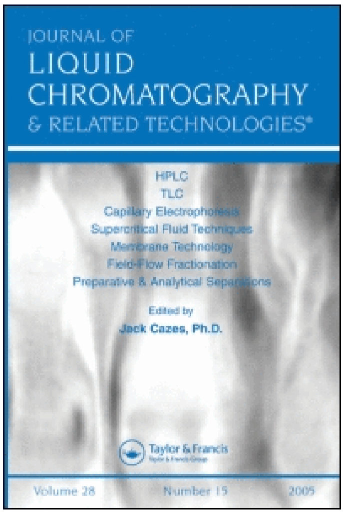

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IDENTIFICATION METHOD OF SYNTHETIC POLYMERS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Polyvinyl chloride (PVC), polyvinyl acetate (PVAc), and their copolymers and blends, polystyrene, poly(methyl, ethyl, and butyl) acrylates and methacrylates were dissolved in tetrahydrofuran (THF), respectively, and the solutions were injected into a column of silica gel having a pore diameter of 30 A and eluted with the mobile phases of THF, chloroform, ethyl acetate, methanol, methylethylketone, acetonitrile and 1,2-dichloroethane (DCE). Some polymers eluted from the column and the rest were retained in the column. The identification of the polymers was not based on the difference in the retention volumes of the polymers, but the elution of the polymers from or the retention in the column were a measure of the identification. This technique was termed as "On-Off Elution Method". Two retention mechanisms were proposed: hydrogen bonding between silica gel and the sample polymers, and the precipitation of polymers in the column. In case of the former, some polymers were retained in the column even though a good solvent to the polymers was used as the mobile phase. When poor solvents to the polymers were used as the mobile phases, the polymers were precipated in the column, except PVC with DCE. The physical blend of PVC and PVAc could be discriminated from the copolymer having the same composition by this procedure.

INTRODUCTION

High-performance liquid chromatography (HPLC) of polymers is recently taken interest in by several chromatographers and polymer chemists. Poly(alkyl acrylate) and poly(alkyl methacrylate) homopolymers and copolymers have been separated and detected by HPLC of silica gel/toluene-2-butanone/evaporative light-scattering detector (1) or /dichloroethane-ethanol/UV detector (2). Styrene-alkyl acrylate and styrene-alkyl methacrylate copolymers have been separated according to their composition by HPLC of slica gel/ chloroform-ethanol/UV detector (3,4). Styrene-acrylonitrile copolymers have been separated by high performance precipitation liquid chromatography (HPPLC) of silica-ODS/tetrahydrofuran-isooctane/UV detector (5). Polystyrene homopolymers have also been tried to separate according to their molecular weight by HPPLC of silica gel/dichloromethane-n-heptane or methanol (6). Theory and mechanism of the separation of polystyrenes have been discussed in detail (7-10).

Polymers and copolymers have been separatd by HPLC according to their molecular weights or compositions and the gradient elution method has usually been apllied. The difference of retention volume is the key of the identification of separated species. Because of the application of the gradient elution method to separate these polymers and copolymers, a differential refractive index detector (RI) cannot be used and an ultra-violet absorption detector (UV) can be used to detect the polymers having chromophors. The use of an evaporative light scattering detector is the only possible way to detect polymers having no chromophors by gradient elution HPLC (1).

The present paper reports the identification method of several homopolymers by HPLC using an RI detector. The identification of polymers in the present report is not based on the difference in retention volume of polymers. The phenomena whether the polymers are retained in the column or elute from the column have been used to identify the polymers. This technique is termed as "On-Off Elution Method". The composition of the mobile phase is constant in this method (isocratic elution) and thus an RI detector can be used and it is applied to the identification of polymers which do not absorb radiation in the UV region.

