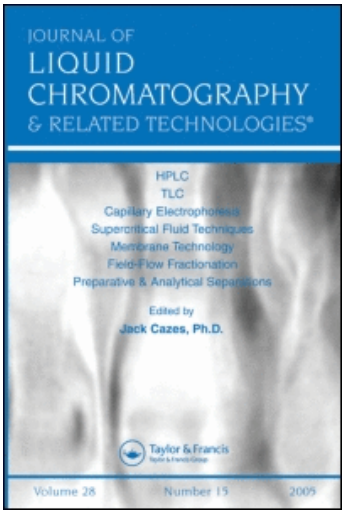

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INTERPRETATION OF THE GEL PERMEATION CHROMATOGRAPHY BEHAVIOUR OF THREE TYPES OF COPOLYMERS

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ABSTRACT

The chromatographic elution of a series of random, block and graft PVC copolymers (with styrene, butadiene, methylmethacrylate, vinylacetate, vinylidene chloride in a large range of composition) is studied. With the help of three consecutive detectors, the composition, molecular weight and intrinsic viscosity of these products are determined and related to the conditions of the synthesis. Results are compared to those obtained by direct measurements. The elution is different for each type of copolymer, varying with the composition but some viscosity-molecular weight relations have been obtained.

INTRODUCTION

This paper reports results I have obtained by gel permeation chromatography (GPC) with various types of modified PVC, namely the three types of copolymers -block, graft and random- each of them with two comonomers and in series of different molar ratios.The purpose is the determination of molecular weight, the comparison with kinetic results in the case of random copolymers and the evaluation of the efficiency of synthesis reaction for graft and block copolymers. This also may give information on the behaviour in fractionation

attempts and in preparative gel permeation chromatography. The elution is strongly dependent on the chemical nature, the structure, the composition and the molecular weight (MW).

Although it has been stated that"the use of GPC for providing quantitative information on copolymer composition and molecular weight distribution (MWD) is not well advanced" [1] I have already found it useful to obtain compositions of mixtures of components, homogeneity of the copolymer versus the MW and to calculate MW, with the help of several detectors on-line [2]. The comparison of the responses of two detectors answers the first two questions ; the continuous measurement of the viscosity of the eluents -when the Mark-Houwink law is not known- and the application of hydrodynamic volume as calibration parameter leads to the MWD [3].

Chemical aspects of the syntheses will not be developed here.

MATERIALS : SYNTHESES OF COPOLYMERS

Synthetic methods have already been described in a detailed manner for each copolymer, and only brief details are given here. Free-radical initiation is used for random and block copolymers. For random copolymers, suspension -vinylidene chloride (VDC) [4]- or solution -vinylacetate (VAc) [5]- processes were chosen with different molar ratio, limiting the conversion or maintaining the composition constant during the copolymerization. For block copolymers, the prepolymer -polyvinylchloride (PVC)-is prepared in the presence of a transfer agent (CCl_4) which may reinitiate, with a copper chelate, the polymerization of styrene (S) or methylmethacrylate (MMA) [6]. Composition was determined by chemical analysis or gas chromatography analysis when possible. Graft copolymers result from the carbanionic deactivation of living polystyrene (PS) or polybutadiene (PB) by PVC in THF solution [7]. The two series presented here have been made by varying the ratio t' graft/backbone. The effective grafting ratio t is an average value and represents the number of grafts per molecule of the backbone.

METHODS OF ANALYSIS

A classical Gel Permeation Chromatograph built in this laboratory was used with two separate lines (for reference and sample) and three consecutive detectors, namely : differential refractometer (Model R-4, Waters Associates, Milford MA, USA), differential UV absorbance detector at 254 nm (Chromatix 220, Berkeley, USA) and an automatic viscometer designed in our laboratory [4]. Solvent was THF at a flow-rate of about 1 cm^3 min^{-1} and temperature was 25° C. Two sets of 3 or 4 columns (1.3 m x 8 mm) filled with spheric silica beads (Porasil) of various pore sizes allowed a good separation in the investigated molecular weight range. The viscometer is of the flow-type [8], dimensions being chosen (l = 20 cm, ∅ = 0.4 or 0.5 mm) to avoid various corrections necessary at low values of t_o (which is here about 130 sec.).

