity and high refractive index of OCP, solvent purity, sample preparation, and sample degradation. The system has been used to investigate the hydrolysis and degradation of PET during extrusion processes.

INTRODUCTION

The selection of size exclusion chromatography (SEC) solvent for the analysis of poly(ethylene terephthalate) (PET) is an exercise in compromise. PET, especially when crystalline, is difficult to dissolve. The traditional solvent has been hot m-cresol, but concerns about polymer degradation have led to a search for room temperature solvents. Hexafluoroisopropanol is an excellent solvent for PET [3] but suffers from both an extreme safety hazard and a prohibitive cost. Other reported solvent systems include phenol/o-dichloro-benzene, nitrobenzene/tetrachloroethane [4], and o-chlorophenol/chloroform [1,2]. In these mixtures the first reagent listed was used to dissolve the polymer and the second was used as a diluent. Mixed eluent systems, however, pose problems of maintaining constant composition. It was preferred to select as eluent a single solvent which dissolved PET under fairly mild conditions without degradation. For these reasons o-chlorophenol (OCP) was evaluated as a solvent for the SEC of PET.

Previously published studies of hydrolysis and degradation of PET did not use SEC. Indirect analytical techniques, mainly intrinsic viscosity and carboxyl end group determination, were used, generally assuming a polydispersity of two when molecular weight averages were discussed at all. Experimental conditions were usually below the melt temperature and at fairly high water content. For melt processing of PET it is generally recommended to dry below 50 ppm [5] to 200 ppm [6]. This is well below the water level examined in most of the studies. The only work examining degradation during extrusion of PET (recycled PET, in fact) at industrially relevant water levels concluded that moisture should be kept below 200 ppm, and mechanical energy input (i.e. extrusion shear) should be minimized to maintain mechanical properties [7]. In this study the effect on molecular weight of extruding recycled PET containing industrially relevant levels of water, is examined using SEC.

EXPERIMENTAL

Solvent

OCP was obtained from BDH Laboratory Supplies (Poole, England) and Aldrich Chemical Company (Milwaukee, Wisconsin) in the highest quality available, which is only 99%+. Solvent colour as received varied from straw yellow through water white to pale pink. The BDH product appeared slightly cleaner, but the supplier has recently discontinued it. Initial trials with solvent filtered through 0.45 μm Teflon media demonstrated severe baseline fluctuations. A purification technique was developed which removed all noticeable discoloration and resulted in much more stable baselines. The solvent was passed through adsorption alumina (Fisher, 80-200 mesh, chromatographic grade) immediately before filtering directly into the solvent reservoir, which was purged with helium.

OCP has a refractive index of 1.5524 at 20°C, which is quite high. It is also quite viscous, which results in high pressure drops across the columns. OCP is corrosive and toxic but not carcinogenic [8,9]. It has a strong, unpleasant odour. The odour threshold is normally well below the level at which mild symptoms of vapour exposure are noted (headache, nausea). However, it was found that olfactory fatigue can temporarily change this situation. Mild chemical burns were reduced by the use of a solvent-resistant hand cream in addition to protective gloves.

Standards

SEC calibration was carried out as discussed below using narrow polystyrene (PS) standards and broad PET standards. Ten PS standards (Toyo Soda, Japan) were selected with molecular weights from 2,750 to 1,270,000. Two broad PET standards were provided by Eastman Chemical Co. (Kingsport, TN). One, designated 39K, had known M_n, 21,000 and M_w, 39,000, determined by SEC and by light scattering respectively in hexafluoroisopropanol by the supplier (American Polymer Standards). The second, designated X20147-2A (referred to here as standard 47K) had M_w estimated at 47,240 by Eastman, using intrinsic viscosity.

Extruded Samples

Extruded PET samples were prepared on a 1.5" single screw extruder equipped with two static mixers to give a total extrusion residence time of about four to five minutes at a screw speed of 60 RPM. Two temperature levels, 270°C and 290°C, were selected. Recycled PET resin (St. Jude Polymer, green) was prepared at three moisture levels by drying in a vacuum oven at 124°C for 24 hours, then adding known amounts of water with mixing and allowing eight days for equilibration. Moisture levels of 0, 100 and 200 ppm were selected. All samples analyzed in this work were collected eight minutes after the prepared resin was charged into the empty extruder hopper, which was blanketed with argon. Extrudate was quenched in cold water to prevent *crystallization.*

Sample Preparation

Samples and standards of PET and PS were prepared at 0.2% w/v in 3.5 mL vials with Teflon-lined septum caps. PS dissolved at room temperature within 15 minutes to five hours, depending on molecular weight. PET samples were dissolved at 100°C in an oven equipped with a rotating rack. All PET samples analyzed dissolved within 45 minutes. Each sample was filtered through a 0.2 μm Teflon disposable filter unit into 1 mL sample vials.

