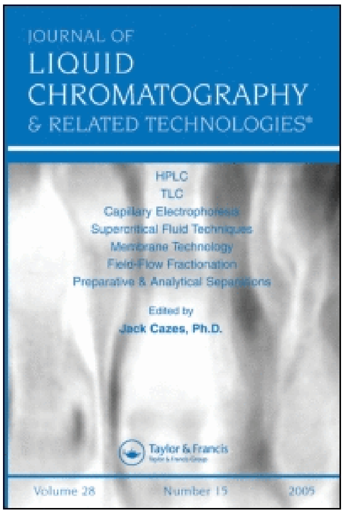

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Column Liquid Chromatography in Polymer Degradation Studies

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To cite this Article Chiantore, Oscar(1990) 'Column Liquid Chromatography in Polymer Degradation Studies', Journal of Liquid Chromatography & Related Technologies, 13: 15, 2957 — 2972
To link to this Article: DOI: 10.1080/01483919008049080
URL: http://dx.doi.org/10.1080/01483919008049080

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(15), 2957-2972 (1990)

COLUMN LIQUID CHROMATOGRAPHY IN POLYMER DEGRADATION STUDIES

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ABSTRACT

Column liquid chromatography performed on polymer samples subjected to degradation reactions makes up an important source of information for determining the polymer degradation mechanisms. In the present paper it is shown how molecular weight distribution changes and formation of new compounds due to degradation reactions can be conveniently analyzed by size exclusion and adsorption/partition chromatography. The sensitivity and uniqueness of the approach is demonstrated with proper examples. Particularly, it is reported how liquid chromatography has been helpful in establishing the presence of weak links in polystyrene samples, in modelling the thermal degradation mechanisms of poly(alpha-methyl styrene) and of poly(methyl methacrylate), in showing the occurrence of termination reactions by radical coupling in poly(methyl methacrylate) samples and the influence of acrylonitrile content on the degradation of styrene-acrylonitrile copolymers.

INTRODUCTION

In the modern development of polymeric materials the control of structures and properties is becoming more and more compelling and tailored to the different applications in order to optimize performances in the desired fields. It is therefore clear that when complete characterization of polymer is dealed with, the behaviour under conditions of degradation, which can be thermal, photochemical, mechanical or of some other kind, must be considered. The chemical reactions taking place when polymer molecules are in some degrading environment may be grouped under different classes: homolytic chain scissions, depolymerizations via unzipping and backbiting, intermolecular radical transfers, side group reactions or eliminations, interactions with small molecules, crosslinking, etc. The mechanisms through which all the above reactions can affect the polymer structures are of different types, their characteristics depending on the nature of the macromolecules and the kind of degradation involved; however, in all cases the net results always are changes of average molecular weights in the polymers, and sometime changes of their chemical structures and formation of medium and low molecular weight molecules, i.e. chain fragments, oligomers, monomers. The tracking of how these molecular and chemical changes occur in the polymers is essential for understanding the degradation mechanisms. A powerful tool for this task is provided by column liquid chromatography because this technique allows performing both detailed analysis of molecular weight distribution (MWD) changes and separation/quantitation of the new molecules produced during degradation, with the use of size exclusion chromatography (SEC) and of adsorption/partition chromatography .

In this paper the applications of liquid chromatographic analysis to the investigation of polymer degradation processes are described, with examples obtained in the degradation, mainly thermal, of different polymers having industrial interest.

EXPERIMENTAL

The degradation of many polystyrene, poly(alpha-methyl styrene) and poly(methyl methacrylate) samples was investigated by measuring the MWD changes during the process. Styrene-acrylonitrile copolymers, with acrylonitrile content ranging from 17 to 39 weight

%, were also degraded and the chain fragment composition analysed. The degradation experiments were carried out at the desired temperatures either in dynamic vacuum on a Cahn RG thermobalance, or under nitrogen flow on a DuPont 951 thermobalance coupled with a DuPont 1091 control unit. After given weight losses, the degraded samples were dissolved in tetrahydrofuran (THF) for MWD measurements. Analysis of oligomers and of chain fragments was performed on the fractions evaporated at high temperatures from the degraded samples and condensed at the outlet of the degradation oven.