Calibration of elution volume (V_e) was accomplished using polystyrene standards, together with the measurement of the intrinsic viscosities of these known polymers, for application of the universal calibration hypothesis. Depending on the molecular weight, solutions were prepared at 0.2 to 2 % in weight. Correction of the Mark-Houwink coefficients K and a for limited chromatographic resolution was made with the help of the equations proposed by Benoit et al. [9]. Calibration curves were obtained for each composition of the random copolymers.

For block copolymers, the prepolymer (PVC) was first characterized, so that its chromatogram could be substracted from that of the products of the reaction. Moreover, if only one component of the copolymer has a UV absorption, the composition of the copolymer is directly obtained. For the graft copolymers, the two components may be characterized, allowing their definite location in the chromatogram of the mixture.

Effectively, for block and graft copolymers, there are two chromatographic peaks, more or less distinct : effective copolymer (at higher MW) and unreacted homopolymer. They must be decomposed

for instance by using the 310 DuPont Curve Analyzer (Du Pont de Nemours & Co Inc., Wilmington 98 Del. USA). After calibration of the responses of the various components, the measurement of the peak areas allows the calculation of the composition of the mixture and of the copolymer. This is necessary to determine the concentration c in the viscosity measurements where two peaks are visible. If the separation is sufficient, one may determine the viscosity of copolymers and homopolymers related to that of the mixture apparent viscosity ($([\eta]_{app.}$) by :

$$[\eta]_{app.} = \frac{([\eta]c)_{homo} + ([\eta]c)_{copo}}{c\ (homo + copo)} \qquad \text{(equation 1)}$$

which is obtained by direct measurement, with the automatic Fica Viscomatic (ARL, Le Mesnil-St-Denis, France) or by summation fo the viscosities of the fractions.

Complementary UV spectra have been obtained with Beckman DB-G (Scientific and Process Instruments Division, Fullterton, Cal. USA or the Carry 1115 (Applied Physics Corporation, Monrovia Cal. USA .

RESULTS AND DISCUSSION

The three types of copolymers are different and must be examined separately. The only common features are the large change of MW for different copolymers having similar chromatographic peaks and the applicability of the peak area method for determination of the composition.

Graft copolymers

Preliminary results on the method have been published elsewhere [10] and mechanistic interpretation of the grafting reaction according to different parameters is the subject of the next paper [11]. Figure 1 represents the chromatograms of : the initial reagents (c), the graft either polystyrene (PS) or polybutadiene (PB)

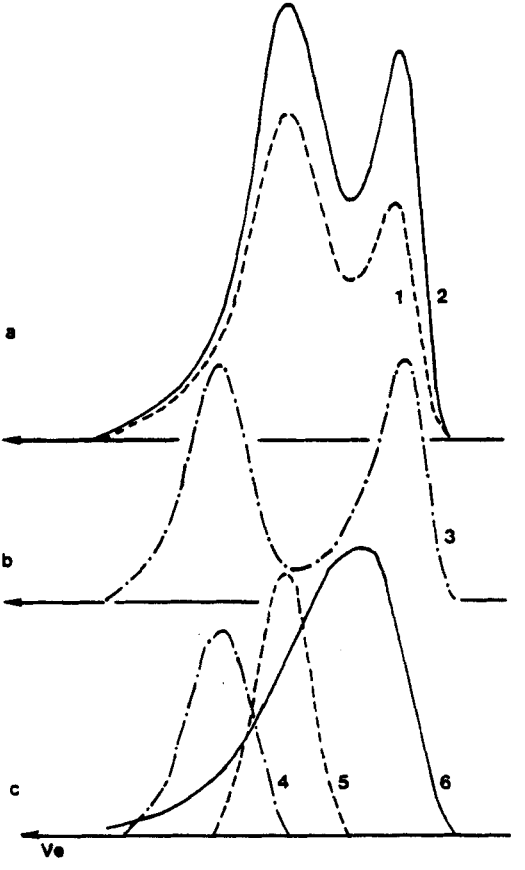

Figure 1

Chromatograms of graft copolymers : 1 - UV ; 2 - refractometric with PS graft --- ; 3 - refractometric with PB graft —— · ; 4 - PB graft —— ·; 5 - PS graft --- ; 6 - PVC backbone ——

and polyvinylchloride (PVC) backbone -an example of final product with PB graft (b) or PS graft (a).