Chromatography

The SEC equipment used in this work consisted of a Waters 510 pump, a Hewlett Packard Series 1050 autosampler, three Waters Linear columns heated to 90°C, and a Waters 410 refractometer. Data was collected with an ADALab A/D conversion card and a PC. Eluent flowrate was 0.5 mL/min. The pressure drop across the three heated columns at this flowrate slowly climbed from about 500 psi to almost 2000 psi over about eight weeks of discontinuous use and several months in storage (in methylene chloride). Sample injection volume ranged from 5 to 50 μL, with 50 μL used routinely. Refractometer sensitivity setting was usually 1024, the highest available. At this setting the differential refractive index detected ranged from 10^{-6} to 10^{-9} ΔRIU. The signal-to-noise ratio was at least 500 at typical peak maxima.

RESULTS AND DISCUSSION

Calibration

The SEC system was calibrated for PET using two methods [10]: a calibration curve search based upon the universal calibration curve and a search for a linear molecular weight calibration curve. These are discussed in turn below.

Universal Calibration

In the method based upon the universal calibration curve, narrow polystyrene (PS) standards were injected to determine the PS calibration curve. The Mark-Houwink equation was then used to convert from PS to PET molecular weights.

$$M_{PET} = (K_{PS}/K_{PET})^{1/(a_{PET}+1)} \cdot M_{PS}^{(a_{PS}+1)/(a_{PET}+1)} \qquad (1)$$

Normally, the Mark-Houwink constants, K and a, for both polymers in the solvent of interest are used to convert the curve directly. In this case, however, the constants for PS in OCP are not known. Therefore, the broad PET standards were used to provide the information required to search for the K and a values for PS. In-house software employing the Simplex search was used, as described in previous publications [11].

The PS calibration curve was fitted with a quartic polynomial. Mark-Houwink constants for PET in OCP used in the search were $K=6.31 \times 10^{-4}$ and $a=0.658$ [12], which were measured at 25°C. Other values in the literature range from 0.69 to 0.83 for a and 4.25×10^{-4} to 1.7×10^{-4} for K [13], with the two constants being strongly correlated. Using two chromatograms for each of the broad PET standards, giving a total of three known molecular weight averages in duplicate (M_n and M_w for standard 39K as well as M_w for standard 47K), the search program estimated values of a and K of 0.488 and 1.43×10^{-3} for PS in OCP. The converted calibration curve matched all three known PET molecular weight averages within 1.8%. The calibration curve for PET is shown in Figure 1.

Despite the physically unrealistic value of a, this technique gives a good calibration curve for PET. As is evident from Equation 1, the conversion to PET molecular weight calibration curve is determined by groups of Mark-Houwink constants [14]. The value of a obtained for PS reflects error in the constants used for PET (which should have been measured at 90°C, the column temperature). In addition, the assumption that the universal calibration is valid for PET may not hold [15].

Linear Calibration Curve Search

The calibration curve obtained above was fit by a quartic polynomial. It can be seen, however, that it is nearly linear over a broad range of retention volumes. One concern in the study was that OCP would cause some gradual change in the system (e.g. column degradation) which could significantly affect results. To enable faster recalibration of the SEC system, a single chromatogram for a broad PET standard of known M_n and M_w was used to search for a linear calibration curve. A program was written to use a Fibonacci search to find the values of D_1 and D_2 (in Eq. 2) which minimize the sum of the squares of the differences between the known and calculated polydispersities for standard 39K.

$$M = D_1 e^{-D_2 v} \tag{2}$$

Figure 1 shows the results of this search superimposed on that obtained from the universal calibration curve method. M_w calculated for other chromatograms (obtained the same day) for the second broad standard, which was not used in the search,

