Basic Gel-Permeation Chromatography Studies.   I. Polymer Degradation

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Synopsis

Polymer degradation has been studied by using gel-permeation chromatography (GPC) to measure the product distribution.   The method is rapid and has a good accuracy that permits one to see most of the degradation products, as they elute at a point different from the starting material.   In the cases studied, polystyrene cleavage has the result of random cleavage, as judged by the product distribution.   A GPC curve to be expected from random cleavage has been put together to aid in the evaluation. Both wide and narrow molecular weight distribution polystyrenes have been studied after degradation.   The narrow distribution products were degraded by peroxides, irradiation, and weathering.   With the latter, the combination of simple fragments to form the starting portions of crosslinking were measured in small amounts.   In none of the cases studied did degradation in solution produce crosslinked products.   Kinetic rate studies were made that concerned the action of peroxides and inhibitors.

INTRODUCTION

Gel-permeation chromatography (GPC) has become a very valuable tool for the study of polymer molecular weight distributions since its introduction.[1]   Recent studies have concerned the nature of the separation,[2,3] its efficiency,[4,5] and the applicability of the method.[6]   In basic terms, the separation is due to the depth to which molecular species penetrate into the column packing, a crosslinked polystyrene gel.   The large molecules penetrate the least, and they are eluted first.   The method gives quite good separation of species in the 100,000 molecular weight region from species in the 150,000–200,000 molecular weight range; hence it should be a very valuable tool in studying relatively small changes in molecular weight due to degradation, polymer coupling and related processes.

There are many reasons for studying polymer degradation.   The importance of commercial degradation of polymers is obvious, but several other considerations motivated the current study, in which a vital role was placed by gel-permeation chromatography (GPC).   Firstly, a new test needed, one that would more accurately reflect the molecular weight distribution (MWD), one that was quicker and applicable to a wide range of products and test conditions.   Also, one can postulate a degradation mechanism and an inhibition mechanism; then, one is in a better position to predict the amount of degradation and to inhibit it.   Indeed, studies

of the kinetics and mechanism of inhibition at moderate temperatures are rare, if available. Of major importance, one can establish a basic technique to aid others in their studies. This can include the choice of solvent, degradation agent, and GPC conditions that appear to be optimum for such studies.

The current work also leads to a better evaluation of GPC results. Early work in the GPC analysis of polyethylene showed that inhibitors were needed in the elution solvent to prevent product degradation.[7] One should inquire about the degradation of the polystyrene samples used for calibration. Do they similarly degrade, and how can one differentiate curve broadening due to polymer diffusion versus degradation?

Most prior work on polymer degradation has been based on changes in product viscosity and/or ultracentrifuge molecular weight results.[8] The former lack specificity and accuracy, and the latter consume considerable time. There is another proposed method, oxyluminescence;[9] it is used at above 150°C., which limits its use and specificity.

EXPERIMENTAL

Weathering

Polymer samples were commercial products and were used in the weathering tests as 1-mm. sheets, about $^3/_4$ in. by 6 in. long. These were weathered in an accelerated aging setup with the use of an AH-6 mercury lamp, 10 cm. from the source. Three samples of each plastic were run; these included a control, a 500-hr. and a 2000-hr. degraded sample. A control and a 1500-hr. sample were also prepared in runs, 1 mm. $\times$ $^3/_8$ in. $\times$ 4 in. molded S-108 and S-103 polystyrene sheets being used.

Polymer Identification

Polystyrenes of the S series were prepared by anionically catalyzed polymerization. The S-108 had a weight-average molecular weight of 267,000 and a $\bar{M}_w/\bar{M}_n$ of 1.08; the S-103 had a weight-average molecular weight of 125,000 and a $\bar{M}_w/\bar{M}_n$ of 1.05; the S-105 had a weight-average molecular weight of 154,000 and a $\bar{M}_w/\bar{M}_n$ of 1.04.

