

CHROM. 11,614

SEPARATION OF VINYL CHLORIDE-VINYL ACETATE COPOLYMERS ACCORDING TO THEIR CHEMICAL COMPOSITION BY THIN-LAYER CHROMATOGRAPHY

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(Received November 13th, 1978)

SUMMARY

The separation of model samples of vinyl chloride-vinyl acetate copolymers by thin-layer chromatography was investigated. Model samples with vinyl acetate contents ranging from 6 to 28% (w/w) were prepared by copolymerization carried out to low degrees of conversion to ensure high homogeneity of chemical composition. No separation was achieved in simple solvents; the samples either migrated with the solvent front or remained at the start. Reasonable separations of samples containing 10-28% of vinyl acetate were attained with the mixed solvent 1,2-dichloroethane-tetrahydrofuran (100:1-5.5), while samples containing 6-15% of vinyl acetate were separated by isocratic elution with 1,2-dichloroethane-tetrahydrofuran-*n*-heptane (100:3:30). Gradient elution gave reasonable separations with vinyl acetate in the range 0-28% contents using as the solvent methyl ethyl ketone-1,2-dichloroethane-carbon tetrachloride. It was shown with fractions of copolymers with various molecular weights that the molecular weight does not affect the separation under the experimental conditions adopted.

INTRODUCTION

The thin-layer chromatography (TLC) of polymers has recently experienced considerable advances. Numerous polymers and copolymers have been successfully separated by TLC according to differences in molecular weight, chemical composition or chain structure¹. The advantages of TLC are its relative experimental simplicity and its rapidity. In the semi-quantitative and quantitative evaluation of results, the chromatograms of the sample being analysed are usually compared with those of standard samples. TLC is a very suitable and rapid checking method in the industrial

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production of important polymers and copolymers, but so far has seldom been employed.

During the synthesis of the important random copolymer vinyl chloride-vinyl acetate (VC-VAc), a product with a relatively broad distribution of chemical composition is formed owing to the changing composition of the comonomer mixture, which is caused by the more rapid consumption of vinyl chloride in copolymerizations carried out to high degrees of conversion. The distribution of chemical composition of this copolymer considerably affects its applicability in the plastics industry, but has been determined only seldom and with difficulty. Reviews^{1,2} with extensive bibliographies do not mention the application of TLC for this copolymer.

The separation of polymers by TLC is based on the different rates of migration of the individual components with respect to their different retentions by the stationary phase during development. The action of the stationary phase, which retards the migration of the sample, can be expressed by various mechanisms with contributions of molecular interactions.

In adsorption, the interaction between the sample molecules and the active sites of the stationary phase prevails. The solubility of the sample in a solvent retained by the stationary phase is of use in the phase-separation mechanism (this mechanism is sometimes described as extraction or precipitation). In the molecular-sieve mechanism, the exclusion of macromolecules by a porous material forming the stationary phase is preferred. In general, all of these mechanisms take place in the chromatographic separation. However, one of the separation mechanisms usually prevails, which can in principle be taken advantage of by the selection of suitable experimental conditions, *i.e.*, of the type and activity of the adsorbent and the composition of the elution system. Considering the various types of gradients that occur in the thin layer as a result of the preferential sorption of some components of the eluent mixture, by evaporation from the layer, etc., the geometric arrangement of the experiment may have an important influence.

With regard to the separation of VC-VAc copolymer according to its chemical composition, the prevailing adsorption mechanism is desirable, or the phase-separation mechanism with respect to the extent to which the solubilities of copolymers of different composition differ. The operation of the molecular-sieve mechanism, which leads to separations exclusively according to the effective dimensions of the macromolecules, is undesirable in the present case. The technique of gradient development is often applied in the TLC of copolymers and consists in the gradual change of the composition of the elution system in such a way as to attain optimal conditions of migration corresponding, *e.g.*, to the polarities of the separated components. The aim of this study was to investigate the possible application of TLC to the characterization of the chemical composition or its distribution in VC-VAc copolymers and to establish the conditions for carrying out routine analyses.