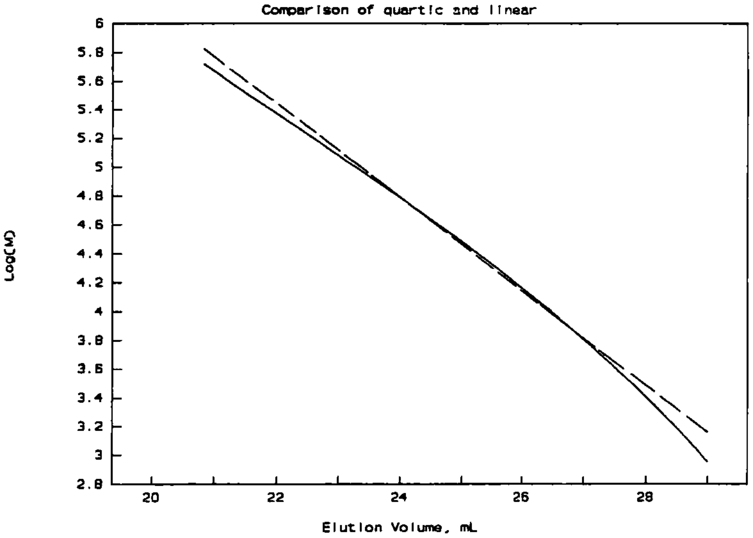

Figure 1 Calibration curves for PET: quartic (universal calibration) (solid line) and linear (dashed line).

differed from the known values by 4.8% or less. The features of the two calibration techniques are summarized in Table 1.

System Evaluation

The reproducibility of the SEC system was tested in two ways. First, the best possible reproducibility was evaluated by repeated injections of the same sample. Figure 2 shows six chromatograms collected over five days. The standard deviation of the area is less than 7%. The standard deviations of the mean M_n and M_w are 2.5% and 1.5% respectively.

In addition to these well-matched chromatograms, however, two chromatograms were collected with a distinctly different low molecular weight tail, as shown in Figure 3, and larger areas. This was traced to the vial septum material, rubber thinly lined with Teflon, which did not stand up well to repeated punctures. A new grade of septum is being sought. When such a chromatogram appeared among the repeated analyses in this work, it was discarded.

Table 1

Comparison of Calibrations for SEC

Form of calibration curve	Linear	Quartic
Information used	one chrom. for broad PET std, M_n, M_w	PS cal. curve, chrom(s) for broad PET stds, M_n(s), M_w(s), K & a for PET
Number of SEC injections required	1	10 to 15
Information searched for	D_1, D_2 in Eq (2)	K & a for PS in Eq (1)
Search technique	Fibonacci	Simplex
Predicted M_w of Standard 47K* using calibration	49,510	48,090

* *The vendor value of the M_w for this standard is 47,240.*

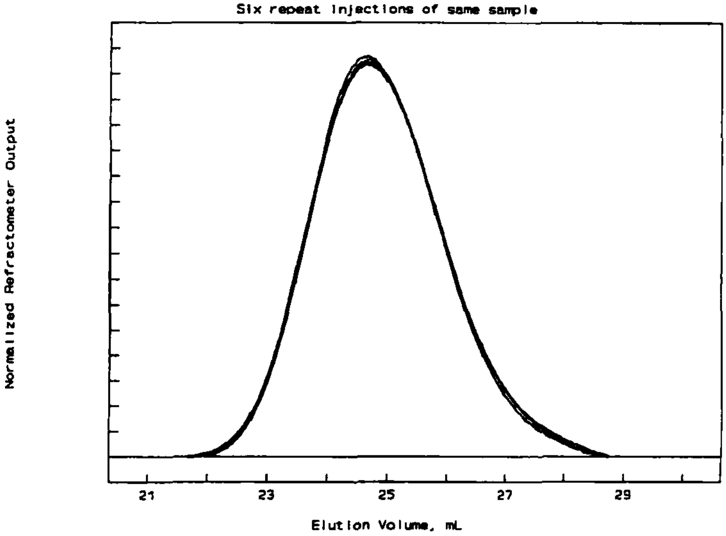

Figure 2 Reproducibility of SEC.

