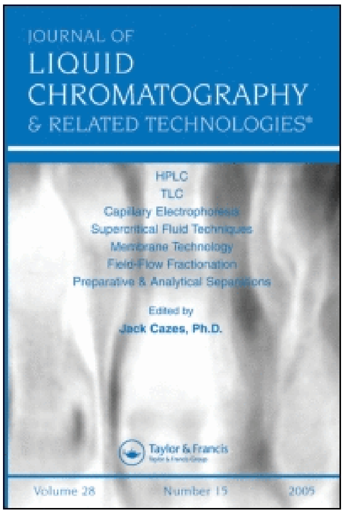

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STUDY OF THE DEGRADATION OF HIGH MOLECULAR WEIGHT POLYSTYRENE IN THE COURSE OF SIZE EXCLUSION CHROMATOGRAPHY (SEC)

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ABSTRACT

The possibility of degradation of large macromolecules in their motion through a porous medium in the course of SEC decreases considerably the range of application of this highly productive and highly selective analytical method for the determination of the MWD of polymers. In fact, the MWD determined by SEC with the existence of degradation is mainly the distribution according to degradation fragments and does not reflect the initial molecular characteristics of the polymer.

The dependence of the degree of degradation of maccromolecules on the main parameters of the chromatographic experiment: the rate of the eluent flow, the size and shape of sorbent particles and the size of their pores was studied in detail. A non-monotonic change in the degree of degradation with increasing flow rate of the eluent was detected.

It is shown that the degree of degradation increases with decreasing particle size and the size of their pores. A new concept of the degradation of high polymers in SEC is formulated. It is related mainly not to the existence of local rate gradients in the interparticle volume but, rather, to the entire combination of hydrodynamic and adsorption effects accompanying the process of interaction between the macromolecules and the surface of sorbent particles. Practical recommendations are given for carrying out SEC, including that of super-high molecular weight samples under "non-degradative" conditions.

INTRODUCTION

The study of degradation of high molecular weight polymers is of considerable interest, mainly because as a result of the scission of macromolecules during SEC, the MWD determined with the aid of this highly productive and promising method is the function of molecular weight distribution of fragments and does not reflect the characteristics of the initial sample. The determination of the degradation mechanism makes it possible to control and, if necessary, to exclude this process in the SEC of polymers because it is undesirable from the standpoint of analytical practice. Several experimental papers (1-3) dealing with the study of degradation in the course of SEC, show that a direct relationship exists between the degree of degradation and the hydrodynamic and thermodynamic characteristics of the chromatographic system. Giddings' review (4) is concerned with the behavior of macromolecules of super-high molecular weights. In this review the main reasons for the perturbation of the molecular-sieve mechanism of SEC have been considered to be hydrodynamic and polarization effects, the draining effect of large pores and, finally, the degradation resulting from "shear" deformations of anomalously large macromolecules. At present it is assumed that the shear degradation of large macromolecules proceeds in the course of their motion in interparticle channels of the granulated sorbent layer through regions with high rate gradients in the cross-section of the channels. Giddings' attempt to evaluate the shear stress in "effective channels" of the sorbent layer of the column by analogy with "pure" hydrodynamic experiments in capillaries, a rotation viscometer and a homogenizer (5-7) has led to an almost thousand-fold discrepancy in the values being compared.

This work deals with the experimental study of degradation mechanism of high molecular weight PS in the SEC process and is also an attempt to establish the physical model or the mechanism of degradation.

EXPERIMENTAL

A special installation was mounted for carrying out chromatographic experiments. It had the following main features: high stability of eluent flow, in particular at low linear rates of $5\cdot10^{-3}$ - $5\cdot10^{-2}$ cm/s and high detector sensitivity (10^{-8} refraction units for a differential refractometer of the raster type). The detector sensitivity made it possible to use low concentrations c ($\sim$ 0.01-0.03%) of the super-high molecular weight polymer in solution in order that the conditions existing in the dilute solution of this polymer, $[\eta]\cdot c < 1$, would be obeyed. Standard stainless steel columns 30 cm in length with an inner diameter of 0.4 cm were used. They were packed with silica sorbents with predetermined characteristics under the conditions ensuring sufficient column efficiency and excluding particle destruction during packing.

Viscometric measurements were carried out with a standard Ubbelohde viscometer.

It should be noted that since the precise values of the eluent flow rate are very important, in each experiment they were additionally checked by relating the retention time (or volume) of the polymer to these values for a low molecular weight standard (orthodichlorobenzene) specially introduced into the sample. It should also be noted that the fact of degradation of super-high molecular weight polymers (PS and PMMA) at high elution rates has also been confirmed by direct experiments (8) in which the intrinsic viscosities of the initial sample and the same sample obtained from the eluate after solvent evaporation were compared.