EXPERIMENTAL

Thin-layer chromatography

The silica gels used to prepare the thin layers were Kieselgel G (E. Merck, Darmstadt, G.F.R.) and KSK, 7-11 μm (U.S.S.R.) after treatment with hydrochloric acid. The required amount of silica gel was mixed by vibration for 90 sec with

3 parts by weight of distilled water (Kieselgel) or with calcined gypsum and water (KSK) and applied with a Unoplan apparatus (Shandon Scientific, London, Great Britain). Glass plates of two sizes (10×20 and 5×10 cm) were used as bases after washing with acetone and diethyl ether; the thicknesses of the applied layers were 0.2 mm with the small plates and 0.3 mm with the larger plates. The coated plates were activated in an oven at 110° for 30 min and stored in a desiccator.

The solutions of samples (0.5%, w/v) were applied in amounts of 1–5 μ l by means of a Hamilton microsyringe. A well sealed chamber (Desaga, Heidelberg, G.F.R.) was used for development after equilibration for at least 30 min by means of a filter-paper coating the side and rear walls of the chamber.

The chromatograms were developed by the ascending technique at room temperature. For gradient elution, another solvent (or a mixture of solvents of given composition) was added continuously to the starting solvent in the chamber by means of a linear dosing pump. Perfect mixing of the solvent in the development chamber was achieved with an electromagnetic stirrer.

The chromatographic spots were detected by spraying with a 3% solution of potassium permanganate in concentrated sulphuric acid or with a 1% solution of iodine in methanol using a glass atomizer. When the former reagent was used, the plates were heated in an oven at 150 – 160° for 5–10 min.

Samples

The model samples of VC-VAc copolymers used were prepared by copolymerization carried out to low degrees of conversion to ensure their chemical homogeneity, as described in a previous paper³. To check the effect of molecular weight on the TLC separations, some fractions of these model copolymers that were obtained by preparative gel-permeation chromatography (GPC) and characterized by a GPC method on the analytical scale were also used³. A poly(vinyl chloride) (PVC) fraction was obtained by precipitation fractionation of commercial PVC (Geon, Japanese

TABLE I
CHARACTERISTICS OF THE SAMPLES OF POLYMERS AND COPOLYMERS STUDIED

Sample	$\bar{M}_w \cdot 10^{-3}$	\bar{M}_w/\bar{M}_n	Vinyl acetate content (% w/w)
<i>Copolymers VC-VAc</i>			
C1	118	1.83	6.00
C2	87	1.78	7.50
C3	70	2.03	10.04
C4	69	1.75	15.18
C5	71	1.51	23.95
C6	67	1.78	28.06
PVC	75	1.21	0
PVAc	290	3.34	100
<i>Fractions of VC-VAc copolymers</i>			
C3a	99	1.51	10.04
C3d	75	1.45	10.04
C3f	59	1.70	10.04
C4a	129	1.34	15.18
C4c	80	1.50	15.18
C4f	51	1.61	15.18

Geon Co., Tokyo, Japan) in the system tetrahydrofuran (THF)–water and characterized earlier⁴. The sample of poly(vinyl acetate) (PVAc) was prepared by polymerization of vinyl acetate and characterized by a GPC method as described elsewhere³. The most important data on the samples used are given in Table I.

Solvents

The following solvents of analytical-reagent or pure grade were used in all experiments: acetone, cyclohexanone (CHX), carbon tetrachloride, chloroform, diethyl ether, methyl ethyl ketone (MEK) and methanol (Lachema, Brno, Czechoslovakia); cyclohexane and *n*-heptane (LOBA-Chemie, Vienna, Austria); and 1,2-dichloroethane (DCE) (PPH-Polski Odczynniky Chemiczne, Gliwice, Poland). THF (VEB Laborchemie, Apolda, G.D.R.) was distilled with copper(I) chloride and potassium hydroxide before use.