SEC and HPLC separations were performed on modular chromatographic equipments, with a Waters M45 and an Altex 110A pump. An Erma differential refractometer, model ERC 7510, and a Zeiss UV spectrophotometer, model PM 2 DLC, were used as detectors.

High efficiency SEC columns (300 x 7.5 mm i.d.) packed with crosslinked semi-rigid polystyrene particles from Waters (UltraStyragel) and from Polymer Laboratories (PL gel 5 µm) were employed. For the molecular weight determinations polymer samples were generally eluted in THF at 1 cm^3/min flow rate with o-dichlorobenzene as internal standard. The output from the detector was sent to a Linseis L8500 A/D converter interfaced with an Apple personal computer for acquisition and treatment of data. All routines for data reduction, flow rate normalization and molecular weight analysis were developed in the laboratory.

Reversed phase liquid chromatography was performed on two Separon Six C18 50 A (150 x 3.2 mm i.d.) glass cartridges connected in series. Normal phase separations were run on a Lichrosorb SI 60, 5 µm (250 x 4 mm i.d.) column.

RESULTS AND DISCUSSION

Molecular weight and molecular weight distribution changes in polymer degradations

Molecular weight (MW) is a property very sensitive to the changes induced by degradation. In fact, when in a polymer sample one main chain chemical bond per macromolecule is broken, so that two shorter chain molecules are produced, the number of molecules doubles and the number average MW, M_n, halves independently of the width of the distribution of MWs and of the bond position into the original polymer. There is a simple straightforward relation between the polymer MW and the number of chain scissions, s, per initial number of macromolecules:

$$s = \frac{M_{n,o}}{M_n} - 1$$

where $M_{n,o}$ is the initial number average MW.

When changes in other MW averages or, generally speaking, in the overall MWDs are considered, they are not only related to the number of scissions but also to the position of the broken bonds in the macromolecules, to their probability of scission, to their molecular weight dependence, and to other factors. Therefore, for a complete picture of the degradation mechanism taking place in a given polymer, the determination of different MW averages is always necessary; furthermore the analysis of the MWD changes, in some cases, may reveal peculiarities of the degradation process otherwise undetectable. For these reasons SEC is such an important technique in polymer degradation studies: with the same experiment on a degraded sample any desired MW average can be obtained and the overall MWD may be directly observed.

A typical separation system employed for investigation of the MWD changes during degradation of polymers consists of 3 columns with nominal pore dimensions of 10^5, 10^4 and 10^3 A, respectively, connected in series. The fractionation capability and the calibration curve relative to this column set are shown in Fig. 1. A separation system like that is specifically designed for degradation studies where, in general, the polymer molecular weights decrease often drastically: we have in fact high overall efficiency with particular very good specific resolution at the intermediate and low molecular weights.

Let us consider two polymer samples with the same initial number average MW, $M_{n,o}$ = 200000, and different MWD. The first sample has a narrow distribution with initial weight average molecular weight $M_{w,o}$ = 220000, whereas the second has a broad distribution with $M_{w,o}$ = 400000. If both polymers undergo degradation so that only random chain scissions take place along the polymer chains, the MWD of the original polymers will change as a function of the increase of the number of scissions in the way shown in Fig. 2; the number and weight average MWs corresponding to these distributions are reported in Fig. 3. It can be seen that the M_n values of both samples are always equal between them in the course of the degradation, whereas the M_w values, initially