Four facts are visible (i) there is not only one peak (in a or b), which means that some unreacted polymer is present together with the graft copolymer ; (ii) it may be seen that the elution volume of the copolymer is not largely modified versus that of

the PVC backbone, except at high grafting ratio. This is normal since the increase in MW is due to side chains ; (iii) the separation between homo- and copolymer is not total (1a) except if the MW of the graft is low (1b) ; (iiii) finally, the grafting efficiency is independent of the chain length of the backbone, since the UV and refractometric chromatograms of the copolymers are similar and similar to that of the backbone.

At low grafting ratios, the copolymer peaks only present a shoulder. The peaks of copolymer and residual monomer become more distinct when the MW of the components are more different. They may also

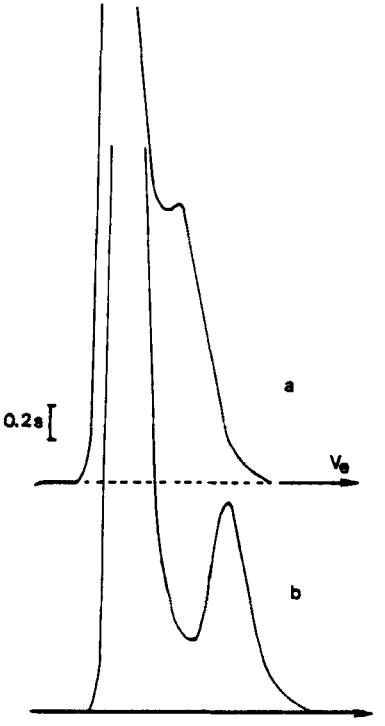

Figure 2

Graft copolymers : viscometric detection
a) with PS graft ; b) with PB graft

become distinct at high grafting ratios when the shorter chains of the backbone have fixed several grafts, which is shown on fig. 2b : the two peaks are almost separated since the MW of the graft (PB) is low (4,200). They are not separated with the PS graft (fig. 2a) since its MW is 8,000 versus 33,000 for the backbone. With PS grafts, the UV chromatogram immediately gives the percent of reacted fixed polymer since it has been verified that the UV trace is only due to PS. With PB graft, the two viscosimetric peaks are distinct (homopolymers of S and B have similar viscosities but different MW) and allow the calculation of the two viscosities of homo PB and graft copolymers (fig. 2). In the case of PS, equation 1 must be used under the form :

$$[\eta]_{copo} = \frac{[\eta]_{app.}\,(m_{homo} + m_{copo}) - ([\eta]m)_{homo}}{m_{copo}} \quad \text{(equation 2)}$$

For the refractometric peak area, it has been supposed that the refractive index of the backbone is equivalent to that of initial PVC and that of the copolymer is a linear combination of those of the components. At high grafting ratio of PB, a UV trace has also been obtained, proportional to the amount of fixed PB, and is due to formation of conjugated double bonds in the backbone. In all cases, under our conditions of synthesis, the yield is about 50 %, so that direct measurements on the product lead to erroneous conclusions : the apparent viscosity is decreased, then remains constant versus PB content, and continually decreases for PS (fig. 3). The $\overline{Mn}$ is calculated from the MW and amounts of the components. On the contrary, osmometric measurements do not show an increase of $\overline{Mn}$.Correct interpretation of viscosity and MW leads to the results of figure 8. Viscosity remains constant for PS and PB at moderate grafting ratio, then increases for PB. It is not possible to determine the number and nature of grafts by measuring the viscosity. The similar behaviour of PS and PB may be explained by similar values of : viscosity of the grafts,

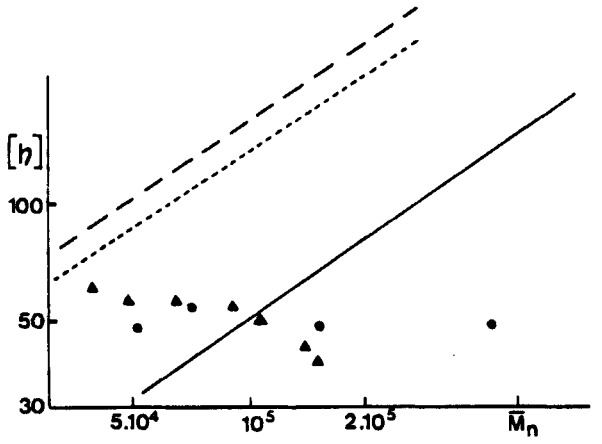

Figure 3

Graft copolymers : intrinsic viscosity of the reaction products versus theoretical molecular weight

--- homo PVC ; .... homo PB ; —— homo PS ; copolymer with PS graft ▲ and PB graft ●

a, and (solubility parameter). At high levels of PB, the viscosity of the copolymer tends to increase since pure homo PVC and PB have higher viscosities : conversely, the viscosity of pure homo PS is lower than that of the copolymer.