EXPERIMENTAL

Apparatus

A Jasco TRIROTAR high performance liquid chromatograph (Jasco Corporation, Hachioji, Tokyo, Japan) with an RI detector Model RI-401 (Waters Inc., Milford, MA, USA) was used. Silica gel with a pore size of 30 A and a mean particle diameter of 5 um (Nomura Chemical Co., Seto, Aichi 489, Japan) was packed in 4.6-mm-i.d.x25-cm-length stainless-steel tubing. The number of theoretical plates of the column was 3600 plates, which was obtained by injecting 0.1 mL of a 0.2% benzene solution in tetrahydrofuran (THF).

Samples

Polystyrene (PSt) SRM 706 was obtained from NIST (Washington, DC, USA), polyvinyl chloride (PVC) and P(VC-VAc) copolymers (VAc content 5.5% and 11.6%) from Mitsui Chemical Co., polyvinyl acetate (PVAc) from Nacalai Tesque Inc., respectively. Polymethyl acrylate (PMA), polyethyl acrylate (PEA), polybutyl acrylate(PBA), polymethyl methacrylate (PMMA), polyethyl methacrylate (PEMA), and polybutyl methacrylate (PBMA) were kindly supplied by Toa Gosei Co. PVAc, PMA, and PEA were dissolved in chloroform and precipitated in n-hexane. PMMA, PEMA, and PBMA were dissolved in chloroform and precipitated in methanol. Low molecular weight materials in PBA were removed by steeping PBA in n-hexane. PSt and

PVC were used without any purification processes. These polymers had weight average molecular weights between 10^5 and $3x10^5$.

Elution

Mobile phases used in this experiment were THF (0.05% butylated hydoxytoluene (BHT) included), chloroform ($CHCl_3$) (1% ethanol included), methanol (MeOH), ethyl acetate (AcEt), methylethyl ketone (MEK), acetonitrile (AcCN), and 1,2-dichloroethane (DCE). They were all guaranteed reagents and used without further purification. The flow rate of the mobile phases was 0.5 ml/min. Sample polymers were dissolved in THF in the concentration of 0.1% and the injection volume of the solution was 0.1 ml. Elution was performed at room temperature. After several injection of sample solutions, the column was washed with THF to remove all the sample polymers retained in the column.

RESULTS AND DISCUSSION

Elution Behavior of Polymers

Sample polymers used in the present experiment are all soluble in THF, and therefore, THF was selected as a solvent to dissolve them before injection into the column. Because, the purpose of the present study is to develop the indentification method of the sample polymers by the phenomena whether they elute from or are retained in the column with a specific solvent used as the mobile phase and therefore, it is preferable to use only one good solvent to dissolve all the sample polymers tested. When THF was used as the mobile phase, all the sample polymers eluted from the column without any interactions with the stationary phase.

Examples of elution behavior of the sample polymers in the mobile phase of chloroform are shown in Figure 1. The chromatog-