RESULTS AND DISCUSSION

In the selection of solvents and non-solvents for the separation of copolymers by TLC, it is necessary to take into account the solubility of the copolymer and the solubility of both homopolymers. The choice of solvents for PVC and PVAc or for the copolymer VC–VAc is relatively limited. Several readily available solvents that differ in their dielectric constants were chosen (Table II).

TABLE II

SOLVENTS AND NON-SOLVENTS OF PVC AND PVAc HOMOPOLYMERS AND VC–VAc COPOLYMER

<i>Solvent</i>	<i>Non-solvent</i>	<i>Dielectric constant</i>	<i>Solvent strength parameter</i> ⁶ , $\epsilon_{Al_2O_3}^0$
Acetone		20.7	0.56
Methyl ethyl ketone		19	0.51
Cyclohexanone		18.3	—
1,2-Dichloroethane		9–11	0.49
Tetrahydrofuran		7.4	0.45
Chloroform		4.7–4.8	0.40
Carbon tetrachloride		2.2	0.18
	Methanol	33	0.95
	Cyclohexane	2.0	0.04
	<i>n</i> -Heptane	1.9	0.01

Some mixtures of solvents of high elution power (THF, MEK or acetone) with a solvent of low elution power (chloroform, carbon tetrachloride, DCE) should permit the required separations. Another method is to increase the concentration of a non-solvent in a good solvent. Both polar and non-polar non-solvents (methanol and *n*-heptane) were used and the results are given in Tables III and IV. In the first instance, a very rapid change in R_F values occurred at a critical concentration, indicating the precipitation of polymers and copolymer. Virtually no interactions of separated polymers with the sorbent occur here, owing to the high polarity of the non-solvent. Moreover, the R_F values increased at a low concentration of methanol

in THF in comparison with neat THF. On the application of a non-polar non-solvent, *n*-heptane, the R_F values of PVC and C6 samples changed continuously with increasing content of *n*-heptane, but the separation was only slightly sensitive to the copolymer composition for vinyl acetate contents in the range 0-30%.

TABLE III

TLC OF PVC, PVAc AND VC-VAc COPOLYMER SAMPLES WITH THE ELUTION SYSTEM THF-METHANOL (KIESELGEL G)

THF to CH ₃ OH ratio	R_F		
	PVC	C6	PVAc
20:1	0.86	0.88	0.84
20:5	0.90	1.00	0.90
20:7	0.90	0.90	0.90
20:10	0.90	0.90	0.90
20:12	1.00	1.00	1.00
20:15	0	1.00	0.92
20:16.5	0	0.90	0.90
20:17	0	0	0.90
1:20	0	0	0.90
5:20	0	0	0.90
15:20	0	0	0.90

TABLE IV

TLC OF PVC, PVAc AND VC-VAc COPOLYMER SAMPLES WITH THE ELUTION SYSTEM THF-*n*-HEPTANE (KIESELGEL G)

THF to heptane ratio	R_F		
	PVC	C6	PVAc
5:1	0.86	0.86	0.50
5:2	0.72	0.72	0
5:2.3	0.72	0.66	0
5:2.5	0.74	0.64	0
6:5	0.60	0.48	0

The development was further carried out with THF-DCE. We have not found in the literature any data that permit the quantitative expression of the thermodynamic quality of DCE in relation to the polymers and copolymers studied, but it can be judged that it is a thermodynamically poor solvent for both PVC and PVAc. As follows from tabular data⁵, DCE dissolves reasonably well low-molecular-weight PVC, but only poorly high-molecular-weight PVC and partially PVAc (in a mixture with ethanol). The TLC results using THF-DCE given in Table V show that with appropriate proportions of the two components the separation of the samples studied was successful.

Further experiments (in contrast to the previous preliminary experiments) were carried out on large plates. The change in experimental conditions led to certain changes in R_F at the compositions of THF-DCE mixture used. The results obtained under these conditions are summarized in Table VI.

