Gel Permeation Chromatography in the Study of the Molecular Weight Distribution of the Copolymer Vinyl Chloride–Vinyl Acetate. II. Influence of Copolymer Chemical Composition

J. JANČA, L. MRKVIČKOVÁ, and M. KOLÍNSKÝ, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia,* and A. S. BRAR, *Indian Institute of Technology, Chemistry Department, New Delhi, 110 029 India*

Synopsis

A set of statistical vinyl chloride–vinyl acetate copolymers of various vinyl acetate content was prepared. The samples were fractionated by preparative gel permeation chromatography (GPC), and the fractions were characterized by analytical GPC, light scattering, and viscometry. The original samples were characterized also by osmometry and chemical analysis. The molecular parameters calculated from GPC analysis using the universal calibration were correlated with those of light scattering measurements and viscometry. It was found that in the range of chemical compositions and molecular weights studied, the chemical composition does not significantly influence the results of GPC analysis.

INTRODUCTION

In our earlier paper[1] we studied some anomalous results obtained by Chen and Blanchard[2] at their GPC measurements of molecular weight distribution (MWD) of vinyl chloride–vinyl acetate (VC–VAc) copolymers. These authors found a considerable discrepancy between the universal calibration curve[3] obtained by using $[\eta] \times M$ parameter for polystyrene standards and that for fractions of VC–VAc copolymers. They further observed a substantial disagreement between the MWD curve calculated from GPC data for unfractionated sample and that obtained from GPC and fractionation data of individual fractions. One of the possible reasons of the anomalous results could be the different solution behavior of the individual fractions of the commercial high-conversion copolymer raised by variable chemical composition. The distribution in the chemical composition of a commercial VC–VAc copolymer is due to the fact that during the copolymerization of vinyl chloride–vinyl acetate mixture the content of vinyl chloride in the batch diminishes faster. Therefore, with advancing conversion the content of vinyl acetate in the resulting copolymer increases. At the same time the copolymer molecular weight decreases owing to an increasing content of the terminating agents.

For a determination of the Mark-Houwink equation needed for calculation of the universal calibration curve in our earlier paper,[1] we chose fractions of the commercial copolymers with the vinyl acetate content ranging from 10% to 13%. Using the Mark-Houwink equation fixed in this way, we reached a good agreement of the weight-average molecular weights $\overline{M}_w$ and of the intrinsic viscosities

0021-8995/78/0022-2661$01.00

$[\eta]$ calculated from GPC data and the universal calibration curve based on the measurements of polystyrene standards with those obtained from light scattering and viscometry. The coincidence of $\overline{M}_w$, $[\eta]$, and number-average molecular weights $\overline{M}_n$ for unfractionated copolymer samples measured directly by GPC and those calculated from GPC data of individual fractions was also very good.

In order to reach more definite conclusions about the influence of the chemical composition of the copolymer fractions on the GPC results, and in consequences of the formerly observed anomalies, we studied prepared samples of the statistical VC–VAc copolymer of different vinyl acetate contents.

The polymerizations were carried out to very low conversions, which warranted a high chemical homogeneity of the copolymer samples. The prepared samples were fractionated by preparative GPC, and both the fractions and the unfractionated copolymer were characterized by analytical GPC using the universal calibration based on the measurements of polystyrene standards by light scattering, osmometry, viscometry, and chemical analysis.

EXPERIMENTAL

Vinyl Chloride–Vinyl Acetate Copolymer Samples

A set of six statistical VC–VAc copolymers of different chemical composition (marked C-1 to C-6) was prepared by copolymerization in a glass autoclave (Ing. Büro, Switzerland) at constant vigorous stirring. Vinyl chloride of usual purity (CHZWP Nováky, Czechoslovakia) was used, and vinyl acetate (of the same origin) was purified by shaking with aqueous sodium hydroxide and water to the neutral point and successive distillation. α-Azobisisobutyronitrile purified by recrystallization was used as an initiator. All the copolymerizations were carried out at 50°C with an initial amount of 500 g of both monomers and 0.5 g of the initiator. To the weighted amounts of vinyl acetate and initiator, a known amount of vinyl chloride was condensed at 15°–20°C, and the polymerization was started by heating the reaction mixture to 50°C. After the defined reaction time (determined by experiments), the copolymerization was finished by venting vinyl chloride of the mixture and lowering the temperature to 10°–15°C. A soluble part of the copolymer was precipitated by methanol. After that, all the copolymer was filtered off, washed several times with methanol, and dried for 24 hr at room temperature. After weighing (to determine the conversion) it was dried further under vacuum (13.33 Pa) at room temperature in order to remove possible traces of methanol and vinyl acetate.