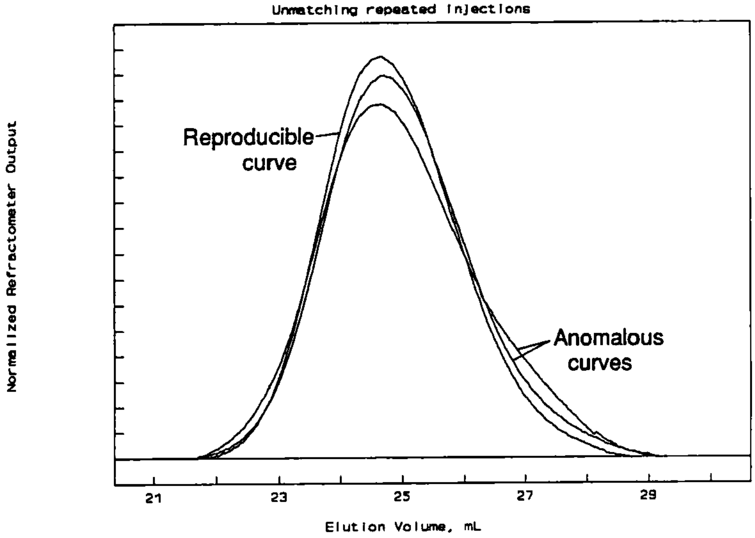

Figure 3 Non-reproducible chromatograms.

The effect of various experimental parameters on the resulting molecular weight averages and mass recovery (area under the chromatogram) was evaluated using a factorial design. The sample-to-sample variation, the time the sample spent in the oven for dissolution, the room temperature ageing of solutions, and possible chromatography system drift over the course of a few days can all affect results. The factors investigated and the levels used are summarized in Table 2.

The broad PET standard 47K was used to prepare the samples. All analyses were repeated in triplicate. The anomalous low molecular weight tail mentioned earlier was found once, and that chromatogram was discarded. The area under the chromatogram, M_n, M_w, M_z, and polydispersity index (PDI) were calculated for each chromatogram and averaged for each experiment. Statistical analysis of variance was carried out using the software package SAS-STAT. In this analysis the effect of each factor was compared to the random between-sample experimental error and an F-test used to determine if the effect was statistically significant. A 95% confidence level was selected. In this way the maximum information can be elucidated from 24 chromatograms.

Table 2

Factorial Experimental Design To Test Reproducibility of SEC

FACTOR	LEVEL 1	LEVEL 2
Time in oven	45 minutes	2 hours
Age of sample	same day	two days
Day chromatogram obtained	Day 1	Day 3

The initial analysis showed that all the molecular weight averages, when calculated with the same calibration curve, were affected by the day the chromatogram was obtained. This was caused by a shift in elution volumes which occurred between Day 1 and Day 3. The six repetitions over five days shown in Figure 2 suggest that the columns were changing little over such a time span, but another chromatogram obtained two days later had the same shape yet eluted about 25 seconds (0.2 mL) earlier. The cause of this sudden shift is probably abrupt column degradation: this particular set of columns had been used in a high temperature SEC before being subjected to this method development, including service in unpurified OCP and storage for months at a time. Recalculation of the molecular weight averages, using calibrations based on standards analyzed on the same day as the samples, eliminated the effect of analysis day. There is every expectation that new columns handled properly should be stable for six months service in OCP.

In the final result, the factors tested did not have any statistically significant effect on the area under the chromatogram (recovery), M_n, M_w, M_z, or PDI. The implications are that the solvent does not significantly degrade the polymer at elevated or room temperature. The necessity of recalibrating daily under certain conditions was verified. Figure 4 shows four typical molecular weight distributions, calculated using the appropriate calibrations, for samples analyzed at different sample ages and analysis days. The differences have been attributed to sample-to-sample variation and not to the experimental parameters examined. Standard deviations of M_n and M_w are both 6.4%.

