

SIZE EXCLUSION CHROMATOGRAPHY OF SUBSTITUTED ACETYLENE POLYMERS: EFFECT OF AUTOOXIDATIVE DEGRADATION OF THE POLYMER DURING THE ANALYSIS

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The degradation of poly(phenylacetylene), a typical autooxidatively degradable polymer of substituted acetylene, is shown to take place inside the SEC (size exclusion chromatography) columns during the polymer analysis carried out with eluent (THF) not protected from air. Three types of experimental evidence are given based on the comparison of results of SEC analyses carried out: (i) with the eluent kept under air or argon atmosphere; (ii) with different flow rates of the eluent; and (iii) with and without the interruption of the analysis for a few hours. Other degradable polymers of substituted acetylene are mentioned and recommendations for their SEC analyses are given.

Key words: Size exclusion chromatography; Poly(acetylene)s; Polyalkynes; Molecular weight determination; Autoxidative degradation.

The SEC analyses of polymers, including polymers of substituted polyacetylene, are usually carried out without any analyte and eluent protection from air by an inert atmosphere. As the most frequently used SEC eluent, tetrahydrofuran (THF), is oxygen-sensitive, it is usually stabilized with 2,6-di-*tert*-butyl-*p*-cresol (DTBC).

The simple SEC technique is fair by sufficient for the analyses of overwhelming majority of polymers which visibly do not degrade in the SEC analysis time scale (within ca 1 h). However, polymers of monosubstituted acetylene are well known to undergo autoxidative degradation when exposed to air even in mild conditions at room temperature¹⁻⁶. For example poly(phenylacetylene) (PPhA), which is entirely stable in vacuum⁵, degrades without any induction period when exposed to air^{4,5,7}. In either state (solid and dissolved) the autoxidation of high-molecular-weight PPhA (75% *cis*) obeys the kinetic laws of random degradation of polymers⁸⁻¹⁰. The rate constant of PPhA degradation, v , was ascertained⁵ to be $2 \cdot 10^{-8} \text{ min}^{-1}$ in the solid state at room temperature and approximately hundred times higher in solution: $4.2 \cdot 10^{-6} \text{ min}^{-1}$ in freshly distilled chlorobenzene, $2.5 \cdot 10^{-6} \text{ min}^{-1}$ in freshly distilled THF, and $1.6 \cdot 10^{-6} \text{ min}^{-1}$ in both

chlorobenzene and THF stabilized with DTBC (0.2% w/v, concentration ten times higher than the one usually used in THF for SEC).

If the rate constant v is known, the half-time, $t_{1/2}$, of the decay of macromolecule of degree of polymerization, X , can easily be calculated: $t_{1/2} = (\ln 2)/vX$. The half-time values for PPhA fractions of various X and DTBC contents in THF eluent are summarized in Table I. An inspection of the values shows that half-times of high-molecular-weight PPhA fractions fall into a typical time scale of SEC analysis. This means that the majority of high-molecular-weight fractions should vanish during the SEC analysis if the polymer degrades inside the columns as fast as in the solution exposed to air. As a result, the measured molecular weight distribution should be more or less distorted and the determined molecular weight averages should be lower in a comparison with the corresponding characteristics of the injected polymer sample. It is therefore of interest to know: (i) whether (and how fast) an oxygen-sensitive polymer under analysis degrades in the SEC columns; and (ii) to what extent this process can distort the results of the SEC analysis. The aim of the present study is to find answers to these questions.

EXPERIMENTAL

Materials

High-molecular-weight poly(phenylacetylene) (PPhA, ca 75% *cis*) samples were prepared by a polymerization of phenylacetylene (PhA) induced by $\text{WOCl}_4/2 \text{ Ph}_4\text{Sn}$ metathesis catalyst in benzene-1,4-dioxane (1 : 2 v/v) mixed solvent using the vacuum breakseal polymerization technique^{5,7,11}; the isolated polymers were stored in sealed, evacuated glass ampoules. Narrow poly(styrene) (PS) standards (MW 18 100 and 2 050 000) were the products of Polymer Laboratories, Bristol, G.B. (PL). 2,6-Di-*tert*-butyl-*p*-cresol (DTBC) and argon (purity grade 99.99%) were used in some cases for the stabilization (0.02% w/v DTBC) and protection of tetrahydrofuran (THF) as the eluent, respectively.