Fractionation of VC–VAc Copolymers by Preparative GPC

The fractionations were performed on a GPC apparatus developed in this Institute. The system of two separation columns of 25-mm diameter and of 2400-mm length was packed with Sphérosil (Produits Chimiques, France) types B, C, D, E, and F of different porosities. The separation region of this mixture lay between the molecular weights of 5×10^3 and 2×10^6. Tetrahydrofuran (THF), distilled under nitrogen with an addition of cuprous chloride and potassium hydroxide to remove peroxides and water, was used as solvent.

Flow velocity of the solvent in preparative GPC fractionation was kept at 6 ml/min; 25 ml of 5% (w/v) solutions of copolymer was injected repeatedly until a sufficient amount of fractionated sample would be gathered. The identical fractions of the individual injections were joined, and the polymer was precipitated in an excess of distilled water. The precipitated fractions were dried to constant weight under vacuum at 40°C.

Copolymer samples C-1 and C-3 to C-6 were fractionated by preparative GPC. The whole quantity of the individual fractionated samples amounted to 3.75 g. From 11 to 18 fractions were obtained depending on the polydispersity of the fractionated copolymers (Table II). The above experimental conditions for GPC preparative fractionation were chosen in accordance with the results of our earlier studies.[4]

Analytical GPC, Light Scattering, Viscometry, and Chemical Analysis

Procedures and experimental conditions used with these methods have been given in detail in the earlier paper.[1] The evaluation procedure of GPC data and a discussion of the applicability of the universal calibration with the use of PS standards have also been described in our earlier papers.[1,5]

Osmometry

All the measurements were performed on a Knauer high-speed membrane osmometer (West Berlin) at 45°C with THF as solvent.

RESULTS AND DISCUSSION

Preparation of VC–VAc Copolymer Samples of Constant Chemical Composition

All data concerning the preparation of VC–VAc copolymers are shown in Table I. The polymerizations were carried out to very low conversions (about 3.5%–5.5% of both comonomers). The reason for that was a requirement of a maximal chemical homogeneity of the samples. Using the copolymerization parameters of the VC–VAc pair[6] ($r_1 = 1.68, r_2 = 0.23$ at 60°C) the average chemical composition as well as the limiting compositions of the copolymer at the beginning and at the end of the copolymerization (columns 5–7 in Table I) were calculated. It follows that the inhomogeneity in the chemical composition of the copolymer

TABLE I
Preparation of VC–VAc Copolymers of Variable Chemical Composition

Sample	Batch composition, % VAc	Yield, g	Conversion, %	Theoretical composition of prepared copolymers, % VAc		
				Initial	Final	Average
C-1	10	27.7	5.5	6.0	6.2	6.1
C-2	15	27.0	5.4	9.1	9.3	9.2
C-3	20	21.5	4.3	12.3	12.5	12.4
C-4	30	25.0	5.0	18.7	19.1	18.9
C-5	40	24.2	4.8	25.5	26.0	25.7
C-6	50	17.0	3.4	32.7	33.1	32.9

samples is very low; the differences cannot be proved by usual analytical methods.

Characterization of Unfractionated VC–VAc Copolymer Samples

The unfractionated copolymer samples C-1 to C-6 were characterized by light scattering, osmometry, viscometry and by GPC. Their chemical composition was determined by chemical analysis. All the measured data are shown in Table II.

GPC data were calculated from the universal calibration curve by using the Mark-Houwink equation $[\eta] = 6.72 \times 10^{-4} M^{0.611}$, obtained[1] for VC–VAc copolymer containing 10%–13% of vinyl acetate in THF solutions at 25°C. The values of $\overline{M}_w$, $\overline{M}_n$, and $[\eta]$ of samples C-2 to C-4 calculated from GPC measurements agree, in the limits of experimental error (ca. ±5% for the individual methods used), with those obtained by light scattering, osmometry, and by viscometry. These samples contained from 7.5% to 15% of vinyl acetate. The samples with higher or lower vinyl acetate contents gave the differences between GPC results and those of light scattering, osmometry, and viscometry somewhat higher than the experimental errors.

The differences (ca. 10% on average) between the calculated average contents of vinyl acetate in samples C-1 to C-6 (see Table I) and those actually found (see Table II) could be caused by some differences in polymerization conditions (comparing our experiments with ref. 6) and to some extent by experimental errors of the chemical analysis methods used. However, the above differences are irrelevant from the point of view of GPC results because the chemical homogeneity of copolymers should not be influenced in a decisive manner.