TABLE V

TLC OF PVC, PVAc AND VC-VAc COPOLYMER SAMPLES WITH THE ELUTION SYSTEM THF-DCE (KIESELGEL G)

THF to DCE ratio	R_F		
	PVC	C6	PVAc
1:5	1.00	0.90	0
2:5	0.96	0.86	0.18
3:5	0.90	0.90	0.90
4:5	0.90	0.86	0.94
5:5	0.80	0.80	0.86
0.5:20	0.88	0.44	0.10
1:20	0.92	0.51	0.10
1.5:20	0.90	0.72	0.10
2:20	0.90	0.64	0.20
3:20	0.88	0.84	0.10

Table VI shows that an effective separation of VC-VAc copolymers according to the vinyl acetate content occurs with DCE to THF ratios ranging from 100:1 to 100:5.5. With increasing concentration of THF in the mixture, also samples with higher vinyl acetate contents are gradually released from the start, but the separation of samples containing 6–15% of vinyl acetate is less efficient. The elution system used obviously has a high eluting power, so that the samples with a low content of vinyl acetate migrate with the solvent front and the separation becomes ineffective. To decrease the eluting power of system, *n*-heptane (the non-solvent of low polarity) was added as a third component. Prior to this, the binary system DCE-*n*-heptane

TABLE VI

TLC OF VC-VAc COPOLYMERS AND PVC AND PVAc HOMOPOLYMERS WITH THE ELUTION SYSTEM THF-DCE (KIESELGEL G)

THF to DCE ratio	R_F							
	PVC	C1	C2	C3	C4	C5	C6	PVAc
1:100	0.93		0.85		0.17	0.02	0	0
1.5:100	0.90		0.85		0.46	0	0	0
2:100	0.92		0.87		0.35	0.03	0	0
2.5:100	0.97	0.92	0.94	0.87	0.37	0.09	0	0
2.7:100	0.88	0.85	0.84	0.83	0.40			0
2.8:100	0.91	0.81	0.82	0.82	0.43			0
3:100	0.96		0.90		0.61	0.27	0.07	0
3.3:100	0.88		0.85		0.81	0.32	0.08	0
3.5:100	0.91		0.87		0.82	0.35	0.09	0
3.7:100	0.95		0.87		0.85	0.37	0.11	0
4:100	0.92		0.81		0.77	0.45	0.12	0
4.3:100	0.91				0.89	0.50	0.20	0
4.7:100	0.95				0.87	0.52	0.31	0
5:100	0.95				0.89	0.65	0.28	0
5.2:100	0.93				0.85	0.70	0.37	0
5.3:100	0.91				0.86	0.56	0.25	0
5.5:100	0.97				0.89	0.57	0.32	0

TABLE VII

TLC OF VC-VAc COPOLYMERS AND PVC AND PVAc HOMOPOLYMERS WITH THE ELUTION SYSTEMS DCE-*n*-HEPTANE AND DCE-*n*-HEPTANE-THF (KIESELGEL G)

DCE to <i>n</i> -heptane to THF ratio	R_F					
	PVC	C1	C2	C3	C4	PVAc
100:1:0	1.00	1.00	(0.2)*	0		
100:2-10:0	1.00	(0.5)	0	0		
100:20:0	(0.5)	0	0	0		
100:30:0	0	0	0	0		
100:30:1	1.00	(0.2)	(0.1)	0	0	
100:30:3	0.97	0.95	0.78	0.42	0.13	0
100:30:4	0.94	0.92	0.76	0.57	0.22	0

* Parentheses indicate that the sample exhibited stronger spreading along the path.

was tested. The results obtained with these elution systems are summarized in Table VII.

Development with the system DCE-*n*-heptane-THF (100:30:4) proved suitable for separation of the VC-VAc copolymers according to the content of vinyl acetate in the range 6-15% (w/w). Separations of VC-VAc copolymers containing 6-15% and 15-28% of vinyl acetate are shown in Fig. 1.