Size Exclusion Chromatography (SEC)

Two SEC systems were used:

A) A TSP chromatograph (Thermo Separation Products, Florida, U.S.A.) fitted with RI and UV ($\lambda = 254 \text{ nm}$) detectors and series of two PL-gel columns (Mixed-B and Mixed-C) were used in experiments (flow rate $0.7 \text{ cm}^3 \text{ min}^{-1}$; THF stabilized with DTBC, 0.02% w/v; PS standards, each 0.02 mg cm^{-3}) in argon atmosphere or in air with discontinued flow of the eluent.

B) A Waters 150C chromatograph with a built-in RI detector and series of five PL-gel columns with upper exclusion limits 10^6 , 10^5 , 10^4 , 10^3 , and $5 \cdot 10^2$ fitted with an LALLS detector of absolute molecular weight (Chromatix CMX-100, $\lambda = 632.8 \text{ nm}$ lying behind of the absorption edge of PPhA) were used in experiments (unstabilized THF, 25 °C) in which the flow rate was varied (0.5 and 2.5 $\text{cm}^3 \text{ min}^{-1}$).

Procedures: An ampoule with PPhA sample was opened in argon atmosphere and 0.02 mg of PPhA was mixed with 1 ml of the eluent; the stock solution was kept at room temperature in the atmosphere (argon, air) corresponding to the type of analysis. After a chosen time (time of exposition), 10 μl of the solution was injected into the SEC columns filled with the same eluent. Into SEC system B), 100 μl of PPhA solution of concentration 1 mg/ml was injected.

RESULTS AND DISCUSSION

The effect of the eluent protection with argon atmosphere was examined by performing two analyses of the same sample of PPhA in the SEC system A, the first made by using THF saturated with argon as the eluent and the other by using the aerated THF as the eluent. A fresh solution, prepared for every analysis, was injected 20 min after its preparation. The analysis with the THF protected by argon resulted in \overline{M}_w 477 000 ($\overline{M}_w/\overline{M}_n = 1.62$), whereas the analysis with the aerated THF resulted in \overline{M}_w 406 000 ($\overline{M}_w/\overline{M}_n = 1.70$). The difference in the \overline{M}_w values is evident. It could not be affected by the time of PPhA dissolution because PPhA dissolves in THF completely within a few minutes as ascertained using the solutions prepared in vacuum⁵. The procedures with the aerated THF as the eluent were used, according to the method described earlier⁵, in determination of the rate constant of PPhA degradation in the aerated THF stabilized with DTBC (0.02%), $v = 2.0 \pm 0.2 \text{ min}^{-1}$ (room temperature). The above drop in \overline{M}_w value was found to be in an entire agreement with the determined v .

The SEC analyses of the same sample of PPhA at two different flow rates, 2.5 and 0.5 $\text{cm}^3 \text{ min}^{-1}$, were aimed at obtaining evidence concerning the effect of the analysis duration in the PPhA degradation. To avoid complications potentially arising from the evaluation of SEC records by the calibration curve method, the measurements were accomplished in the SEC system B. A sample of PPhA was mixed with unstabilized THF 30 min before the first injection of the solution into the SEC columns. The start of the mixing of PPhA with THF was set up as zero of the degradation time, t , measured till the moment of the SEC peak passing through the LALLS detector. A few consecutive analyses of the stock solution, exposed to air in the meantime, were made at both flow rates using separate stock solutions. The results of the experiments are given in Fig. 1. At a flow rate of 2.5 $\text{cm}^3 \text{ min}^{-1}$, the first measured value of \overline{M}_w is 850 000 ($t = 45 \text{ min}$), whereas that obtained at a flow rate of 0.5 $\text{cm}^3 \text{ min}^{-1}$ is 520 000 ($t = 100 \text{ min}$).