RESULTS AND DISCUSSION

The elution rate, the mean size and shape of sorbent particles and the mean size of their pores were chosen as the main parameters that affect (or may affect) the degradation value.

In the SEC of super-high molecular weight polymers, the effect of increasing elution rate is mainly manifested in an increasing deviation of the upper part of the calibration curve towards higher retention volumes. The authors of ref.(3) have carried out the chromatography of PS with molecular weights from $2.6x10^6$ to $9.5x10^6$ at a maximum (restrictions were due to the impossibility of using extremely high pressure at the column entrance) flow rate through columns with macroporous glasses (MPG) with the particle size of 30-70 μm and mean pore diameter of 2000 Å and through columns with crosslinked macroporous gels of the TSK PW type. The eluate was collected at the detector outlet and rechromatographed at a relatively low rate (12 cm^3/h at an inner diameter of the column ~ 0.9 cm) at which according to the opinion of the authors (well-grounded in our opinion) degradation should not occur. Degradation actually did not take place on a column with TSK. However, the rate dependence of the deviation in retention volumes was observed in all cases. The authors of ref.(3) have associated the rate dependences without degradation with the deformation of large macromolecules at high flow rate gradients.

Fig.1 shows the calibration dependences obtained in

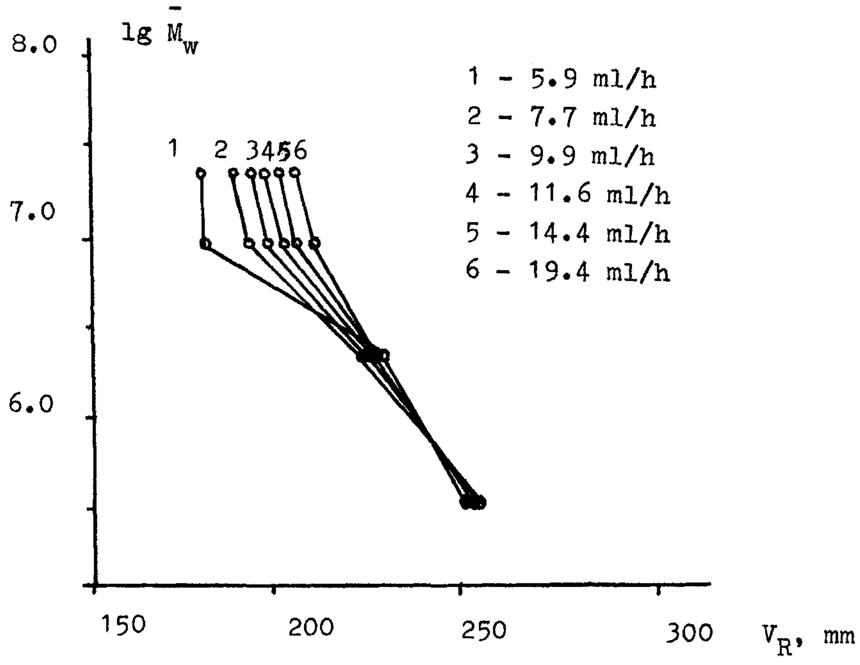


Fig.1 Calibration dependences for narrow-disperse PS in SEC on two columns connected in series and packed with MPG-4000 at different elution rates.

the present work for narrow-disperse PS in SEC on two columns connected in series and packed with MPG with a mean pore diameter of 4000 Å, MPG-4000, at different elution rates. It is clear that with increasing rates the retention volumes of PS with $\bar{M}_w > 2x10^6$ increase.

In order to establish the reasons for the increase in retention volumes with increasing rate, the following experiments were carried out. The solutions of a high molecular weight PS ($\bar{M}_w \sim 10^7$) with a volume of

20 μl were chromatographed at different fixed rates. The corrected rate values were determined from the retention volumes of the above-mentioned internal standard. The eluate was collected, concentrated to the initial concentration and rechromatographed at a rate of 5.9 cm^3/h on a previously calibrated system of columns for which at this rate the absence of degradation (at the accuracy determining average molecular weights of ±5%) was proven. The MWD of the initial PS was obtained for SEC carried out under the same conditions.

Similar experiments were carried out on columns packed with MPG with other pore sizes, MPG-1150 and MPG-250, on columns packed with spherical silica gels with pore sizes of 300 and 4000 Å (Si-300 and Si-4000), on columns packed with non-porous quartz particles and on columns packed with non-porous glass balls. The chromatograms of all eluates were also obtained for repeated chromatography at the above rate of 5.9 cm^3/h on a system of two columns with MPG-4000. The MWD was calculated from calibration dependence 1 in Fig.1. The calculated MWD made it possible to determine the degradation indices $I = (\bar{M}_{no}/\bar{M}_n) - 1$ where $\bar{M}_{no}$ and $\bar{M}_n$ are the number-average molecular weights of the initial sample and the same sample after the second chromatography. Fig.2 shows the results of the corresponding calculations.