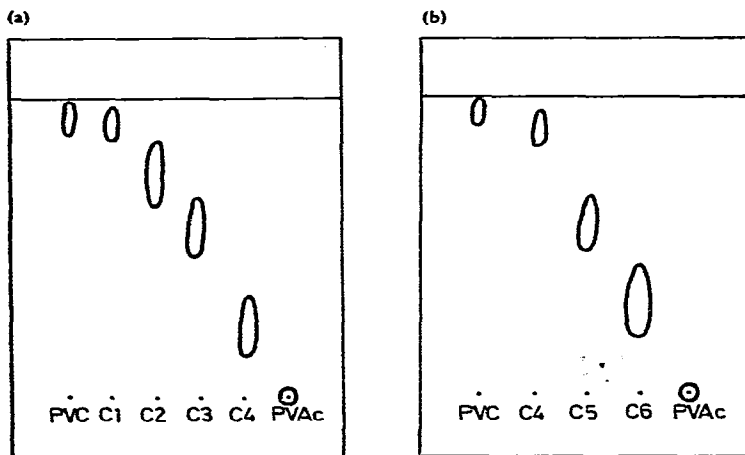


Fig. 1. Separation of VC-VAc copolymers according to their composition by isocratic elution. (a) Vinyl acetate content 6-15%; elution system DCE-*n*-heptane-THF (100:30:4); (b) vinyl acetate content 15-28%; elution system DCE-THF (100:5.5). (Kieselgel G plates, 10 × 20 cm).

To ascertain the effect of molecular weight on the separation, fractions of copolymer C3 and C4 were employed. The R_F values found (see Table VIII) confirmed that the molecular weight does not affect the separation under the given conditions within the limits of experimental error, *i.e.*, that VC-VAc copolymer can be separated with the elution system according to the content of vinyl acetate.

The possibility of the application of the gradient elution technique was tested with the solvent system DCE-MEK-carbon tetrachloride. The starting solvent in the separations was always 6 ml of DCE-carbon tetrachloride (1:1) and 6 ml of the mixture

TABLE VIII

EFFECT OF MOLECULAR WEIGHT ON TLC OF VC-VAc COPOLYMERS WITH THE ELUTION SYSTEM THF-DCE (KIESELGEL G)

THF to DCE ratio	R_F					
	C3a	C3d	C3f	C4a	C4c	C4f
2.5:100	0.90	0.91	0.90			
3.5:100				0.81	0.82	0.82

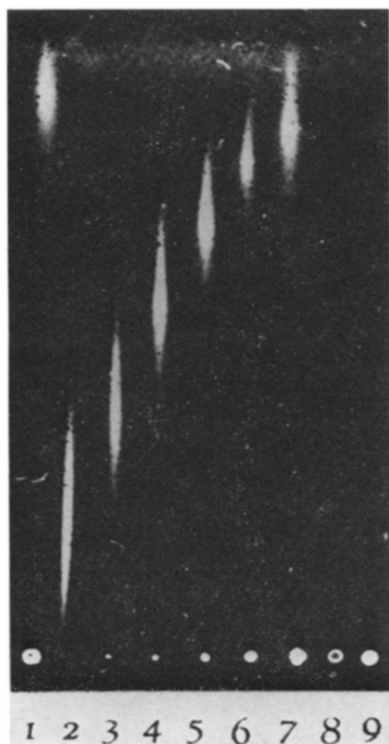


Fig. 2. Separation of VC-VAc copolymers by gradient elution: 1 = C1; 2 = C6; 3 = C5; 4 = C4; 5 = C3; 6 = C2; 7 = C1; 8 = PVC; 9 = PVAc.

DCE-MEK (5:2) was gradually added (0.24 ml/min) during development. The small plates were used for this experiment. The results obtained on KSK are shown in Fig. 2.

The results presented show that the separation of VC-VAc copolymers with various vinyl acetate contents by TLC is possible and that several solvent systems are suitable for this separation.

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