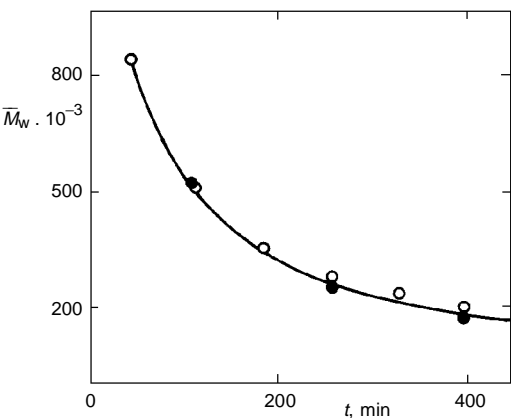


FIG. 1
The dependence of weight-average molecular weight, \overline{M}_w , of PPhA (75% *cis*) on the time of degradation in THF solution, t , for two different flow rates: ○ 2.5 $\text{cm}^3 \text{ min}^{-1}$, ● 0.5 $\text{cm}^3 \text{ min}^{-1}$

The latter value agrees well with the next value measured at a flow rate of $2.5 \text{ cm}^3 \text{ min}^{-1}$, ca 510 000 ($t = 102 \text{ min}$). Also the values for higher t using different flow rates are in an acceptable agreement. The residence time of PPhA in the SEC columns is 14–16 min and 70–76 min at flow rate $2.5 \text{ cm}^3 \text{ min}^{-1}$ and $0.5 \text{ cm}^3 \text{ min}^{-1}$, respectively. The results show that PPhA degrades not only during the exposition of the stock solution to air but also inside the SEC columns, and rates of degradation in both steps of the procedure are comparable. From the observed drop in \overline{M}_w , from 850 000 to 520 000 within 55 min, the value of rate constant v was ascertained to be ca $2.7 \cdot 10^{-6} \text{ min}^{-1}$ (25°C) in a good agreement with the value found earlier⁵ (Table I).

There is no doubt that the decreases in \overline{M}_w , observed in all the above-mentioned experiments, are due to the degradation and not to disentanglement of some aggregates of not completely dissolved PPhA (ref.⁵). Further evidence can be provided by an experiment in which the residence time of PPhA in the SEC columns is prolonged by an interruption of the SEC analysis for some time. Set of experiments, including those with a temporarily stopped flow of eluent, was carried out in the SEC system A using two narrow PS standards as internal calibration marks and THF stabilized with DTBC (0.02%) as the eluent (a fresh solution was prepared for any experiment and, after the exposition of the solution to air for 20 min, 10 μl of the solution was injected into the SEC columns):

First, a blank experiment was carried out with both PS standards (each ca 0.02 mg cm^{-3}) only in which no effect of the eluent flow interruption on the distance between the peaks exceeding common fluctuation in retention time ($\pm 1 \text{ s}$) was observed. Second, an initial reference experiment was carried out in which ca 0.02 mg of PPhA of medium molecular weight ($\overline{M}_w = 305 \text{ 000}$, PS scale) was dissolved in the THF solution of the PS standards and the resulting solution was analysed in a usual way without an interruption. Third, in the main experiment, a fresh solution of PPhA and both PS standards

TABLE I

Calculated halftime, $t_{1/2}$, of the decay of PPhA macromolecule (75% *cis*) in THF solution (various content of DTBC stabilizer is given) as a function of the degree of polymerization, X , and the rate constant v (room temperature)

v 10^{-6} min^{-1}	$t_{1/2}$, min			
	$X = 10 \text{ 000}$	$X = 5 \text{ 000}$	$X = 1 \text{ 000}$	$X = 200$
1.6 (0.2% DTBC) ^a	43.3	86.6	433	2 166
2.0 (0.02% DTBC) ^b	34.6	69.3	347	1 733
2.5 (without DTBC) ^a	27.7	55.5	277	1 386

^a The value taken from ref.⁵. ^b The value determined in this study.