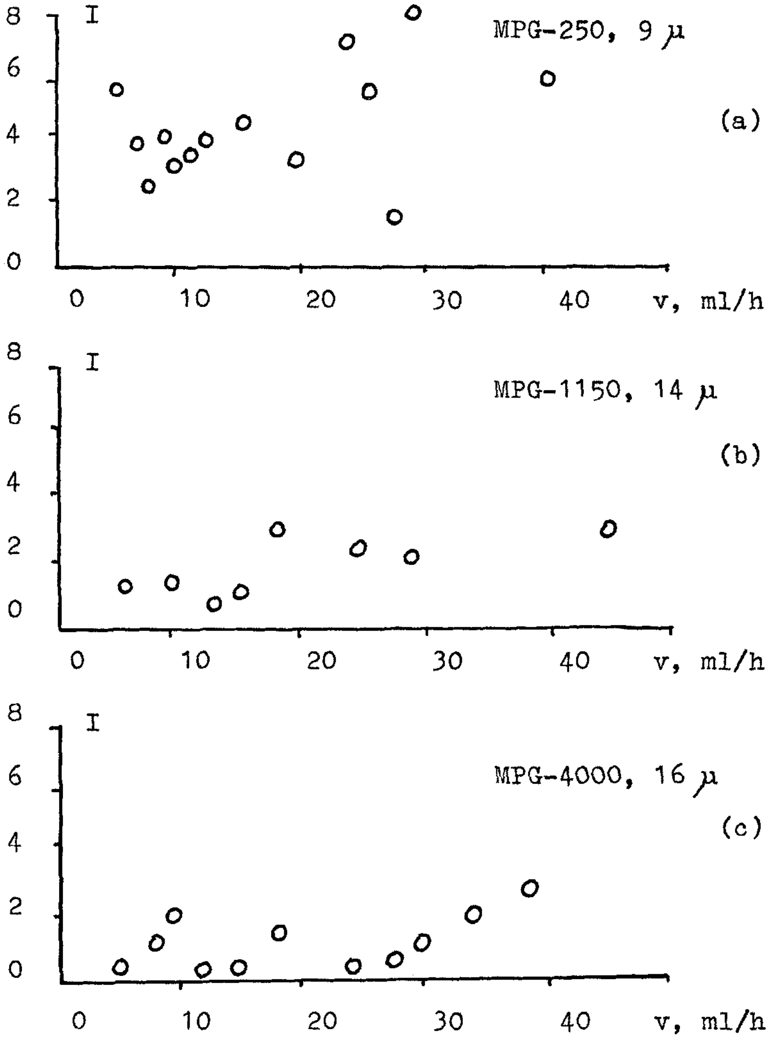


Fig.2 Degradation indices vs flow rate in SEC on MPG with different sizes of pores and particles.

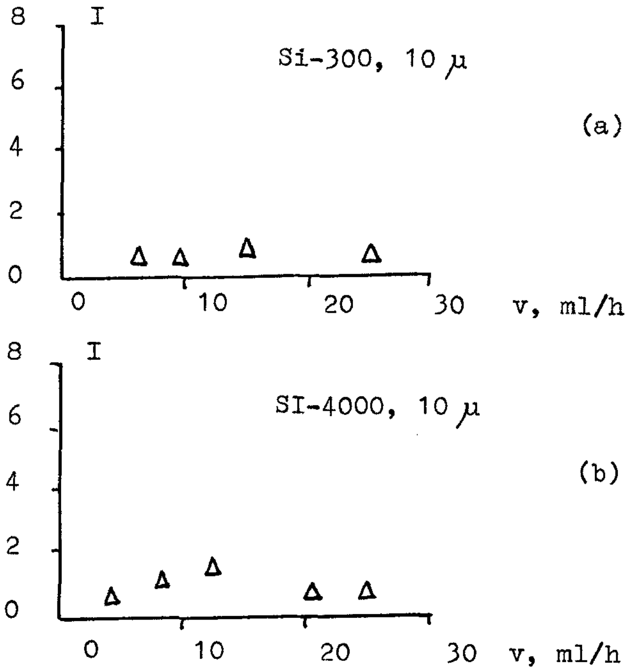


Fig.3 Degradation indices vs flow rate in SEC on silica gels.