Block copolymers

The refractometric chromatogram is generally broad with a shoulder (figure 4), corresponding to the prepolymer which has not added the second monomer. A large intermediate region represents a mixture of two species with different elution behaviours and a constant variation of their relative concentrations (which is easily shown by plotting the ratio of the two instantenous detector traces) [8]. This is not very visible if the efficiency of the reaction is low (curve 6) or high (curve 4). When using S as second monomer, the UV trace gives, directly, the copolymer chromatogram. As seen in figure

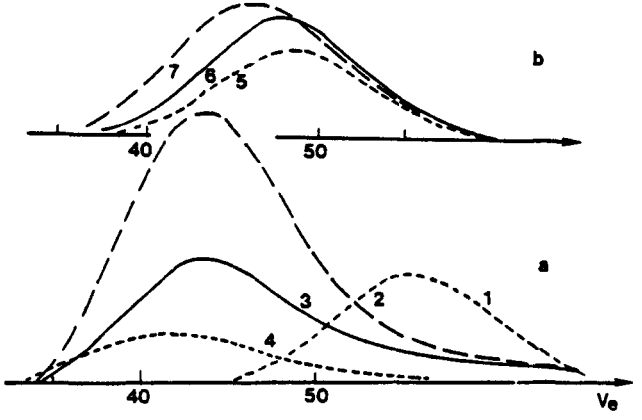

Figure 4

Block copolymers : chromatograms
a) initial PVC --- (1) ; refractometric —— (3) and UV (2) of copolymer with PS ; copolymer with PMMA (4)
b) other initial PVC --- (5) ; refractometric —— (6)and UV --- (7) copolymer with PS

4b, the two refractometric and UV traces may have their maxima at different elution volumes since here the amount of S is low : small effect in refractive index, but large UV absorption.

The measurement of peak areas allows the determination of the composition (only the whole content, not that contained in each species, if only a single detector is used). Since the MW of the prepolymer and copolymer are very different, the copolymer is mainly constituted of the second monomer, an assumption which has been used to calculate its MW. The composition and MW being known, it is possible to determine the number of chains of each species and, from that, the efficiency of the reinitiation and the apparent MW of the mixture.

Depending on the conditions of the reaction, the mixture may contain 20 to 80-90 weight % of comonomer. The efficiency of the reaction varies from less than 0.1 to almost 1. This

efficiency is lower with S than with MMA, and decreases when the MW of the prepolymer increases. The viscosity of copolymers is intermediate between those of the homo PS or PMMA and homo PVC.

Random copolymers

It has already been shown that two copolymers of different compositions having the same chromatograms have different MW and that there is not necessarily parallel variations of elution volume and MW, when the composition is changed. Fig. 5 shows the determination of the composition from the refractometric peak areas and optical density for VAc copolymers, in agreement with gas chromatography analysis results.
Similar tratment for VDC copolymers has been already indicated[4]

Individual calibration curves for each composition are obtained : they move regularly towards lower V_e with decrease of VAc (Fig. 6), the same with VDC [4]. The K and a coefficients

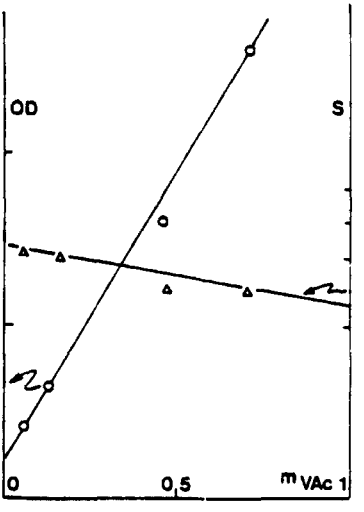

Figure 5

Random copolymers - Evolution of the optical density (O) and refractometric peak area (Δ) with the molar fraction of VAc.