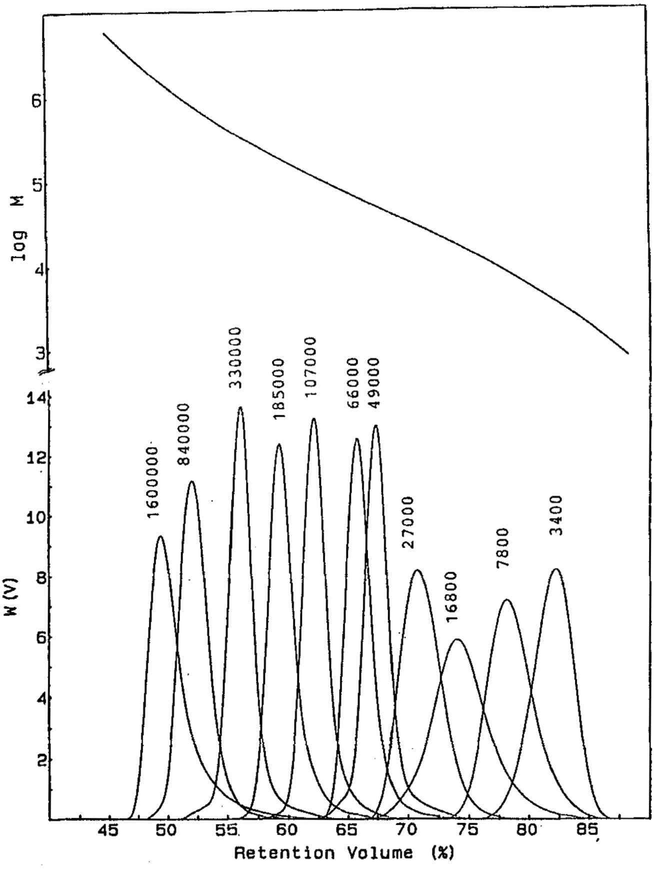
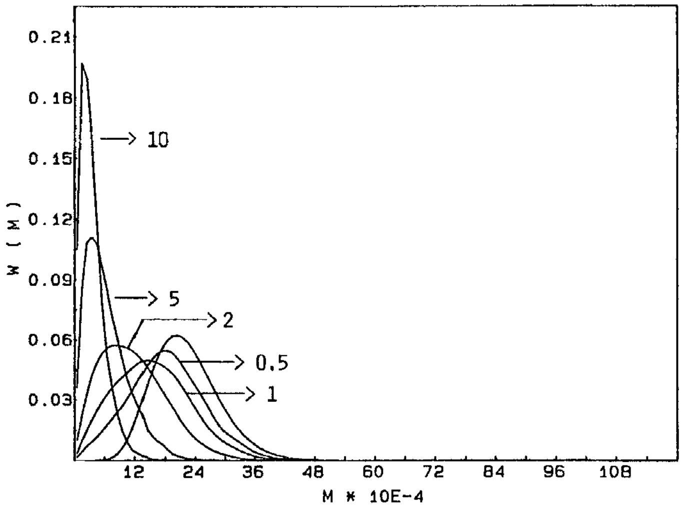


FIGURE 1. Calibration curve and chromatograms of poly(methyl methacrylate) narrow standards eluted in THF on 3 PL Gel columns, $10^5 + 10^4 + 10^3$. Numbers on the peaks are molecular weights of the standards. Retention volumes are expressed as percent of total volume of liquid in the columns.



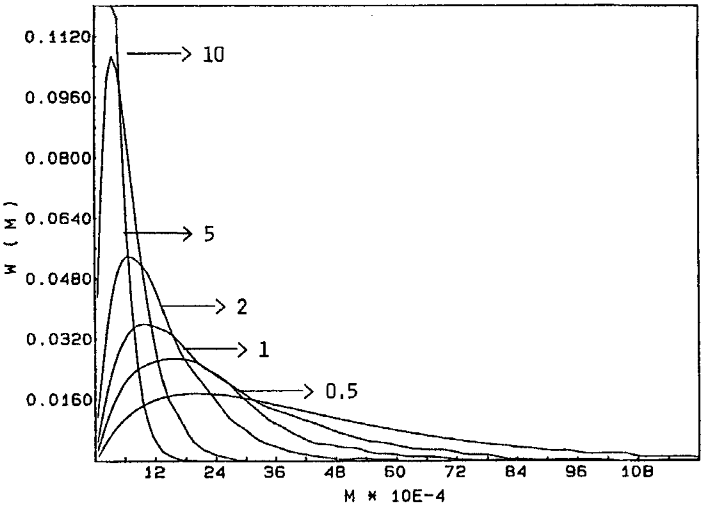


FIGURE 2. Molecular weight distributions of polymers with $M_{n,o}$ = 200000 and initial dispersity index $(M_w/M_n)_o$ = 1.1 (top) and $(M_w/M_n)_o$ = 2.0 (bottom), and ditributions obtained after the given number of random chain scissions per initial molecule.