These figures show mainly that the rate dependences of degradation index are not monotonic. This fact contradicts the generally accepted view most completely expressed in ref.(4) according to which degradation (i.e. the value of I) should increase with elution rate as a result of shear deformation. However, a great number of experimental data obtained by us suggests that it is not an artefact but a phenomenon requiring an explanation. Similar rate dependences of degradation indices

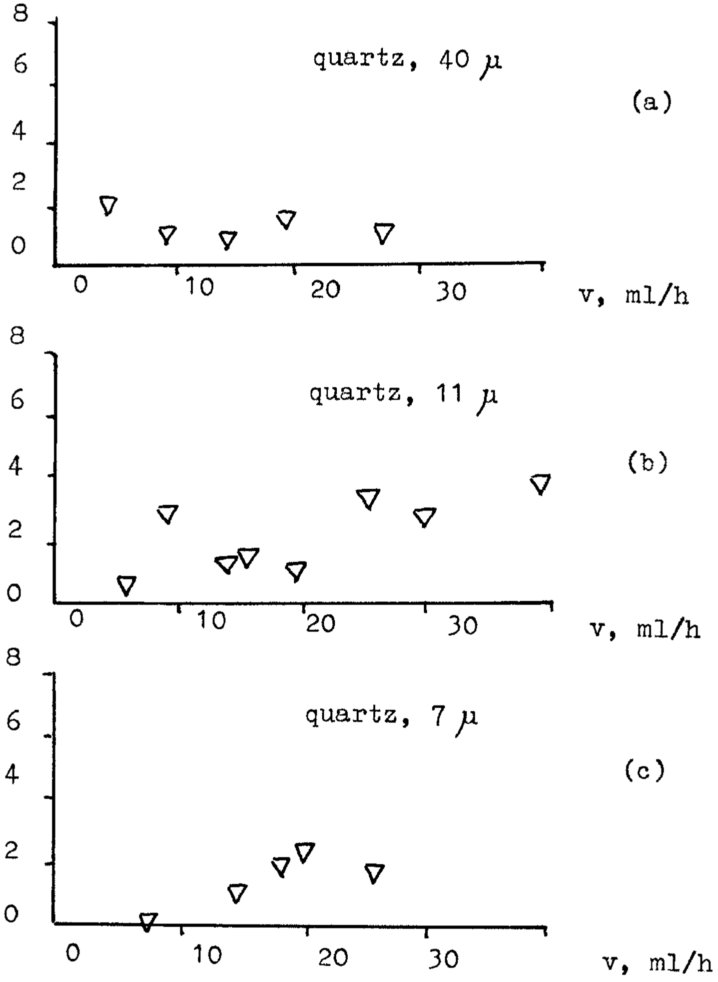


Fig.4 Degradation indices vs flow rate in SEC on non-porous quartz particles.

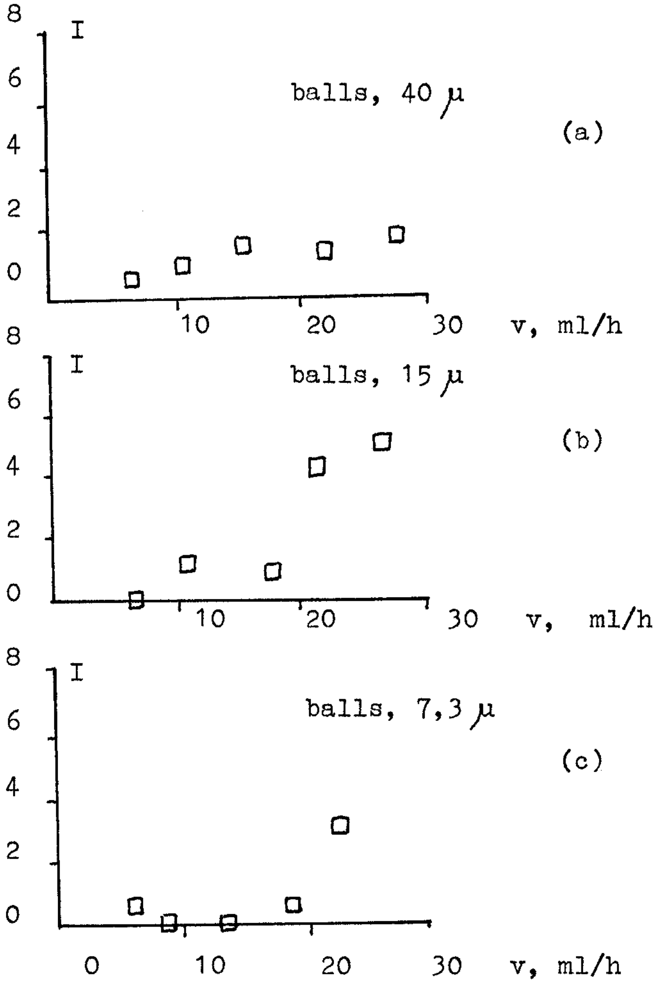


Fig.5 Degradation indices vs flow rate in SEC on non-porous glass balls.

were also obtained for two PMMA samples (with $\bar{M}_w \sim 5x10^6$ and $\bar{M}_w \sim 10^7$) (Fig.6). Although the degradation indices for PMMA are on the average lower than those for PS in SEC under similar conditions, the character of dependences indicates that this is a general phenomenon for polymers with different chemical natures.