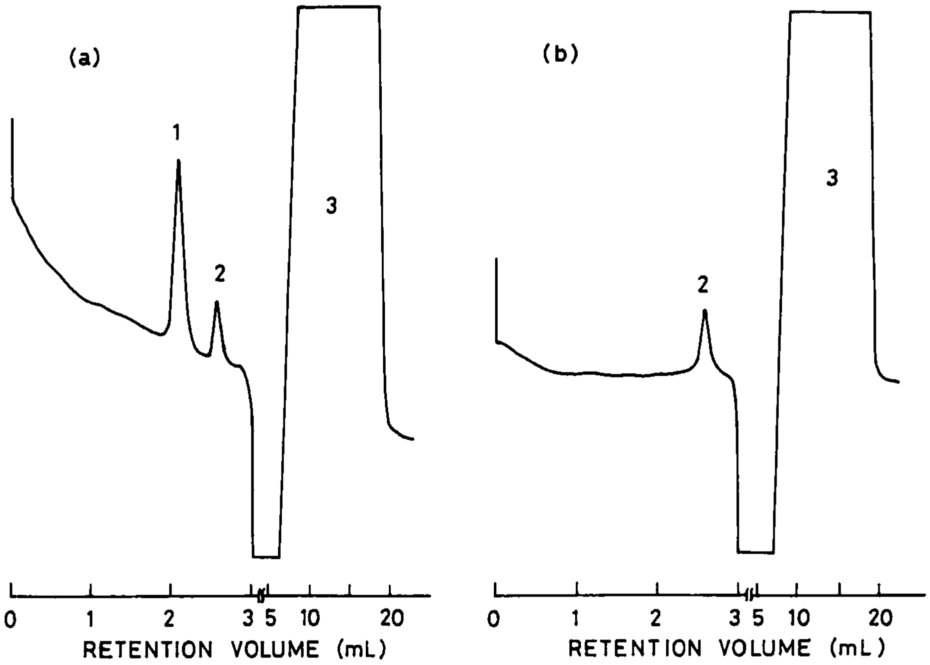

FIGURE 1. Chromatograms for PBMA and PEMA in the chloroform mobile phase: (a) PBMA; (b) PEMA; peak 1, PBMA; peak 2, additives in THF; peak 3, THF; attenuation of RI, x16.

ram for PBMA is shown in Figure 1, a and that for PEMA in Figure 1, b, respectively. Peak 1 is PBMA and is appeared at retention volume 2.05 ml which corresponds to the retention volume at the exclusion limit in size exclusion chromatography (V_o). Silica gel of pore size 30 A has the exclusion limit of 2000 molecular weight as polystyrene (11) and therefore, all the sample polymers eluted at the exclusion limit on this silica gel. Peak 2 is additives in THF and peak 3 is THF used to dissolve the sample polymers. Low molecular weight materials such as additives in THF could enter the pore of the silica gel and therefore, eluted at the retention volume 2.8 ml which corresponds to the volume of the mobile phase in the column ($V_o + V_i$ (= V_M)). This peak would

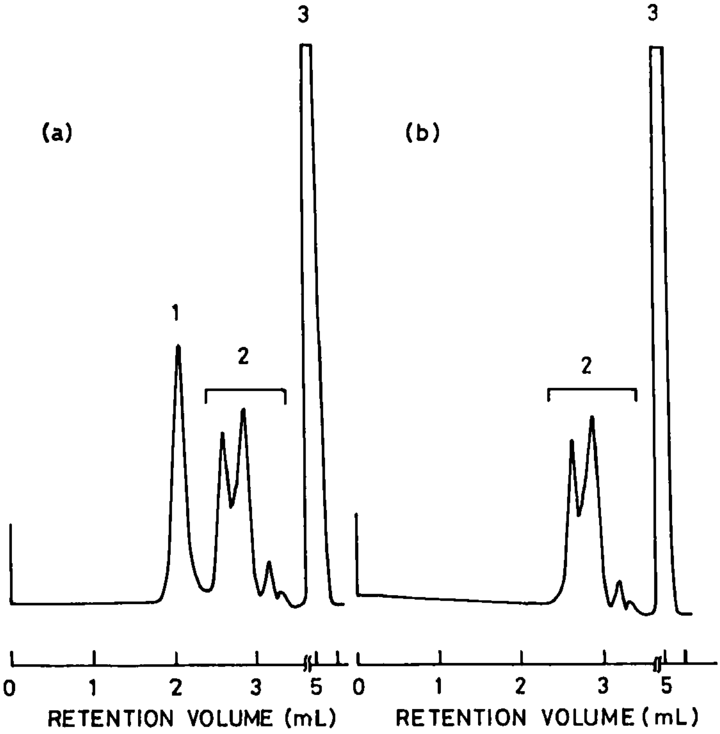

FIGURE 2. Chromatograms for PEA and PMA in the ethyl acetate mobile phase: (a) PEA; (b) PMA; peak 1, PEA; peaks 2, additives in THF; peak 3, THF; attenuation of RI, x16.

disappear or get smaller when the freshly prepared solvent is used for both the mobile phase and the sample solution. The THF peak was negative first and then became positive. PEMA was retained in the column and was not appeared at V_0 of the column system.