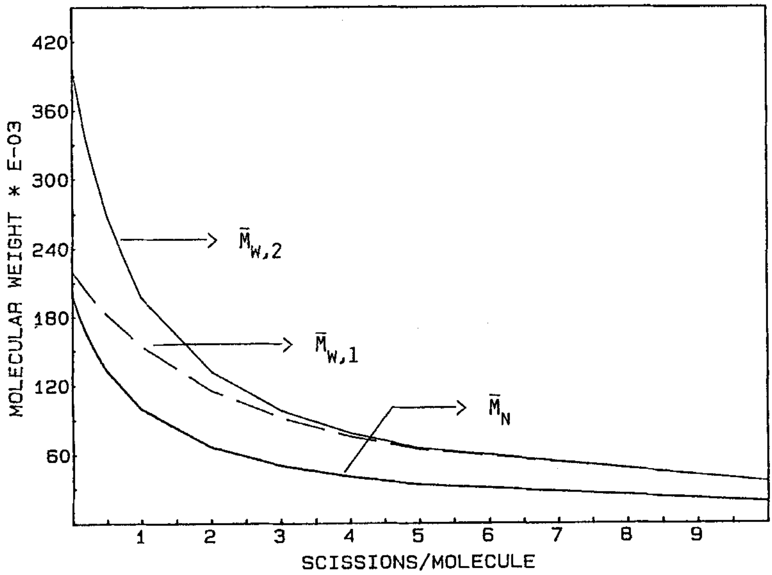


FIGURE 3. Molecular weights as a function of number of random chain scissions for the two polymers of Fig. 2. The M_n line is relative to both polymers; $M_{w,1}$ is relative to the narrow distribution sample, $M_{w,2}$ to the broad distribution one.

different, become equal only after ca. 6 scissions per molecule. The bigger changes, especially evident looking at the average MWs, occur at low values of chain scissions.

When the MWD of a polymer is known the SEC chromatographic curve which would be obtained by eluting the sample on a given column system can be easily calculated through the relationship:

$$W(V) = - W(M) M \frac{d\log M}{dV} 2.303$$

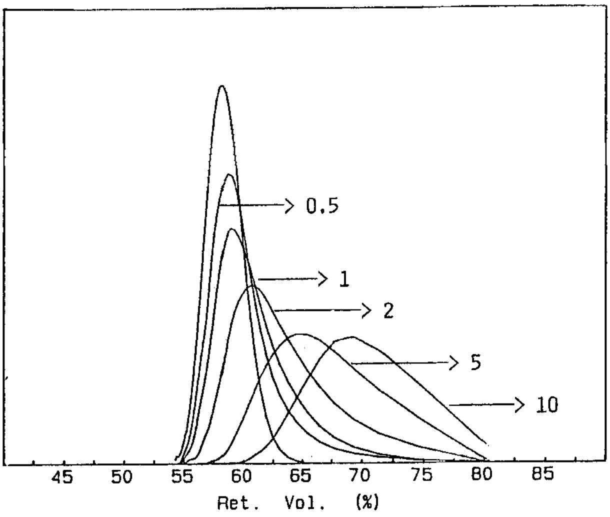
W(V) is the chromatographic height at each retention volume V and W(M) is the corresponding polymer weight fraction, M is obtained from the calibration function log M = f(V) relative to the SEC columns, and -dlog M/dV represents the local slope of the calibration.

The chromatograms corresponding to the MWDs reported in Fig. 2 and which would be obtained from the system giving the separation of Fig. 1 are shown in Fig. 4: it can be seen, also from simple inspection of the chromatograms, that even small amounts of chain scissions are very efficiently detected.