Consequently, since with increasing flow rate gradient degradation cannot only increase but also decrease, it might be suggested that it is associated with the interaction between the macromolecules and the surface of the pore volume of sorbent particles. These interactions are naturally related to rate gradient. In fact, the experimental results for SEC on MPG (Fig.2b) show that the highest degradation is observed when MPG-250 is used which has the largest surface area as compared to other MPG.

When an eluent containing macromolecules flows past a sorbent particle, three possible situations may be visualized. First, the macromolecule can enter a stagnant zone near the particle surface, which should lead to an increase in retention time (Fig.7a). Secondly, the macromolecule can pass into a "stretching" hydrodynamic field near the particle surface and undergo degradation (Fig.7b). Third, the macromolecule coming into contact with the particle surface and/or its internal pore volume (e.g. as a result of the reversibility of physical

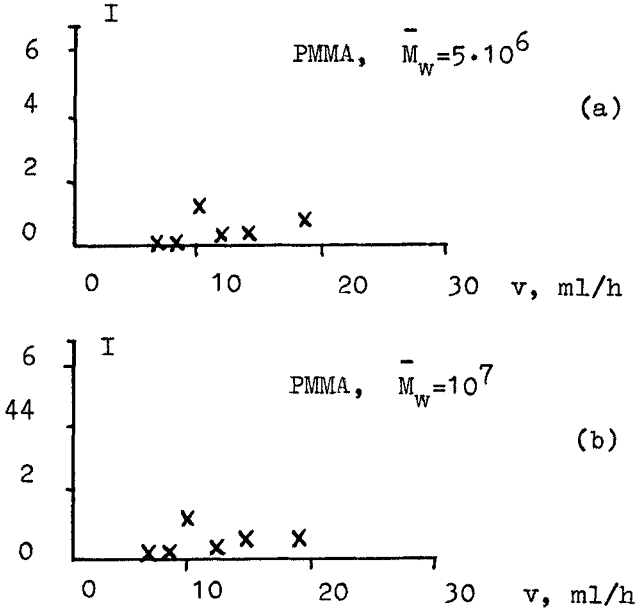
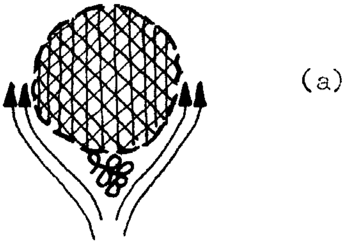


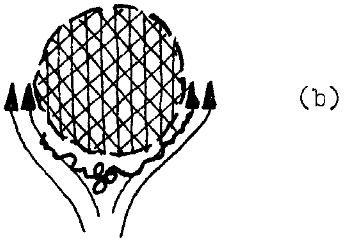
Fig.6 Degradation indices vs flow rate in the SEC of PMMA samples MPG.

adsorption) can be stretched by the flow along the particle surface, which can also lead to degradation.

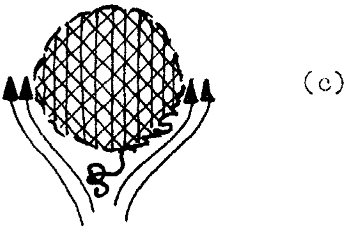
It is clear that all three situations can occur simultaneously but the contribution of each of them depends on the shape and size of the particle, the existence of internal pores and the rate of the flow passing along the particle. Other conditions being equal, i.e. for the same sorbent, it is the rate of the flow moving past the particle that can change the ratio of the con-



arrival in the stagnant zone



stretching along the flow lines



simultaneous motion of the chain along the surface and interaction with it

Fig.7 Possible situations of the behavior of the macromolecule near the surface of sorbent particles.

tributions of the three above situations and hence may lead to a dependence of degradation indices on the flow rate, which seems surprising at first.