Oneofthecharacteristics of this method istouse the silica gel having a pore diameter of 30 A, and by using this silica gel, a polymer peak could be clearly separated from peaks originated from THF used for the dissolution of samples. This silica gel is commercially available. On 60-A or 100-A pore-size silica gel, both peaks, a polymer peak and a solvent related peak, com-

TABLE I.

The Elution from or The Retention in a Column for The Sample Polymers with Several Mobile Phases

Mobile phase	Polymer PSt	PVC	PVAc	PMA	PEA	PBA	PMMA	PEMA	PBMA
THF	o	o	o	o	o	o	o	o	o
$CHCl_3$	o	x	x	x	x	o	x	x	o
AcEt	o	o	x	x	o	o	o	o	o
MeOH	x	x	o	x	o	x	x	x	x
MEK	o	o	o	o	o	o	o	o	o
AcCN	x	x	x	o	x	x	o	x	x
DCE	o	o	x	x	x	x	x	x	x

Note: (o), eluted from the column; (x), retained in the column.

bined in one peak and the confirmation of polymer elution became uncertain.

Sample polymers which eluted from the column with chloroform are PSt, PBA and PBMA, and the rest of the sample polymers were retained in the column. Although PVAc, PMA, PEA, PMMA, and PEMA are all soluble in chloroform, these polymers were retained in the column with the mobile phase of chloroform containing 1 % ethanol and began to elute from the column with increasing the content of ethanol in chlororom (3, 4). The retention of the polymers in the column is due to the hydrogen bonding between the silanol groups on the surface of silica gel and the carbonyl groups of the polymers (12). On the contrary, PVC was insoluble in chloroform and therefore, it was assumed that PVC precipitated in the column (the phase separation), though the pressure increase due to the precipitation of PVC in the column was not observed.

Figure 2 is the example of chromatograms obtained with ethyl acetate as the mobile phase. The chromatogram for PEA is shown in Figure 2, a and that for PMA in Figure 2, b. Peak 1 is PEA, peaks 2 are additives in THF, peak 3 is THF, and no peak for PMA. PEA eluted from the column and PMA was retained in the column.

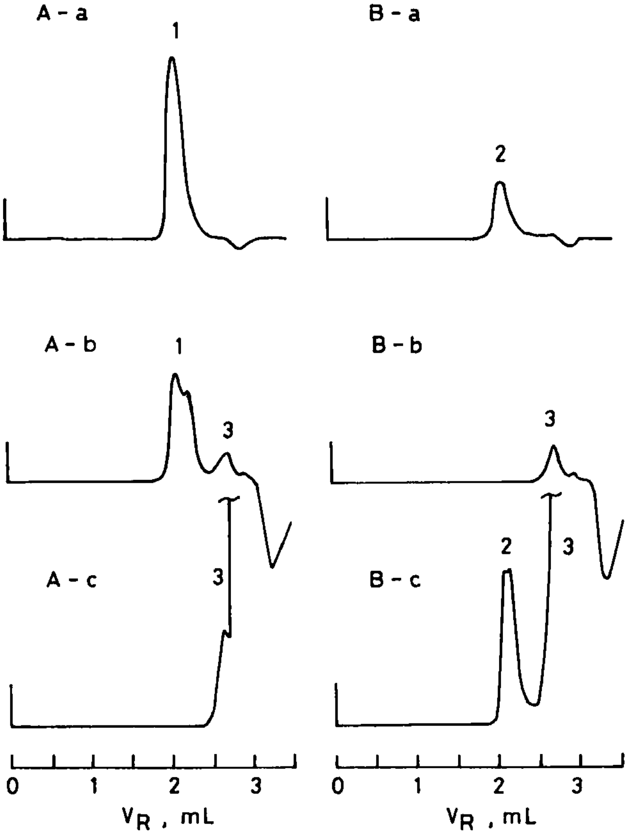

FIGURE 3. Chromatograms of PVC and PVAc in three mobile phases. Polymer: A, PVC; B, PVAc; mobile phase: a, THF; b, DCE; c, methanol; peak identification: 1, PVC; 2, PVAc; 3, THF and additives in THF.