Sample Preparation and Analysis

About 0.25 g. of polymer and 49.75 ml. of tetrahydrofuran (THF) from the solvent reservoir were placed in a 2-oz. bottle having a polyethylene-lined cap and shaken vigorously for 1 hr. to dissolve the samples. A Waters Associates GPC machine was used for the current work, $^1/_2$ ml. injections every 2 hr. being used. The elution solvent was THF flowing at 1 ml./min. through four column sections in series, each 4 ft. long. The calibration standards and their elution times are listed in Table I for the 10^4 A. permeation limit columns of the current work. With the weathered samples, duplicate runs were made to confirm the results, and the run with the most stable baseline was used. The original molecular weight distributions are shown as the shaded portion of Figures 1a and 1b.
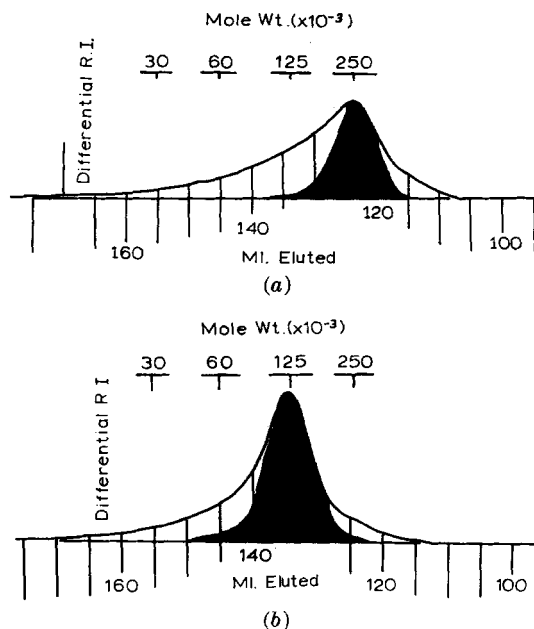
Fig. 1. GPC curves of (a) weathered polystyrene S-108 and (b) weathered polystyrene S-103.   Samples treated (0.5 ml. of 0.5% sample in THF) × 2; column H, 10⁴ A., 16,000 plates.

TABLE I
Calibration of Column H, 10⁴ A.

Calibration standard	Molecular weight	Length, A.	Elution (10 A. column)[a]			
			Peak, ml.	Leading edge[b]	Bench mark[c]	Base, ml.
S-108	262,000	6,200	123.2	117.5	121.0	13.04
S-109	197,000	4,650	130.4	—	—	—
S-105	154,000	3,650	130.4	124.5	129.0	12.62
S-103	125,000	2,950	133.8	127.8	132.0	12.66
S-102	82,000	1,920	141.2	—	—	—
PS-20	19,750	460	159.3	—	—	13.66
P-4000	4,000	258	167.3	—	—	—
P-2000	2,000	133	169.6	—	—	9.64
P-400	400	33	184.7	—	—	—
Acetonitrile			201.9	—	—	6.27

[a] Just permeable to ¹/₂ million molecular weight polystyrene (see Figure 7).
[b] Intercept of line drawn tangent to leading edge of curve, used as a calibration point.
[c] A calibration point for measuring peak heights.

Yield Calculations

Basically, the per cent unreacted polymer was calculated from the ratio of the peak height of the total reacted sample at a specified elution volume divided by the height which the starting sample would have given at the same calibration point.   This ratio was corrected by the area of the

reacted product divided by the area of the original sample, since an exactly constant amount of sample did not reach the columns each time. Further, the position of the curves shifted by a few tenths of a milliliter between runs; hence, the calibration points shifted. The curve shift was measured as a shift in the zero intercept of the leading edge of the GPC curve, and the calibration point was adjusted by this difference. A further very small change in the calibration point was caused by the "highs" degrading faster than the balance of the sample. Hence, the position of the calibration point was adjusted also by 1.0 ml. times the conversion. This latter correction made a difference at times of 1–4% in the computed yields, and a correction of this type would change with the slope of the calibration curve and the width of the molecular weight distribution.

Irradiation Degradation

Samples of S-103 and S-105 were dissolved (0.5%) in the desired solvent in 12-ml. vials having polyethylene liners in the caps. Next, they were deaerated by bubbling nitrogen through them for 2 min. at a vigorous rate. They were then quickly sealed and irradiated for the indicated dosage. This typically took 17–78 hr. The samples were analyzed and evaluated as discussed above.

Peroxide Degradation

Samples of S-105 and S-103 polystyrene were dissolved (0.5%) in o-dichlorobenzene that had been purged with nitrogen and then shaken with it. A sample of 0.1% peroxide in the 0.5% solution was prepared, and the desired peroxide concentrations were prepared by blending solutions under nitrogen by use of hypodermic syringes. The containers were 2-dram vials with Teflon liners. After the blending, the vials were purged for 3 min. with nitrogen and quickly capped with nitrogen flowing at the mouth of the vial. The vials were aged for 4 hr. at 145°C. in a thermostated oven and then cooled, and from them samples were taken for analysis by the above technique.