The "hindrance effect" is most pronounced for SEC on non-porous balls with $d_p = 7.3\ \mu m$ (Fig.8a). Fig.8a shows overlapping chromatograms of a mixture of PS with orthodichlorobenzene obtained at different flow rates on a column packed with non-porous glass balls with $d_p = 7.3\ \mu m$. Since the sorbent is non-porous, the retention volume should be slightly lower for the polymer than for a low molecular weight substance or at least identical for them. However, the reverse situation is observed (Fig.8a). Some literature data indirectly confirm the hindrance effect in chromatography. Thus, it has been found in ref.(10) that retention volumes of a low molecular weight substance and PS with different molecular weights increase with elution rate. In ref.(11) the hindrance effect has been detected in the investigation of the mobility of DNA fragments in electrophoresis in gel.

The hindrance effect is much weaker on particles with an average size of $40\ \mu m$ (Fig.8b).

These results are quite comprehensible from the standpoint of the effect of stretching of the macromolecule along the particle surface, in particular at the possible physical adsorption of individual segments of

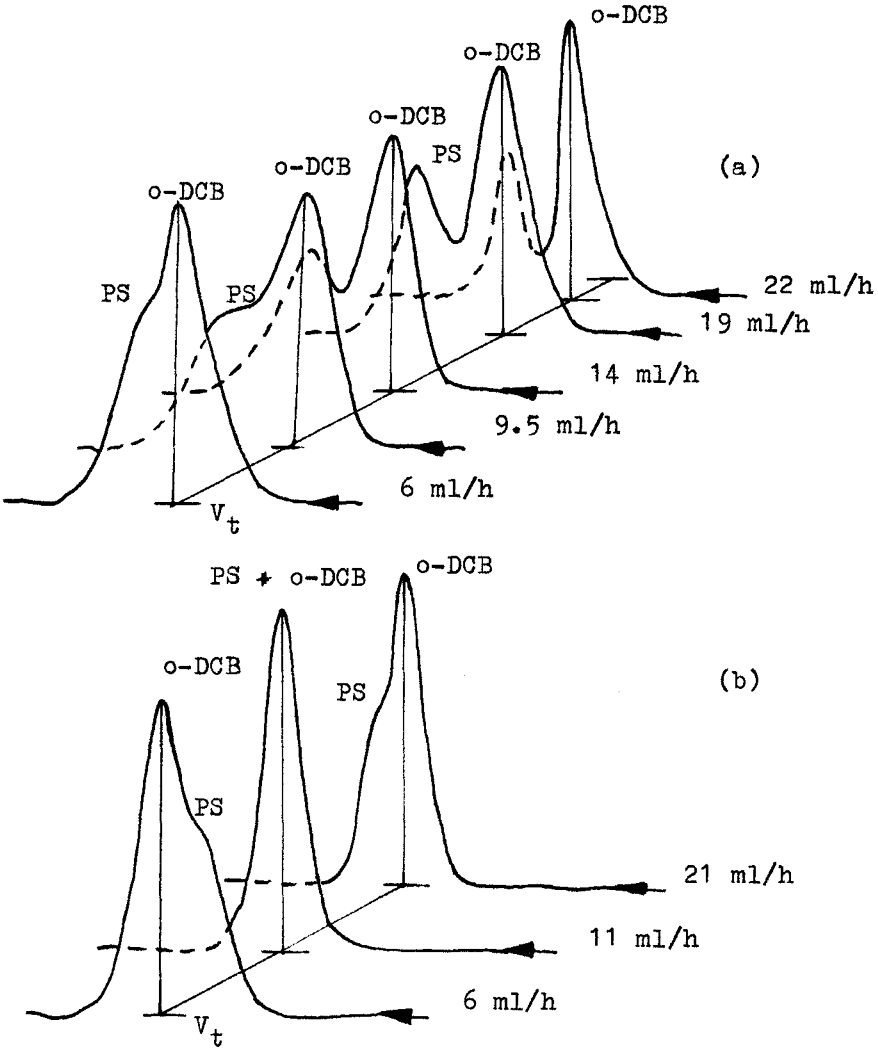


Fig.8 Overlapping chromatograms of a mixture of PS and orthodichlorobenzene obtained in SEC on non-porous glass balls with a mean pore diam. (d_p) of (a) 7.3 µm and (b) 40.0 µm.

the macromolecule on surface "unevennesses". Further, it may be assumed that with increasing flow rate the probability of a direct approach of the macromolecule to the particle surface decreases. If this assumption is true, then at low rates degradation should be affected by the shape of sorbent particles and the quality of their surface. In fact, degradation indices for particles of irregular shape (quartz) are higher than for balls of the corresponding sizes with a smoother surface (Figs.4 and 5) just at low rates. At high rates, degradation indices are comparable.