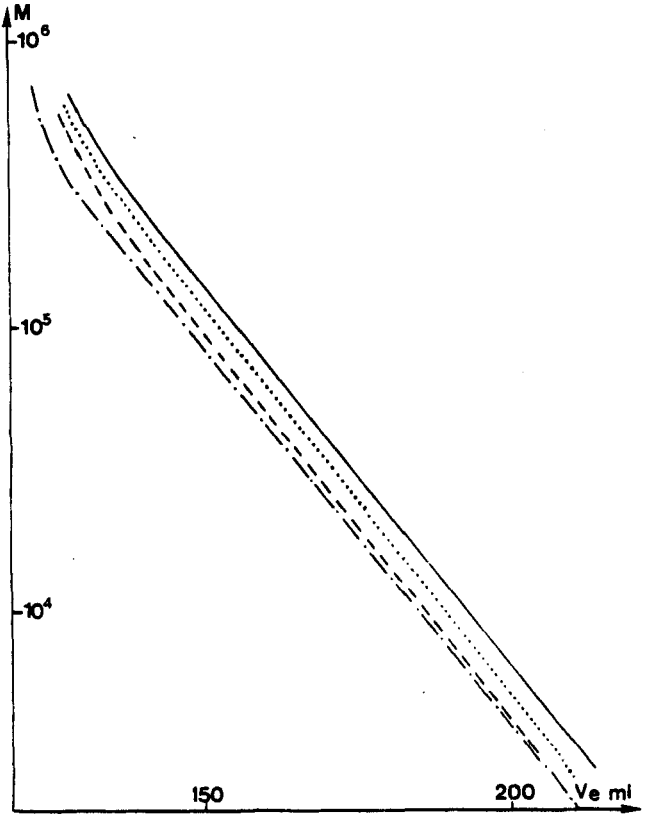

Figure 6

Random copolymers - GPC calibration curves for the different molar fractions of VAc : 0.70 —— ; 0.47 ... ; 0.10 --- ; 0.05 — · —

of the Mark-Houwink law show a continuous evolution with composition : they increase with the CV content [2,4] (Fig. 7). Despite the very different K and a values for a given homopolymer[12], the semilog plot of K versus a allows to draw an average straight line from which are close the values obtained for the copolymers. Yet, there is no regular evolution of the viscosity with M, when the composition is changed (Fig. 8). One may appro-

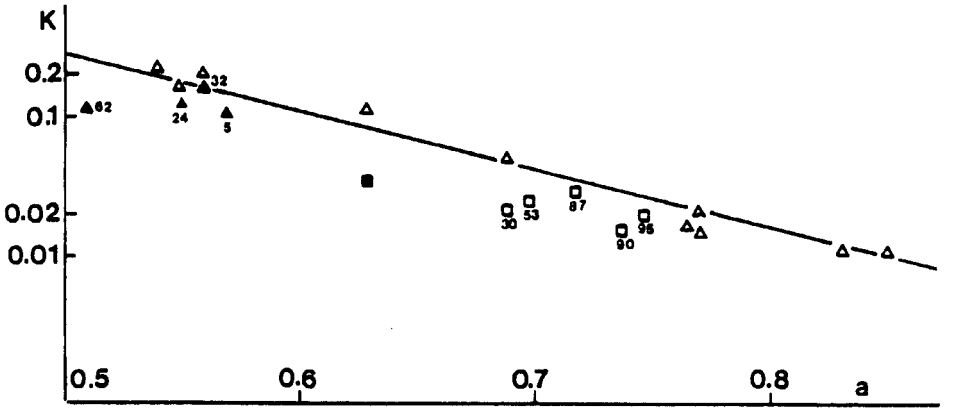

Figure 7

Random copolymers - Semilogarithmic plot of K versus a for homopolymers PVC (Δ), PVAc (■) and copolymers with CVD (▲) and VAc (□). (Figures indicate the molar percent of comonomer).