DISCUSSION

Gel-permeation chromatography (GPC) has been used to measure polymer degradation in a group of polymer samples, and it was a preferred technique for such a study. The method had accuracy, speed, a range of applicability, and a degree of confidence not present in other methods. The technique measured the amount of degradation and crosslinking separately and without ambiguity, and it did not require excessive temperatures or mathematical interpretations of M_w/M_n data.

Initial runs were made with an accelerated Weather-Ometer, using commercial polystyrene (Styron 666) and poly(methyl methacrylate) (Lucite), and runs after 0, 500, and 1000 hr. were compared. The object was a better understanding of the degradation process with the ultimate aim of

an improved plastic of the type being studied.   The current study has led to some improved techniques for studying degradation and to a better understanding of the process.

A broad molecular weight polystyrene (Styron 666) was degraded for 500 and 2000 hr. of accelerated weathering. The 2000-hr. Styron produced molecular weight distribution (MWD) broadening, since some THF-soluble, coupling products were formed in the 2000-hr. run.   The exact amount of "highs" was almost impossible to estimate by GPC,[10] due to the possibility of medium molecular weight original polymer being coupled to form a higher molecular weight product that would indeed replace some of the higher mole weight polymer that degraded.   One may con-clude that a narrower MWD polymer would be preferred, to obtain a clearer picture of what happens during degradation; and this became another part of the current study.

In contrast to Styron, Lucite formed no detected amount of higher molecular weight products.   Cleavage did occur with it, but no monomeric fragments were detected, in contrast to degradation at elevated tempera-ture, where an unzipping is the prevalent reaction.[11]   A comparison of the 500-hr. and the 2000-hr. runs with Lucite indicate that much more degradation occurred during the first period than might be predicted by a kinetic comparison of the two runs.   This may reflect some weak links in the product.

Narrow MWD polystyrene were degraded, and a mechanism for the reaction proposed.   Unfortunately, one cannot intuitively predict with ease the GPC curve that would be observed with degraded polystyrene, since several people knowledgeable in the field have predicted greatly different results.   The literature indicates that random cleavage would be the expected manner of scission, and that degradation of a gaussian MWD polymer would produce a gaussian MWD polymer.   The author has not been able to find reports of either the use of GPC to study polymer degradation or the prediction of the product distribution curve with a nar-row molecular weight polymer by a random cleavage mechanism.   Draw-ing such a curve will now be explored.

Figure 2 characterizes the degradation products from various view-points.   Consider the degradation of polystyrene of 105,000 molecular weight, which equals a degree of polymerization (DP) of 1001.   If one observes the random cleavage results with 1000 molecules, then 2 molecules of each DP from 1 to 1000 would be made.   The weight distribution of these products would vary linearly from 2 at DP = 1 to 2000 at DP = 1000, as shown in Figure 2b.   However, the GPC results are seen as a function of log molecular weight.   The data of Figure 2b are replotted on a logarithmic basis; this is the uncrosshatched line in Figure 2c; the data are shown in numerical sequence (serially, hence not linearly with regard to the baseline) and indicate that one would expect to see only 10% as much by weight of polymer with 10% of the peak molecular weight compared to the latter, as a result of random cleavage.   In terms of the
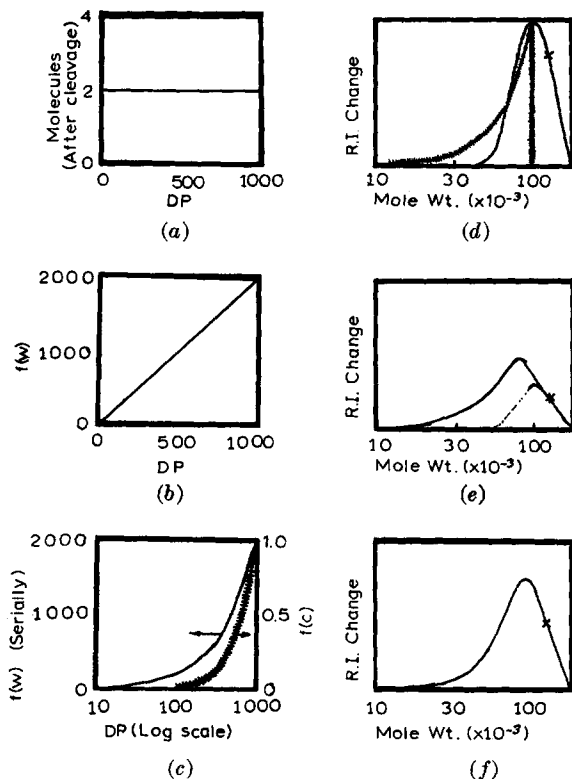
Fig. 2. Random cleavage degradation, 1000 molecules of 1001 DP (= 105,000 molecular weight polystyrene).