PVAc was also retained in the column and the rest of the sample polymers eluted from the column.

PVAc and PEA eluted from the column with methanol and the rest of the sample polymers were retained in the column. In order to know the mechanism of the retention of the sample polymers in the column, polymer solutions were added to methanol dropwise and the formation of precipitates was exmined. The solutions of the

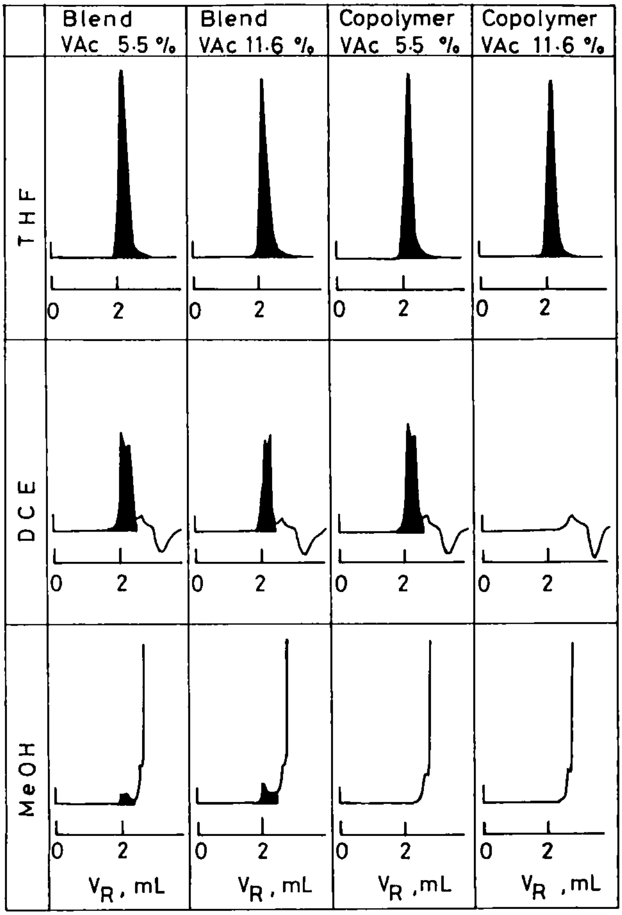

FIGURE 4. Schematic diagrams of the copolymers and the physical blends of PVC and PVAc. VAc contents were 5.5% and 11.6%.

sample polymers retained in the column formed the precipitates in methanol. This precipitation experiments suggest that the retention of the polymers was due to the formation of the precipitates in the column (the phase separation).

The elution behavior of the sample polymers in MEK as the mobile phase was the same to the mobile phase THF and all the sample polymers eluted from the column. PMA and PMMA eluted from the column with acetonitrile as the mobile phase and the rest of the sample polymers were retained in the column. PVAc, PMA, PEA, PMMA, and PEMA were soluble in acetonitrile and the rest were insoluble. Therefore, the retention of PVAc, PEA and PEMA in the column was assumed to be due to the formation of the hydrogen bonding between the silanol groups and the carbonyl groups as in the case of chloroform mobile phase and that of the rest of the sample polymers due to the precipitation in the column.

When DCE was used as the mobile phase, PSt and PVC eluted from the column and the rest were retained in the column. Only PVC was insoluble in DCE and the rest of the sample polymers were soluble. The retention of the sample polymers was, therefore, estimated to be due to the formation of hydrogen bonding between the silanol groups and the carbonyl groups (4). In order to examine the reason of the elution of PVC, the precipitation experiment was performed as follows: one drop of 1% PVC solution in THF was placed in 5 ml DCE. No precipitation was found. Therefore, the reason why PVC eluted from the colum in spite of PVC being insoluble in DCE is assumed that THF moleclules in the PVC solution surround PVC molecules firmly and DCE molecules are not replaced by THF molecules during the elution of PVC moleclules from the column.