The hindrance effect was also studied on porous sorbents.Fig.9 shows overlapping chromatograms of a mixture of PS and orthodichlorobenzene at different flow rates for spherical silica gels d_p = 10 μm with pore sizes of 300 Å and 4000 Å (Si-300 and Si-4000). For the Si-300 silica gel, the hindrance effect is greatly complicated by degradation. In this case at a rate of 15 cm^3/h, high molecular weight PS is eluted after low molecular weight orthodichlorobenzene. For Si-4000 the hindrance effect is virtually absent or very weak at high rates.

These facts may be explained from the standpoint of multicenter adsorption of macromolecules on a sorbent with a more developed surface when the macromolecule is

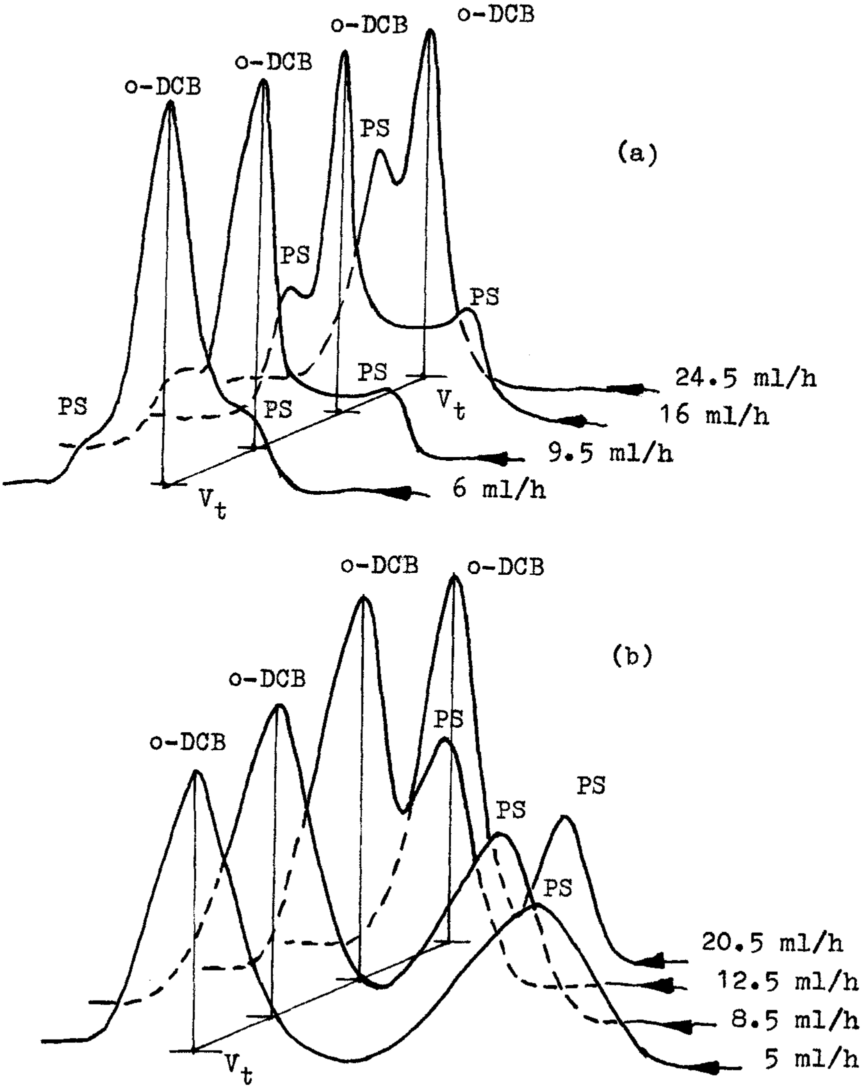


Fig.9 Overlapping chromatograms of a mixture of PS and orthochlorobenzene obtained at different flow rates on (a) Si-300 and (b) Si-4000 silica gels.

adsorbed simultaneously at several units (or segments) located at different distances along the chain. When the pore size (Si-4000) is comparable to that of the macromolecule or exceeds it, the mass transfer between the pore volume and the flow takes place for the macromolecule as a whole during its relaxation time. At a smaller pore size (Si-300) and a more developed surface, multicenter adsorption becomes possible. Description acts will take place with a displacement in time, moreover, the adsorption of other segments can take place simultaneously. As a result, the macromolecule can be retained much longer than its own relaxation time. Furthermore, in multicenter adsorption, when the free part of the macromolecule is entrained by the flow, degradation can take place with the formation of fragments the length of which decreases with the pore size. The possibility of capture of individual segments of the macromolecule by small pores has been considered in ref.(12) in an attemt to explain the higher degradation on microstyragels with narrow pores than that on microstyragels with wide pores (13).