weight per cut, as is actually seen in the GPC cell (average weight × number present), about 1% of the maximum peak height will be observed at the point where polymer has 10% of the peak molecular weight. This concept is mathematically drawn to scale in Figures 2c and 2d as the cross-hatched lines.

The cross-hatched line in Figure 2d represents the theoretical GPC curve for a monomolecular weight polymer of 100,000 mole weight that was degraded by a single cleavage of each molecule. This is a little far from the situation observed, but it offers a point for adapting the theory to evaluate the observed curves. The accompanying curve of the same figure represents a typical curve of the starting materials, the anionically polymerized polystyrenes used in the current studies. Using both curves as models, one can derive the curve given in Figure 2e as the GPC curve expected from the simple cleavage products of a narrow MWD polymer, when subjected to the diffusion and related factors in the GPC process. Figure 2f shows an anticipated GPC curve for 50% degradation products and 50% unreacted sample. The observed curves look very much like this, as shown in Figure 1a.
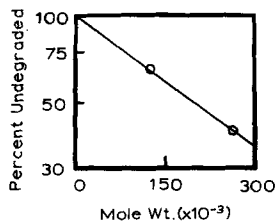
Fig. 3. Comparison of reactivities of polystyrenes during 1500 hr. accelerated aging.

The present techniques do not at present allow a 100% separation of the degradation products away from the starting material. Only 60–80% of these products do not elute in the range of the starting materials. However, a constant correction factor applies, although none has been used in the current work.

Weathering of S-108 and S-103 polystyrene samples were carried out at Midland in an accelerated Weather-Ometer for 1500 hr. These two species were chosen, based on availability and molecular weight. Since their molecular weights differed from each other by about a twofold change, each became a calibration standard for the other, and gross effect due to changing molecular weight could be observed by comparing the products formed from the two samples. With the S-108 sample, 40% of the weathered sample was within the MWD shape and range of the original polymer; and the rest consisted of 49% having a MWD lower than the original (the "lows") and 11% with a MWD range higher than the original sample (the "highs"). With the S-103 sample, 64% of the weathered sample was within the MWD shape and range of the untreated sample; also present were 8% highs and 28% lows. This data were further plotted in Figure 3 to show that it is a rate process; the S-108 had twice as much molecular weight and degradation as did the S-103. The observed curve shape (lows plus reactant) also agreed well with the theoretical model.

S-105 polystyrene was also studied by using irradiation-induced degradation in solution. A part of the object was to observe the molar ratios of the degradation products. In summary, coupling products were made with chloroform plus benzene solvent, and otherwise the curves showed the expected distribution.

The solvent effect paralleled its chain transfer constant[12] as the data in Table II show; but a few exceptions merit further examination. Methyl chloroform showed an unexpectedly high stability, and o-dichlorobenzene was quite unexpectedly low. Irradiation damage of the polymers in the ether-type solvents was significantly low; perhaps the ethers function as an inhibitor in this case. The method also showed major differences in effectiveness between the two inhibitors in chloroform and suggests that this could be a useful device for screening inhibitors.

Figure 4 shows reaction rate data from the degradation of polystyrene S-105 in dichlorobenzene solution. Here, the rate of degradation was a

TABLE II
Degradation of S-105 Polystyrene by γ-Irradiation
(0.5% in the Indicated Solvent)