The elution behavior of the sample polymers with different mobile phases is summarized in Table I. An example for the identification procedures of polymers is illustrated in a mixture of PSt, PVC, PVAc, and PMA as follows: a polymer eluted with chloroform is PSt, that with methanol PVAc, that with acetonitrile PMA, and that retained in the column with these three solvets is PVC.

Inagaki (13) introduced the separation techniques of homopolymers and copolymers by thin-layer chromatography (TLC) and showed the results of the chromatographic behavior of some homopolymers on silica gel plates with several developing solvents. Sample polymers used in his experiment as well as our experiment were PSt, PVC, PVAc, PMMA, PEMA, PBMA, and PMA, and similarly, the mobile phase solvents used in both experiments were THF, chloroform, MEK, and methanol. The migration of the polymers to the upper side in TLC corresponds to the elution of the polymers from the column in HPLC and the immobility of the polymers at the starting point in TLC corresponds to the retention of the polymers in the column in HPLC. His results were similar to our results except PBMA with chloroform. PBMA eluted from the column in our results and remained immobile by TLC. The difference is mainly due to the difference in the adsorption strength of silica gel and /or the content of ethanol in chloroform added as the stabilizer.

Elution Behavior of Copolymers and Blends of PVC and PVAc

When THF was used as the mobile phase, PVC and PVAc eluted from the column without any interactions with the stationary phase. The example is shown in Figure 3, A-a for PVC and B-a for PVAc. When DCE was used as the mobile phase, PVC eluted from and PVAc was retained in the column. The results are shown in Figure 3, A-b and B-b. Peak 1 in Figure 3, A-b is PVC and appeared at V_0, but no peak for PVAc in Figure 3, B-b. A positive peak in peaks 3 is additives in THF and a negative peak is THF. Figure 3, A-c and B-c are the chromatograms for PVC (A-c) and PVAc (B-c) obtained with methanol as the mobile phase. PVAc eluted from the column (peak 2) and was appeared at V_0 and PVC was retained in the column and was not observed on the chromatogram. A solvent peak (peak 3) was separated from a polymer peak (peaks 1 and 2) and didn't disturb the confirmation of PVC and PVAc peaks.

The results in Figure 3 suggest the possibility of the separation of PVC, PVAc and their copolymers according to the compositions, if a gradient elution method was applied with DCE and methanol. They would appear at different retention volumes and P(VC-VAc) copolymers would elute at retention volumes between those of PVC and PVAc. However, an evaporative mass detector must be used to detect the solutes eluted from a column (1), because they do not have UV absorption.

In the present report, polymers can be identified utilizing the phenomena whether the polymers elute from the column or are retained in the column. Figure 4 is the schematic diagrams of P(VC-VAc) copolymers and the mixtures of PVC and PVAc having the VAc content of 5.5% and 11.6%. The copolymers and the blends appeared at V_0 with the mobile phase of THF, showing all the solutes eluted from the column. With the mobile phase of DCE, two blends and the copolymer having a VAc content of 5.5% appeared at V_0 and the copolymer having a VAc content of 11.6% was retained in the column. Portions eluted from the column were only PVC for the blends and the whole for the copolyemr. With the mobile phase of methanol, two copolymers were retained in the column and only a small peak for the blends could be observed at V_{Ro}. The portion eluted from the column was PVAc in the blends.

It can be said from the results shown in Figure 4 that the copolymers having a VAc content of at least 11.6% and less than that were retained in the column with the mobile phase of methanol and that the copolymers having a VAc content of at least 11.6% and more than that were retained in the column with the mobile phase of DCE.

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