The same situation is also observed on MPG in our experiments (Fig.2). Degradation indices are particularly high on MPG-250, are lower on MPG-1150 and are the lowest on MPG-4000. Fig.10 shows overlapping MWD of the

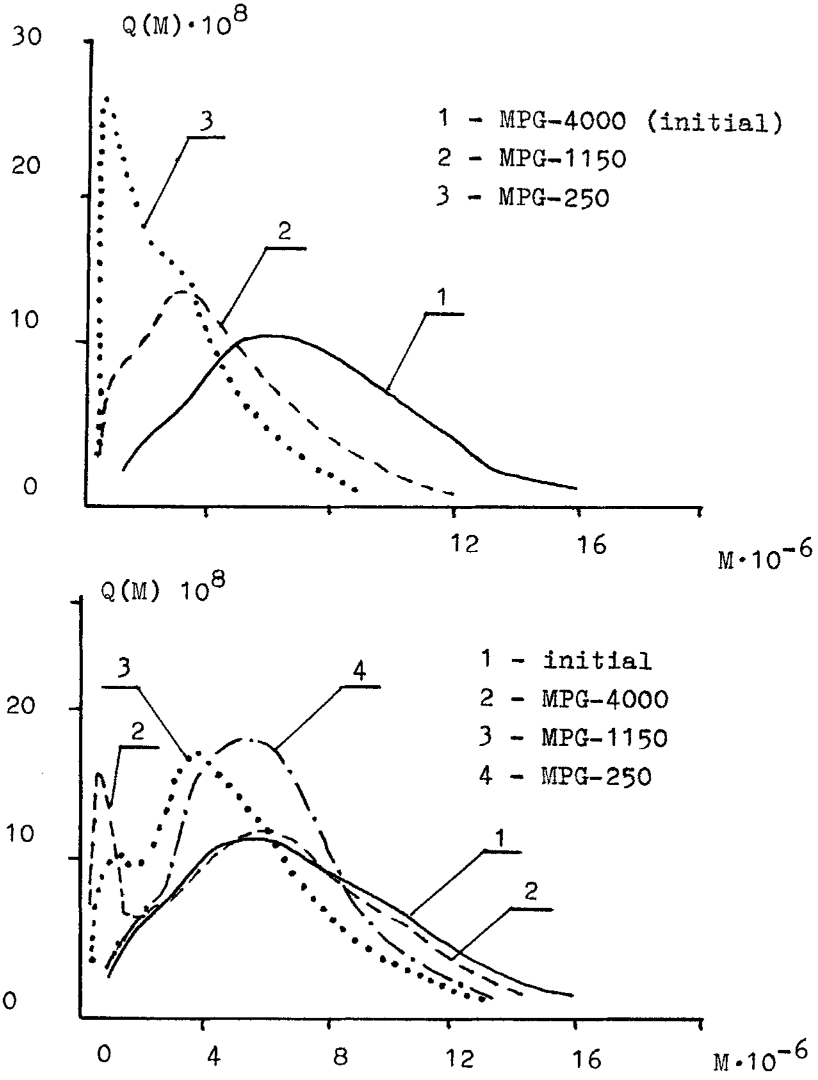


Fig.10 Overlapping MWD of the same PS calculated from the chromatograms of eluates obtained on different MPG at flow rates of (a) ~ 6 cm^3/h and (b) ~ 30 cm^3/h.

same PS from eluates obtained at low flow rates on MPG with different pore sizes. It is clear that the smaller the pore size, the smaller fragments are formed upon degradation. The experiments at rates exceeding almost five-fold the minimum rate (Fig.10b) showed that on a column with MPG-250 (the most capable of inducing degradation in the previous case) PS virtually does not degrade. However, in this case also the smallest fragments were formed (in small amounts) on MPG-250.

CONCLUSION

These investigations on the degradation of macromolecules in SEC make it possible to suggest some practical recommendations on the analysis of polymers with $\bar{M}_w > 2\times10^6$. In the SEC of these polymers, chromatographic systems with mixed sorbents, in particular those containing narrow pores cannot be used. It is necessary to work at "non-degradative" elution rates determined in previous experiments. At these rates degradation indices are close to zero (Fig.2). Because of a strong hindrance effect, the application of sorbents with $d_p \sim$ 5-10 μm to the SEC of super-high molecular weight polymers is problematic. Experiments on balls with $d_p \sim$ 40 μm showed (Fig.8b) that at a flow rate of 6 cm^3/h the hindrance effect is slight or absent.

Hence, the particle size of 5-10 μm is not an optimum size for the chromatography of large molecules.

Moreover, the experimental results showed conclusively that in SEC the degradation of large macromolecules takes place on the surface of the sorbent particle rather than in interparticle channels. In this case the degree of degradation depends on the shape and size of the particles, the pore size and the elution rate.

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