Degradation by simple random chain scission is an important case which may occur during polymer life under the effect of heat, radiation, chemical agents or ultrasonic waves. In some instances, however, depending on the polymers and on the energy levels involved, the breaking of the chemical bonds is followed by depolymerization reactions which affect the MWs of the residues in different ways, according to the type and the extent of these reactions which give rise to low MW compounds such as monomers and oligomers. The analysis with SEC gives in such cases the MW changes as a function of the fractional conversion to non polymeric molecules, as it can be seen in Fig. 5 where the weight and number average MWs experimentally determined with SEC at various degradation levels are reported for samples of poly(alpha-methyl styrene) having different initial polymerization degrees (1). On the basis of these results, and of the knowledge of the low MW products formed during the degradation (in the present case only monomer is formed) the appropriate degradation mechanism can be recovered by computer simulation of the process and comparison with the chromatographic results. The solid lines of Fig. 5 represent the MW changes obtained from the computed model, and it can be seen that the experimental results are fairly well reproduced. It is important to note that for a correct evaluation of the degradation mechanism, samples with wide spectrum of initial polymerization degrees must be evaluated, and this is made easy by the application of the chromatographic technique.

Special cases where the chromatographic investigation has shown his unique capability of detecting degradation reactions in polymer samples will be described now.

The presence of weak links, i.e. some kind of thermally labile bonds, in polystyrene molecules has been postulated for many years (2, 3) but never directly demonstrated, owing to their very small number in the polymer samples (<<1/molecule) undetectable with the ordinary analytical techniques. The destruction of even such small number of weak links, however, plays a non negligible role on the sample MWs, and it has been possible, by means of high performance SEC, to obtain direct evidence of the presence of weak links in different types of polystyrenes and to measure their rate of scission by following the changes of MWD taking place in the polymer samples (4).



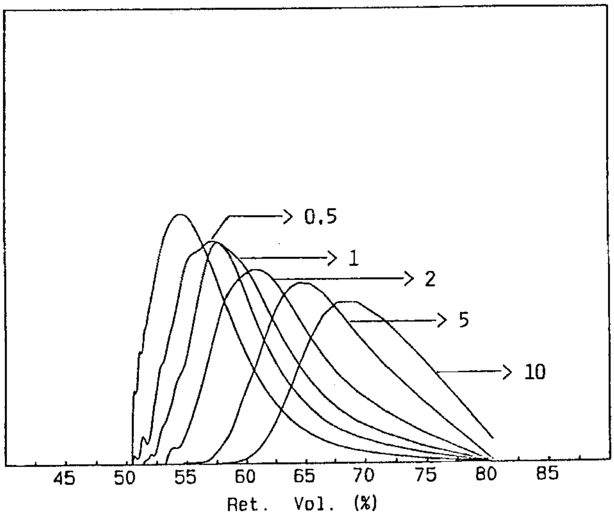
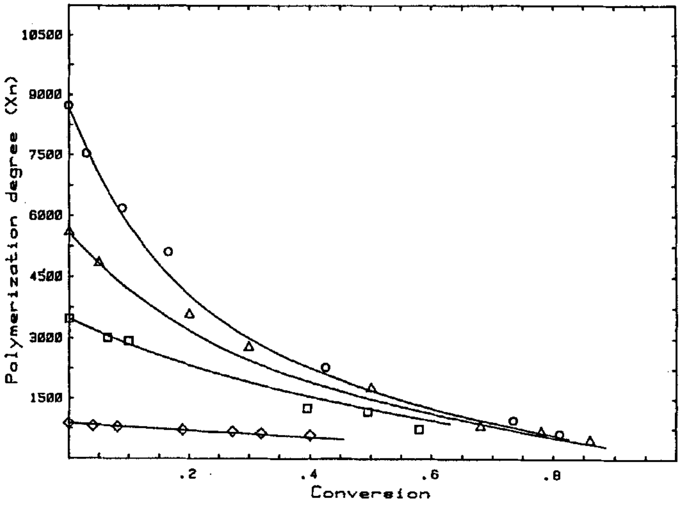


FIGURE 4. Simulated chromatograms corresponding to the molecular weight distributions of Fig. 2 and to the calibration curve of Fig. 1. Polymer with initial narrow distribution: top; with initial broad distribution: bottom. Values of random scissions per initial molecule are indicated on the chromatograms.