Characterization of Fractionated VC–VAc Copolymer Samples

For further study only the fractions obtained in sufficient quantities enabling their characterization by GPC and either light scattering or viscometry were used. A summary of the GPC, light scattering, and viscometry results for all fractions chosen is shown in Table III. The $\overline{M}_w$ and $[\eta]$ values of all fractions (disregarding the vinyl acetate content) were calculated from GPC measurements by using the universal calibration curve and the Mark-Houwink equation obtained in our previous paper[1] for fractions containing 10%–13% of vinyl acetate. The agreement of the $\overline{M}_w$ and $[\eta]$ values calculated from GPC measurements and the same quantities obtained by light scattering and viscometry was evaluated statistically. Standard deviations were calculated by means of the formula

$$S = \sqrt{\frac{(x_i - \overline{x})^2}{n - 1}}$$

and have been cited in Table III in percent of the pertinent average values of $\overline{M}_w$ and $[\eta]$, respectively. The standard deviations shown in Table III are in most cases comparable with, or lower than, the average experimental errors of the used methods. Some exceptions, where the standard deviations are higher than the average experimental errors, are of the statistical character. In the set of experimental data summarized in Table III no systematic deviations could be found exceeding the experimental errors and so being significant for the interpretation of results.

TABLE II
Characterization of VC–VAc Copolymer Samples of Different VAc Content

Sample	Light scattering $\bar{M}_w \times 10^{-3}$	Osmometry $\bar{M}_n \times 10^{-3}$	Viscometry $[\eta]$, dl/g	GPC data $\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$[\eta]$, dl/g	VAc content, %
C-1	118	53	0.88	99	54	0.71	6.0
C-2	87	46	0.76	91	51	0.68	7.5
C-3	70	40	0.68	73	36	0.59	10.0
C-4	69	38	0.62	70	40	0.58	15.2
C-5	71	54		80	53	0.64	23.9
C-6	67	38	0.61	48	27	0.46	28.1

TABLE III
Characterization of VC–VAc Copolymer Fractions

Fraction	GPC data		Light scattering	Viscometry	Standard deviation	
	$\overline{M}_w \times 10^{-3}$	$[\eta]$, dl/g	$\overline{M}_w \times 10^{-3}$	$[\eta]$, dl/g	S_{M_w}, %	S_η, %
C-1a	149	0.93	135	1.06	7.0	
C-1b	136	0.87	135	0.93	0.5	13.8
C-1c	128	0.84	120	0.93	4.6	7.2
C-1d	109	0.77	112	0.79	1.9	1.8
C-1e	92	0.69	90	0.78	1.5	8.7
C-1f	85	0.64	87	0.77	1.6	13.0
					average 2.9	8.9
C-3a	99	0.73	89	0.81	7.5	7.3
C-3b	88	0.68	84	0.82	3.3	13.2
C-3c	84	0.66	81	0.70	2.6	4.2
C-3d	75	0.61	65	0.62	10.1	1.1
C-3e	61	0.55	58	0.57	3.6	2.5
C-3f	59	0.52	48	0.47	14.5	7.1
					average 6.9	5.9
C-4a	129	0.87	133	0.91	2.2	3.2
C-4b	89	0.69	98	0.77	6.8	7.7
C-4c	80	0.64	75	0.65	4.6	1.1
C-4d	66	0.56	64	0.58	2.2	2.5
C-4e	56	0.50	56	0.53	0.0	4.1
C-4f	51	0.48		0.50		2.9
					average 3.2	3.6

C-5a	111	0.77	98	0.77		0.0
C-5b	105	0.76	77	0.74	4.9	1.9
C-5c	89	0.68	67	0.63	10.2	5.4
C-5d	70	0.59	60	0.59	3.1	0.0
C-5e	68	0.58	45	0.53	8.8	6.4
C-5f	49	0.46		0.45	6.0	1.6
					average 6.6	2.6
C-6a	90	0.69	94	0.76	3.1	6.8
C-6b	80	0.64	75	0.67	4.6	3.2
C-6c	69	0.58	69	0.59	0.0	1.2
C-6d	57	0.52	56		1.3	
C-6e	46	0.45		0.44		1.6
C-6f	46	0.45		0.40		8.3
					average 2.3	4.2

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This conclusion seems to be in variance with the results obtained for the unfractionated samples. It is possible, however, that fractions which could not be characterized differ from the others by their structure. This dissimilarity could bring about different solution behavior which results in the disagreement of the molecular parameters measured by different methods with the unfractionated samples.

Nevertheless, it is evident that the variable chemical composition could not influence the GPC results obtained by using the universal calibration to the degree observed by Chen and Blanchard.[2] Another possible cause of the observed anomalies[2] will be the subject of further study.

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