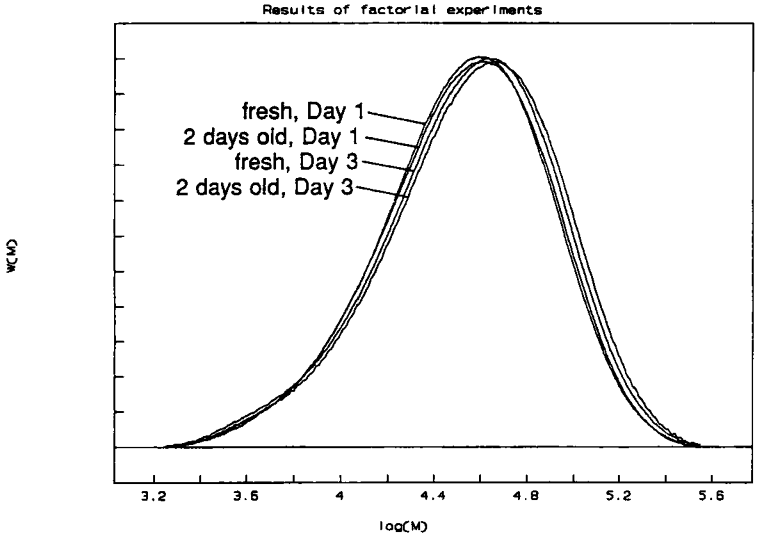

Figure 4 Results of factorial test of reproducibility, showing sample-to-sample variation.

Effect of Water Content and Extrusion Temperature on the Molecular Weight of Extruded PET

Table 3 summarizes the experimental conditions and resulting M_n, M_w, and PDI. Several observations can be made about the extrusion process. A comparison of the starting resin with extruded dried PET indicates that the polymer underwent significant degradation, attributable to thermal and shear effects and any hydrolysis caused by the residual traces of water left after vacuum drying. The lack of difference between extrusion temperatures gives clues to the degradation mechanisms in force. For polymer degradation the temperature coefficient is positive for thermal processes and negative for mechanochemical (shear) [16]. A combination of these mechanisms may result in a lack of temperature effect, as observed here. The decrease in PDI, caused by a much larger decrease in M_w than in M_n, supports the case for shear degradation. The final M_n values are comparable to the lower limit of molecular weights reported for mechanochemical degradation (by milling) [17]. The shear rates achieved in the extruder are approximately 30 s^{-1}.

Table 3

SEC Results of Extrusion Experiments

Extrusion Temperature	Moisture level, ppm	M_n	M_w	PDI
Not extruded	N/A	23,400	45,500	1.94
270°C	0	18,000	33,200	1.84
270°C	100	17,500	32,500	1.85
270°C	200	16,400	31,500	1.92
290°C	0	18,800	33,100	1.76
290°C	100	17,200	31,600	1.84
290°C	200	15,600	30,100	1.92

The lack of difference between temperatures also confirms the effectiveness of the drying process, since the temperature strongly affects M_n and M_w when water is present (as will be shown later). This initial level of degradation attributable to the extrusion process itself was assumed to be constant at each temperature when water levels were varied.

The addition of water from 0 to 100 and 200 ppm resulted in an increase in PDI, at both temperatures. At the 98% confidence level, PDI is a linear function of water. According to solid phase [18,19] and polymerization studies [20], hydrolysis of PET is catalyzed by terminal carboxyl groups. This would result in greater reaction at low molecular weight, broadening the molecular weight distribution and increasing PDI.

Assuming that shear/thermal degradation due to extrusion is independent of and constant at different water levels, the final molecular weight averages can be used to calculate the amount of water consumed in hydrolysis reactions. M_n is defined as the total mass of polymer divided by the total number of moles of polymer chains. Assuming that the total mass of polymer is a constant (which is a fair approximation, neglecting "snipping", which gives small molecule products), for each water molecule that reacts, one new chain forms. Thus the number of chains that exist after hydrolysis

Table 4

Calculated Amount of Reacted Water

Extrusion Temperature	Reacted Water	
	100 ppm added	200 ppm added
270°C	30 ppm	97 ppm
290°C	90 ppm	194 ppm

is equal to the original number plus the moles of reacted water:

$$n = n^0 + n_w \tag{3}$$

$$\frac{M_n}{M_n^0} = \frac{n^0}{n} \tag{4}$$

Therefore,

$$\frac{n_w}{n^0} = \frac{M_N^0}{M_N} - 1 \tag{5}$$

where n_w is the number of moles of reacted water, n and M_n are the number of polymer chains and the number average molecular weight in a sample extruded with water, and n^0 and M_n^0 correspond to the sample extruded without water but under the same conditions otherwise.