Dose = 6 Mrad		Dose = 12 Mrad	
Solvent	Per cent un-reacted	Solvent	Per cent un-reacted
Tetraethylene glycol diethyl ether	97	Aniline	97
β,β'-Dichloroethyl ether	93	Benzene + 0.5% Ionol	96
Tetralin	90	Benzene + 1% MMA	91
Dioxane	87	Tetrahydrofuran	85
Ethyl butyrate	86	Cyclohexanone	85
Methyl chloroform	80	Tetraethylene glycol diethyl ether	84
Benzene	80	$CHCl_2$ + 0.5% β-phenylnaph-thylamine	78
Benzene	75	$CHCl_3$ + 0.5% Ionol	60
2-Butanone	72	Benzene	61
8% benzene in $CHCl_3$	61	Perchloroethylene	24
Perchloroethylene	27	o-Dichlorobenzene	9?
Chloroform	21		
sym-Tetrachloroethane	<5		

function of solvent purity. Since it is difficult to determine whether the rates are different due to peroxides in one or because of inhibitors in one of the solvents. However, the situation warrants further study. Here also the degradation curves corresponded to the theoretical model, given in Figure 2f.

The rate curves gave good agreement with the concept that the amount of cleavage was proportional to the per cent peroxide added, and hence the per cent degraded followed a rate expression where per cent peroxide times a constant equals $\log (1 - x)$, where x was the fraction degraded and the constant a function of the molecular weight of the polymer.
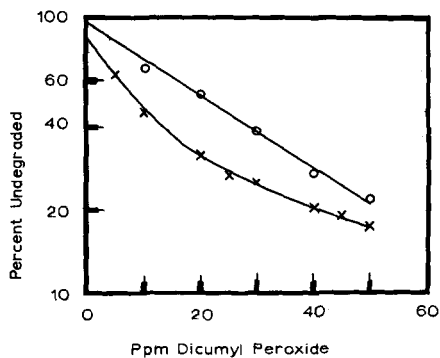

Fig. 4. Degradation of polystyrene S-105 (0.5% in o-dichlorobenzene at 145° C.).

The degradation mechanism was also studied for the weathered narrow MWD polystyrene S-103. The results in Figure 1b show that the "highs" fraction contained only a minor portion with a molecular weight exactly twice that of the initial reaction sample; hence, peroxides or macromolecular dimers formed by coupling two chains were not major constituents of the sample. Indeed, the amount of material increased as the molecular weight decreased from the point corresponding to the dimer. Hence the products represented the incorporation of at least one fragment into the majority of the molecules in the "highs" fraction. The results also indicate that the process is complex and that there may be a selectivity in the cleavage of large peroxide molecules, which favors the formation of two more nearly equal masses.

A major observation in the current work concerned the polycondensation products. In the run with the weathered S-103, a fraction was observed having a molecular weight above 300,000 and it was present in the amount slightly less than 2%. This fraction could only be formed by the combination of residues of more than two polystyrene molecules, and hence the start of the crosslinking process has been seen and measured accurately, at this time. Similarly, a small amount of coupling products (about 2%) were detected in one of the solution degradation runs, by comparing the results of Figures 5a and 5b. However, no crosslinked products were detected at the interstitial volume in either case.
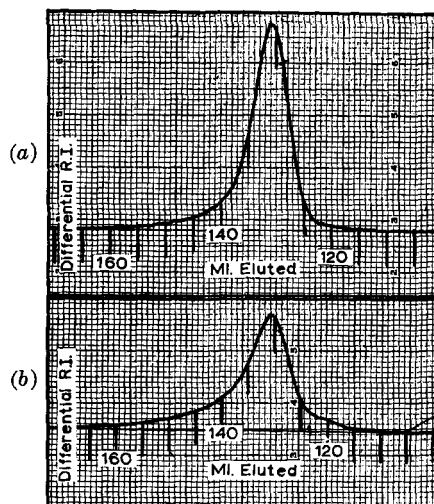

Fig. 5. Degradation of polystyrene of 154,000 molecular weight on irradiation in solution with 6 Mrad dosage: (a) in benzene; (b) in benzene + 8 wt.-% CHCl$_3$.

The current results were based on the proper choice of both polymer studied and the columns used. The plate count should be above 1000 plates per foot and should be an integral part of the description of the experimental technique. The columns chosen for this work had a 10^4 A.
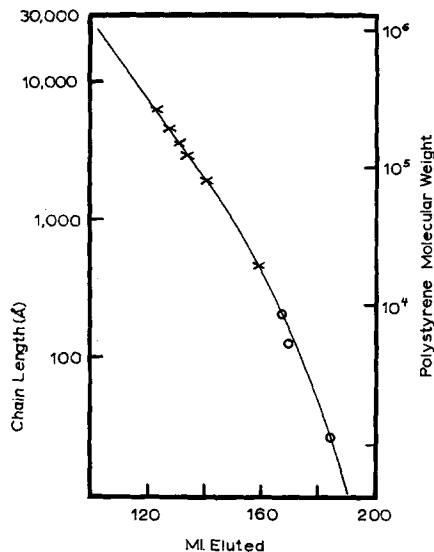
Fig. 6. Calibration curve.   Column H, 10⁴ A., 16,000 plates, 16 ft. long.