(each compound ca 0.02 mg cm^{-3}) was injected into the SEC columns but the eluent flow was stopped after 2.5 min and all three polymers were allowed to stay inside the column for some time (3 to 16 h); the analysis was then completed using original flow rate ($0.7 \text{ cm}^3 \text{ min}^{-1}$). Finally, the stock solution of PPhA and both PS standards, which was during the main experiment in contact with air, was analysed in a standard way (injection 30 min after completing the main experiment) in order to acquire the final reference for the extent of PPhA degradation.

The results of experiments with 16 h interruption are summarized in Fig. 2. A substantial shift of PPhA peak towards the low-molecular-weight PS standard which clearly demonstrates the degradation of PPhA inside the SEC columns is evident (curve 2). This shift is comparable with the one observed for PPhA exposed during the interruption to air (curve 3). This means that PPhA degrades inside the SEC columns approximately as fast as in the THF solution exposed to air.

The equality of both rates of degradation is somewhat surprising. However, it can be explained taking into account that: (i) the mass of PPhA in a sample injected into the SEC column is very low (ca $0.2 \mu\text{g}$); and (ii) polymer autoxidation takes place, on average, in one or a few monomeric units per chain only. The oxygen concentration in THF eluent can thus hardly be lowered in a sensible manner due to the polymer degradation. As a result, the conditions for PPhA degradation both inside and outside the column can be regarded as practically equal.

As to the distortion of results of SEC analyses due to the polymer degradation inside columns, it can take place in solutions of other oxygen sensitive poly(acetylene)s as well. According to our preliminary results, some polymers of substituted phenylacetylene (e.g. *p*-iodo-, *p*-nitro-) and some copolymers of PhA degrade as fast as or even

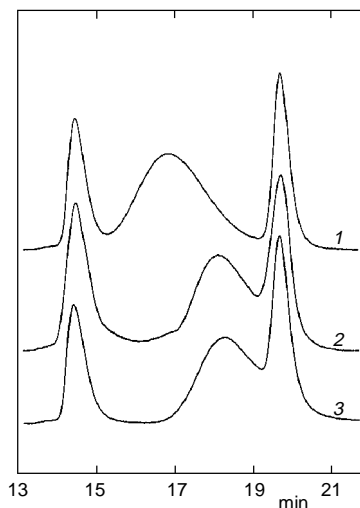


FIG. 2
SEC records of the mixture of two PS standards (MW 18 100 and 2 050 000) and PPhA (MW 305 000): 1 uninterrupted analysis of fresh solution (initial reference experiment); 2 analysis with the eluent flow interrupted for 16 h (the main experiment); 3 uninterrupted analysis of the solution used in the main experiment 2, in the meantime exposed to air for 16.5 h (final reference experiment)

faster than PPhA. The knowledge of the autoxidative stability of the analysed polymer is therefore highly desirable. This information is perhaps most easily available through a series of SEC analyses of a polymer solution exposed to air (cf. refs^{5,7}). High-molecular-weight polymer samples (MW of hundreds of thousands) are the most convenient for this purpose due to low lifetimes of their macromolecules (see Table I). In some cases, extrapolations of molecular weight averages vs time dependencies¹⁰ to zero time can be applied to a partial, additional elimination of the MW values distortion due to the polymer random autoxidative degradation.

Another possibility of revealing and quantifying polymer autoxidative degradation consists in a comparison of the MW values determined with and without protection of the eluent and polymer solution by inert atmosphere (see above). This technique is experimentally more demanding but, on the other hand, it certainly provides more exact and more reliable values of MW of oxygen-sensitive polymers than the simple SEC method.

The theoretical treatment (modelling) of the SEC separation of macromolecules degrading in the random manner inside the columns is the subject of the paper in preparation.

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