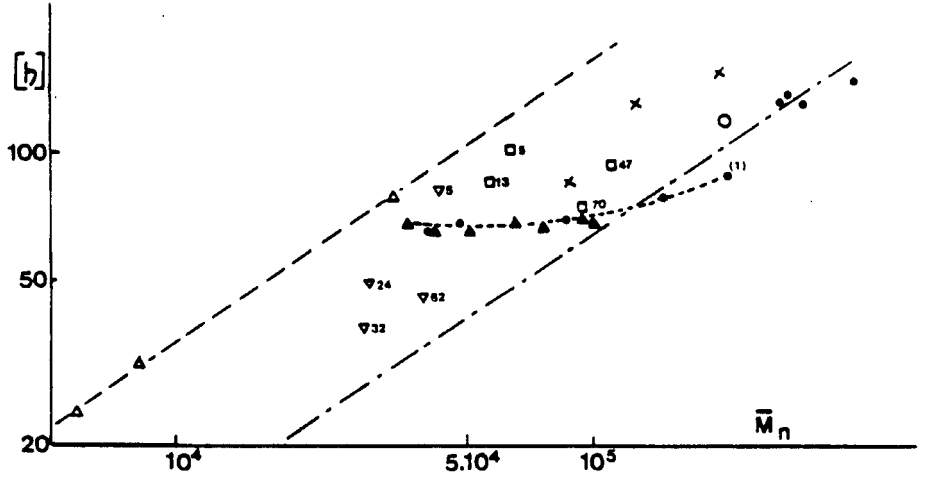

Figure 8

Viscosity - Molecular weight double logarithmic plot
Homo PVC --- ; homo PMMA — · — ; graft with PS (▲) and PB (●) ; random with VDC (▽) and VAc (o) ; block with PS (o) and PMMA (x) (figures indicate the molar percent of comonomer).

ximately say that viscosity increases with CV content but the variation of M is more complex : existence of a minimum in the case of VDC and a maximum with VAc. These evolutions may be compared to those of the copolymerization rates vs the feed composition. Rough evaluation of $\overline{M}$ by the ratio $(\eta)\ M_{PS}/(\eta)_{copolymer}$ leads to a value close to $\overline{Mn}$ for VDC copolymers and to $(MwMn)^{1/2}$ for VAc copolymers.

CONCLUSIONS

Figure 8 summarizes some properties of the various products, namely the relation between solution viscosity and molecular weight. Intrinsic viscosity (η) varies largely with M according to the type of copolymer, its composition and the nature of the components : for a given viscosity, the MW may vary by a factor of 5. A regular evolution may be found for graft copolymers when the number of grafts $\overline{t}$ increases, but it is not possible to correlate directly viscosity and $\overline{t}$ in all the cases. For block copolymers, where a component is in large excess, one approaches its own (η)-M law. The situation is similar for random copolymers, but changes rapidly in a "random" manner with the increase of the comonomer content ; yet, it has been possible to determine K and a values. Since there is a logarithmic relation between elution volume and MW, and between viscosity and M, small changes of elution volume and variation of vicosity by the addition of a second monomer, considerably affect the resulting MW, so that a rapid interpretation of the chromatogram by the position of the maximum is unsufficient and erroneous. Appropriate interpretation of the detector responses leads to a correct description of the products.

REFERENCES

1. DAWKINS,J.V., Block copolymers, ed. Allport,D.C. and Jones,W.J., Applied Science, New York, 1973, p 569

2. REVILLON,A., Chimie Actualités, 1555, 35, 1975

3. GRUBIZIC, Z., REMPP, P. and BENOIT, H., J. Polym. Sci., 35, 753, 1967
4. REVILLON, A., DUMONT, B. and GUYOT, A., J. Polym. Sci. (Chem.), 14,2263, 1976
5. PICHOT, C., GUILLOT, J., PHAM, Q.T. and GUYOT A. J. Macromol. Sci. (Chem.), A7 495, 1973
6. GUYOT, A., CEYSSON, M., MICHEL, A., and REVILLON, A., Informations Chimie, 116,17, 1973
7. LECHERMEIER, G., PILLOT, C., GOLE, J. and REVILLON,A., J. Appl. Polym. Sci., 19,1979, 1975
8. REVILLON, A., Plastiques Modernes et Elastomères, 26, 99, 1974
9. GALLOT, Z., MARAIS, L. and BENOIT, H., J. Chromatog., 88, 363, 1973
10. LECHERMEIER, G., REVILLON, A. and PILLOT, C., J. Appl. Polym. Sci., 19, 1989, 1975
11. LECHERMEIER, G., REVILLON, A. and PILLOT, C., J. Macromol. Sci. (Chem.), PVC Symp., A12(2), 285, 1978
12. KURATA, M., IWAMA, M. and KAMADA, T., Polymer Handbook, Section IV, Brandrup J. and Immergut E.M., ed. Wiley, New York, 1966