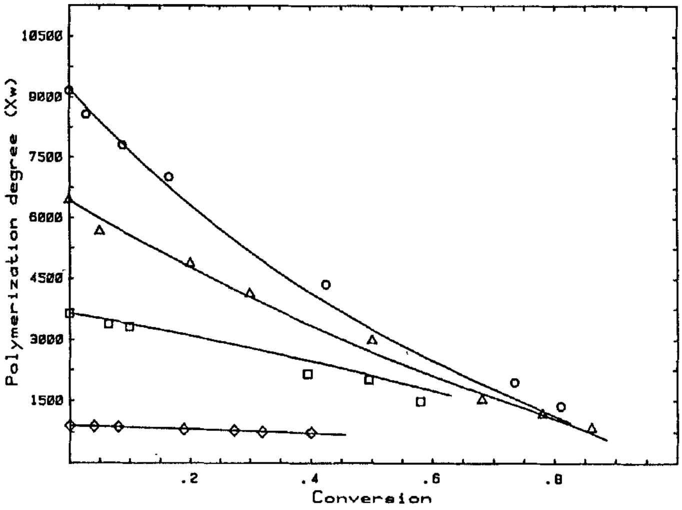


FIGURE 5. Experimental changes of number average (X_n) and of weight average (X_w) polymerization degrees with fractional conversion to volatile products during thermal degradation of poly(alpha-methyl styrene)s having different initial molecular weights. Solid lines are the results from computer simulation of degradation mechanism.

In another case, with a thorough study on the changes of degrees of polymerization occurring during thermal degradation of a series of poly(methyl methacrylate) samples , again performed with SEC, it has been possible to point out the different behaviour of the tertiary and primary radicals formed by polymer chain scissions, and consequently an accurate mechanism of the process could be established (5). The most important chromatographic result, however, was related to the finding that in the peaks of some degraded samples tails at low elution volumes are formed, due to higher molecular weight fractions not present in the original samples. Obviously this is a clear indication that coupling between radicals takes place in termination rections; in addition with other evidences of non complete randomness of the process (5), the influence of diffusion phenomena could be demonstrated. A similar finding would never have been possible with techniques giving only average MWs, whereas it was only obtainable with exclusion chromatography where the overall MWD envelope is revealed.

Analysis of low molecular weight compounds

The use of SEC in the analysis of oligomers and small molecules has been previously described (6) and some applications to degradation problems discussed. Column combinations with very high specific resolution values in the low molecular weight range, up to approximately 1000/2000, are available for these applications. The separation power of one such column system is shown in Fig. 6 where a mixture of n-alkanes ranging from methane to dotriacontane has been resolved into the individual components. Molecular characterizations on similar chromatographic columns have been reported for many low molecular weight resins like polyesters, phenolics, ureics, epoxies, and others. The problem of calibration may be overcome if the polymer structure is exactly known, e.g. from the polymer synthesis, or if identification of the individual peaks present in the chromatogram can be done in some way, so that the results are extrapolated in all the MW range of interest.

Separation power in the region of molecular weights between ca. 100 and a few thousands is also useful for analysis of the molecules formed during degradation of polymers. Unfortunately, in such cases, it is practically impossible to establish a proper calibration function due to the heterogeneity of chemical structures present in these samples: more than one calibration curve should be considered and, furthermore, as compounds differing in structure and molecular weights may have the same hydrodynamic