Using the 0 ppm runs as M_n^0, the calculated amount of water reacted (n_w/n^0) for each experiment is given in Table 4. For a residence time of 4-5 minutes, the hydrolysis reaction almost reached completion at 290°C, but was only partly completed at 270°C. This agrees with results observed in a study examining PET films (at much higher water levels but without shear) [21], where degradation at 280°C was observed only after 10 minutes, but at 290°C was observed immediately. A kinetic study of hydrolysis and thermal degradation of PET melts at 285°C [22] showed a rapid rate of degradation up to about 6 minutes, attributed mainly to hydrolysis, and a much lower rate thereafter, attributed to thermal effects (undried PET, >2,500 ppm water). Presumably the rates would be slower at lower temperatures. Although our limited data cannot be used to evaluate kinetics, it is interesting to note that the extent of hydrolysis observed here is consistent with published work. Note also that the temperature used for PET processing is critical, if the resin contains moisture in the range of 100 ppm or greater.

Using SEC to examine the effect of water and extrusion temperature on the molecular weight of extruded recycled PET enabled the rapid confirmation of a number of results found in the literature for the hydrolysis and degradation of PET. The M_n, M_w and polydispersity of dried, recycled PET decreased upon extrusion. Hydrolysis is significant at 100 ppm, and is probably catalyzed by terminal carboxyl groups since the low molecular weight tail is more strongly affected, causing an increase in PDI. Hydrolysis is incomplete in 4-5 minutes (the extruder residence time) at 270°C but is nearly complete at 290°C. These results have important implications in the selection of drying and extrusion conditions for PET melt processing.

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REFERENCES

1. M.M. Sang, N.N. Jin and E.F. Jiang, *J. Liq. Chrom.*, 5(9), 1665 (1982).
2. S.A. Jabarin and D.C. Balduff, *J. Liq. Chrom.* 5(10), 1825 (1982).
3. J.R. Overton and H.L. Browning, Jr., Size Exclusion Chromatography, ed. T. Provder, ACS Symposium Series No. 245 (1984).
4. E.E. Paschke, B.A. Bidlingmeyer and J.G. Bergmann, *J. Polym. Sci: Polym. Chem. Ed.*, 15, 983 (1977).

5. R. Juran, ed., Modern Plastics Encyclopedia, McGraw Hill (1991).

6 Y.C. Jalandar and S.W. Kantor, Encyclopedia of Polymer Science and Engineering, John Wiley and Sons Inc., New York (1985).

7 J. Curry and A. Kiani, Proceedings of the 49th ANTEC (1990).

8 Aldrich Chemical Co., Material Safety Data Sheet for 2-chlorophenol (1989).

9 Public Health Service, NIOSH, Registry of Toxic Effects of Chemical Substances, RTECS #SK2625000, U.S. Dept. of Health and Human Services (1987).

10. S.T. Balke, Quantitative Column Liquid Chromatography, a survey of chemometric methods, Elsevier Science Publishing, New York NY (1984).

11. R. Lew, S.T. Balke, and T.H. Mourey, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 45, pp.139-176 (1990).

12. American Polymer Standards Co., Polymer Standards Catalog (1991).

13. J. Brandrup and E.H. Immergut, eds., Polymer Handbook, 2nd ed., John Wiley and Sons, N.Y. (1975).

14. O. Chiantore and A.E. Hamielec, *J. Liq. Chrom.*, 7(9), pp. 1753-1767 (1984).

15. T. Havard, private communication.

16. A. Casale and R.S. Porter, Polymer Stress Reactions, Volume 1, Academic Press, New York (1978).

17. A. Casale and R.S. Porter, Polymer Stress Reactions, Volume 2, Academic Press, New York (1979).

18. D.A.S. Ravens and I.M. Ward, *Faraday Soc. Trans.*, 57, 150-159 (1961).

19. A. Ballara and J. Verdu, *Polymer Degradation & Stability*, 26, 361-374 (1989).

20. H. Zimmerman and T.K. Nguyen, *Polymer Eng. & Sci.*, 20 (10), 680-683 (1980).

21. S.A. Jabarin and E.A. Lofgren, *Polymer Eng. & Sci.*, 24 (13), 1056-1063 (1984).

22. K.S. Seo and J.D. Cloyd, *J. Appl. Polym. Sci.*, 42, pp. 845-849 (1991).