permeation limit; this offered several advantages.   Obviously, the samples and their products did not elute at the interstitial volume, but rather near to it.   This results in a minimum amount of peak broadening due to diffusion, yet a portion of the curve was used that had a near-linearity of elution versus log molecular weight.   Since the products were bunched up in the small molecular region, a larger separation factor was obtained in the desired range (see Fig. 6).   The molecular weight distribution of the polymer used in the current method is also a critical factor, since it should be as narrow as possible.   In the current work, the S-103 eluted entirely over a twofold change in molecular weight.   Recent commercially available polystyrene samples (such as one having 97,000 molecular weight), whose MWD spans only about half of the range of the polymers used in the current study.   By choosing the newer products and running the GPC at, for example, 0.5 ml./min., the separation of the products from the reactants has currently been considerably improved.   One thereby also obtains a more uniform polymer degradation rate and a more accurate analysis.

CONCLUSIONS

Gel-permeation chromatography is a superior technique with which to follow polymer degradation.   It allows one to observe unzipping, polymer cleavage, polymer coupling, polymer dimerization, and polycondensation products all at one time if the reactants have a sufficiently narrow molecular weight distribution.   It allows rate studies to be made so that mechanism studies can be made.

The initial steps of the crosslinking of polymers were measured, perhaps for the first time, when fragments were detected that were formed by the combination of several polystyrene molecules or fragments thereof, and each step in the process can be observed and to a degree measured.

The narrow molecular weight polystyrenes were obtained from H. W. McCormick and the samples were degraded in the accelerated ultraviolet weathering apparatus by C. L. Stacy, both of The Dow Chemical Company, Midland, Michigan.

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Résumé

La dégradation de polymères a été étudiée en utilisant la chromatographie par perméation sur gel en vue de mesurer la distribution du produit. La méthode est rapide et a une bonne précision, permettant de suivre la plupart des produits de dégradation à mesure qu'ils sont dilués à des points différents au départ du matériau initial. Dans les cas étudiés, la rupture du polystyrène résulte de la rupture statistique ainsi, qu'il résulte dans les distributions de produits. La courbe G.P.C. attendue au départ d'une rupture statistique a été rassemblée à l'aide de cette évaluation. A la fois des polystyrènes à large et étroite distribution de poids moléculaire, ont été étudiés après dégradation. Les produits de distribution étroite ont été dégradés par des peroxydes, par irradiation et par le vieillissement. Avec ce dernier, la combinasion de fragments simples pour former des portions initiales de ponts ont été mesurés en faible quantité. Dans aucun des cas étudiés, la dégradation en solution n'a prduit de matériaux pontés. Des études de vitesses ont été faites en ce qui concerne l'action des peroxydes et des inhibiteurs.

Zusammenfassung

Der Polymerabbau wurde unter Verwendung der Gelpermeationschromatographie zur Messung der Verteilung in den Abbauprodukten untersucht. Die Methode ist rasch und besitzt eine gute Genauigkeit, welche die Auffindung des grössten Teils der Abbauprodukte erlaubt, da sie an einem anderen Punkt als das Ausgangsmaterial

eluiert werden.   In den untersuchten Fällen ist, nach der Produktverteilung zu urteilen, der Polystyrolabbau ein statistischer Spaltungsprozess.   Zur Erleichterung der Auswertung wurde eine für statistische Spaltung zu erwartende GPC-Kurve konstruiert. Polystyrole mit breiter und enger Verteilung wurden nach dem Abbau untersucht. Die eng-verteilten Produkte wurden mit Peroxyden, durch Bestrahlung und durch Bewitterung abgetaut.   Bei letzterer Methode wurde die Kombination einfacher Fragmente zu Ausgangspunkten für die Vernetzung in kleiner Menge festgestellt. In keinem der untersuchten Fälle führte der Abbau in Lösung zu vernetzten Produkten. Bezüglich der Wirkung von Peroxyden und Inhibitoren wurden kinetische Geschwindigkeitsuntersuchungen durchgeführt.