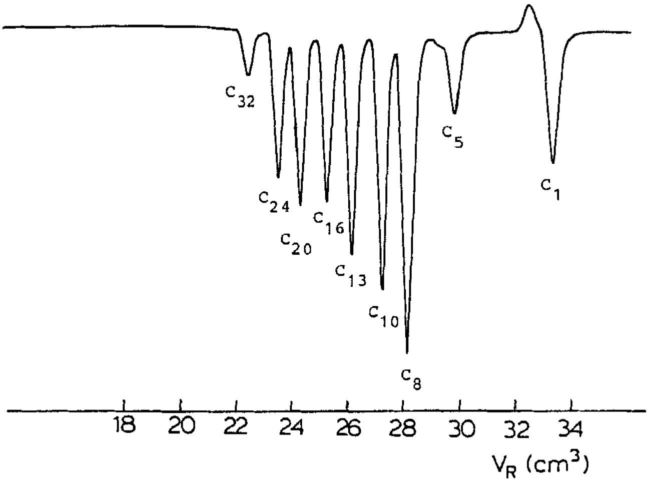


FIGURE 6. SEC separation of n-alkanes, from methane to dotriacontane, in toluene with 3 UltraStyragel columns, 10^3 + 500 + 100. Detector:DRI. Flow rate: 1 cm^3/min.

volume in the solution to be analyzed, they will have same retention volumes in the chromatograms so that complete separation of the mixtures cannot be achieved. Even so, however, SEC gives important informations on the degradation modes of the polymers. An example is given by the analysis of the oligomers formed by thermal treatment of styrene-acrylonitrile copolymers having different initial compositions. In Fig. 7 the chromatograms obtained from these degradation products are shown; all the fractions present in the chromatograms contain acrylonitrile units and it is clearly seen from the figure that by increasing the acrylonitrile content in the copolymer the relative amount of the fractions with higher molecular weights, giving the unresolved broad peak at the lowest retention volumes, increases in comparison with the peaks of the dimers and trimers. This finding, together with other experimental correlations, suggests that the depolymerization reactions are, in the copolymers, the more inhibited, the more acrylonitrile units are present along the chains (7).

When complete resolution of components in mixtures of oligomers or of chain fragments formed during degradation processes is

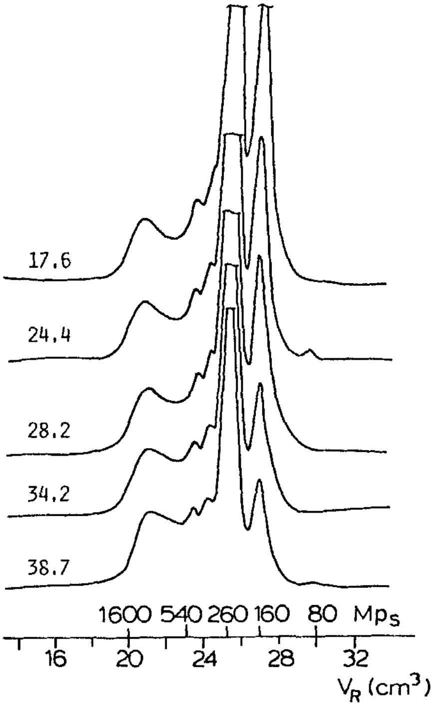


FIGURE 7. SEC chromatograms of oligomeric and chain fragment fractions from thermal degradation of different stirene-acrylonitrile copolymers. Initial copolymer acrylonitrile content (weight %) is given on each chromatogram. Molecular weights relative to polystyrene calibration are indicated on the retention volume axis. Solvent: THF. Detector: DRI. Flow rate: 1 cm^3/min.

desired, adsorption and partition chromatography are also useful. The possibility of obtaining separations of such mixtures on the commercially available HPLC columns is of course greatly influenced by the eluent choice, where in addition to the classical concepts of eluent strength the variation of solubility with the molecular weight of compounds within homologous series has also to be taken into account. A low MW polystyrene standard containing oligomers with degrees of polymerization ranging from 2 to 10 can be fractionated on the same C18-silica column with different

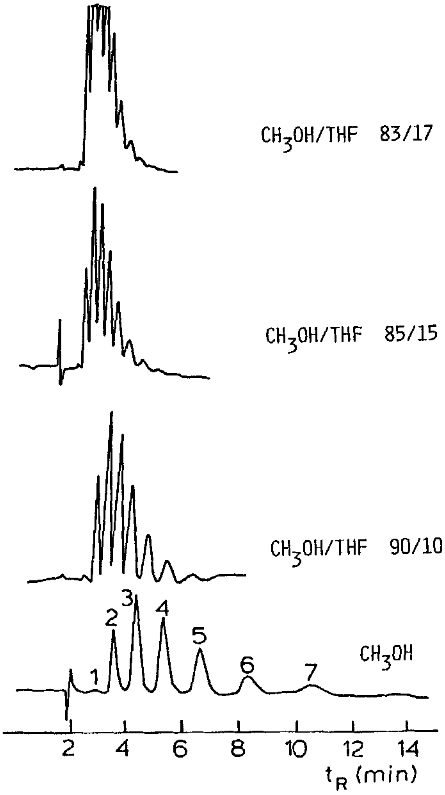


FIGURE 8. Fractionation of low molecular weight polystyrene standard, M_w = 526, on two Separon Six C18 50 A glass cartridges with different eluents. Flow rate: 1 cm^3/min. Numbers on the peaks indicate polymerization degrees.

resolutions depending on the eluents, as it can be seen in Fig. 8, where the results relative to elutions in CH_3OH/THF mixtures and in CH_3OH are compared. The search for optimum conditions in the cases here discussed is always done with isocratic elutions because for applications to polymers and related compounds the differential refractometer is generally used as a detector and therefore elutions with solvent gradients are not feasible. As a consequence of this restriction the results are also limited by the peak

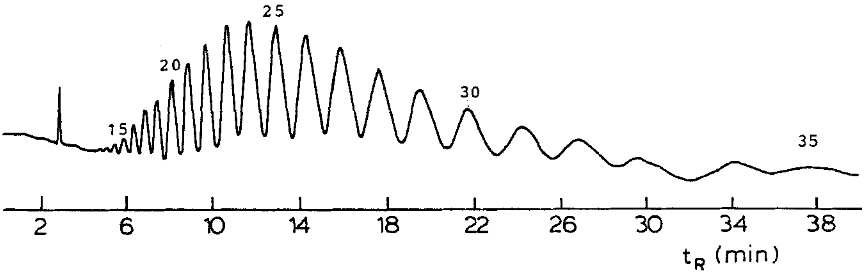


FIGURE 9. Fractionation of polystyrene standard, M_w □ 2800, on a Lichrosorb SI 60-5 µm column. Eluent: n-heptane/THF, 85/15. Flow rate: 1 cm^3/min. Numbers on the peaks indicate polymerization degrees.

broadening which increases with elution time. In Fig. 8 the chromatogram obtained in CH_3OH, where resolution is the highest, shows only 6 peaks, whereas at least 9 may be counted from the elution in the mixture CH_3OH/THF, 83/17 v/v, where separation is fairly poor. Similar results were also obtained in mixtures CH_3CN/THF and H_2O/THF (8). The number of oligomers which can be resolved with HPLC is, when working in the best conditions, very much higher than that one possible with SEC, where for degrees of polymerization higher than ca. 10 individual peaks are generally no more obtained (6). For example, with polystyrene oligomers of the same type described above, but having degrees of polymerizations up to more than 30 very good separations can be obtained on silica gel columns and eluent mixtures n-heptane/THF. A typical chromatogram referring to a polymer sample with M_w = 2800 and dispersity index M_w/M_n □ 1.05 is reported in Fig. 9: more than 20 peaks are visible, covering polymerization degrees between 13 and 35.

Another point relevant for the present discussion is that, with HPLC columns, separations on the basis of structural and isomeric differences can be easily performed, and as it has already been mentioned this is important for the investigation of the great number of compounds originated in the degradation of polymers.

CONCLUSIONS

In the application of column liquid chromatography to the investigation of polymer degradation reactions both SEC and HPLC are essential techniques: the former shows the range of molecular weights over which the sample spans and how the polymer MWDs change during degradations, whereas from the latter a representation of the structural complexity of the mixtures of newly formed molecules may be obtained. A combination of the two techniques in series, similar to that proposed by other authors (9, 10) would certainly be helpful in simplifying the analyses. The most difficult problems still arise from the identification of the revealed substances; detectors giving structural informations are therefore of paramount importance to gain a deeper insight on the results of the separations. To this end the most interesting systems to be coupled with the liquid chromatographic equipment are, for the problems involved in this field, the UV diode array spectrophotometer and the mass spectrometer.

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