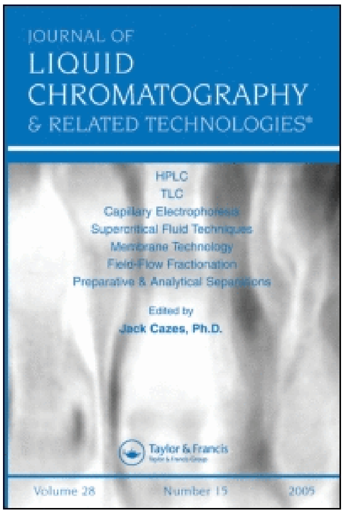

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DETERMINATION OF COMPOSITIONAL HETEROGENEITY OF POLYAMIDE COPOLYMERS

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ABSTRACT

A gel permeation chromatograph equipped with dual detectors provides very useful information on compositional and molecular weight distributions. One copolymer composed of nylon 12 and polytetramethylene ether glycol, and the other of nylon 6 and natural rubber were discussed in this study. By trifluoroacetylation of the amide group, these polymers became soluble in common solvents such as dichloromethane and tetrachloroethane. Good chromatograms were obtained using these solvents for the above copolymers. At the same time, the compositional heterogeneity was determined from the chromatograms obtained with refractive index and ultraviolet detectors.

INTRODUCTION

Gel permeation chromatrography (GPC) is currently the method of choice for measuring the molecular weight distributions of synthetic polymers. In GPC chromatograms, the abscissa is usually expressed by "elution count" and the ordinate by a quantity proportional to weight fraction, which is monitored by a refractive index (RI) detector. If other detectors, such as ultraviolet (UV) detector and/or light scattering apparatus are used, additional information will be obtained. GPC, with dual detectors, is very useful for obtaining information about

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compositional heterogeneity of copolymers.[1,2] It goes, without saying, that the compositional variation curve in the GPC technique does not exhibit the true compositional distribution.[3] However, the larger the magnitude of the variation becomes, the wider is the breadth of the compositional distribution in a similar series of copolymers.

Recently, various polyamide copolymers have been synthesized.[4,5] Some of them are commercially available. A suitable eluent system must be found for the GPC analysis of these copolymers. Unfortunately none has been found yet, even for polyamide homopolymers, except for a few special cases.6-9)

Trifluoroacetylation is an excellent derivatization technique for dissolving nylons in common solvents such as tetrahydrofuran, dichloromethane and tetrachloroethane. This method was presented by Jacobi et al. several years ago.[10] Using the above solvents, good chromatograms are expected for these copolymers under ordinary experimental conditions. This method was reexamined by us for nylon 6 and 66. Good, reproducible chromatograms were obtained using dichloromethane as eluent, when we were sufficiently careful with the reaction conditions. Polyamide copolymers have more or less random compositional distribution. Therefore, homopolymers composed of component monomers should, in principle, be soluble in solvent by assuming the extreme case, because such homopolymers are expected to be present in the copolymerization products. The application of trifluoroacetylation to polyamide copolymers is, therefore, expected to be successful. At the same time, the compositional variation curve should be able to be obtained by using the relationship between the areas of the RI or the UV curve and polymer concentration.

This study is concerned with GPC of polyamide copolymers via trifluoroacetylation.

EXPERIMENTAL

Copolymers

Copolymer I: this copolymer is commercially available. It is prepared with ω-aminododecanoic acid (67.4mol%), decane dicarboxylic acid (18.3mol%) and polytetramethylene ether glycol (PTG, 14.3mol%). In practice, various structure will be considered, differing in the position where dicarboxylic acid reacts. For example, the chemical structure of this copolymer is expressed as $-\!\left[CO(CH_2)_{11}NH\right]_n-CO(CH_2)_{10}COO\!\left[(CH_2)_4O\right]_m-$. These components were confirmed by hydrolysis and ^1H-NMR. Further, the structure was also reconfirmed by synthesis according to patents$^{11-12)}$.

Copolymer II: this copolymer was prepared by mixing mechanically, on a laboratory scale, natural rubber, nylon 6 and a small amount of phenol resin. Thirty three weight percent of nylon 6 is contained in this copolymer. The sample is not homogeneous in a sense of chemical structure, but contains component homopolymers together with grafted copolymer. The molecular weight of the original natural rubber was estimated to be 17000 ($\bar{M}_v$). However, the rubber component will have a lower molecular weight after mixing. The molecular weight of nylon 6 is 15600 ($\bar{M}_n$), which was determined by vapor pressure osmometry.

N-trifluoroacetylation (N-TFA)

Approximately one gram of nylon copolymer was suspended in 30ml of dichloromethane (Copolymer I) or 1,1,2,2-tetrachloroethane (Copolymer II). After introduction of 10g of $(CF_3CO)_2$, the reaction mixture was refluxed for 24hr. The solvent, CF_3COOH and unreacted $(CF_3CO)_2$ were removed by a flash evaporator. Sticky N-TFA polyamide copolymer was quickly subjected to analysis by GPC. Otherwise, N-TFA copolymer was stored in solution in an ampoule. Moisture must be completely excluded. For example, when exposed to air for only one hour, the copolymer reverts to the original material. This conversion is clearly demonstrated by infrared spectra (Figure 1). The water content of dichloromethane used here was less than 0.003wt%, and that of tetrachloroethane was less than 0.006wt%.

Preparation of model compound

A model compound was synthesized for one of the components in Copolymer I: the compound, corresponding to PTG and DDA, was prepared from PTG and n-hexanoic acid. PTG was supplied by Nippon Polyurethane Industries, Ltd., Japan and n-hexanoic acid by Kishida Chemical Co., Japan. After introduction of 1mol of PTG and 2mol of n-hexanoic acid into a flask, the mixture was allowed to react for 3hr at 180°C under nitrogen atmosphere, followed by reaction for an additional 22hr at 220°C under a reduce pressure. The reaction product was confirmed by an infrared spectrum. The product has the structure

$$CH_3(CH_2)_4COO\!\left[(CH_2)_4O\right]_m-CO(CH_2)_4CH_3 \quad (m \approx 16).$$

GPC analysis

A home-made GPC apparatus was used for recording chromatograms. The GPC signals were detected with a Showadenko Model SE-11 RI detector and a Union Giken Model SM-303 UV detector. Dichloromethane CH_2Cl_2 was employed as eluent for Copolymer I, and 1,1,2,2-tetrachloroethane CH_2Cl_2 $-CH_2Cl_2$ for Copolymer II. The wavenumber of 230nm was chosen for UV detection of Copolymer I and that of 260nm for Copolymer II. Two columns packed with cross-linked polystyrene gel Shodex AD-80M/S were employed, which had separation performance ranging from 10^2 to 10^7 in molecular weight of polystyrene. The apparatus was operated with a flow rate of 1.0ml/min, at ambient temperature. In chromatograms, one elution count corresponded to nearly 0.43ml.

Calculations

The area of the UV curve I_{UV} is expressed as a function of content of components A and B.

$$I_{UV} = G_c\left[U_A W_A + U_B(1 - W_B)\right] \cdots\cdots (1)$$

where G_c is the weight of polymer in injected solution, W_A is the weight fraction of component A in the polymer sample. U is the proportionality constant between UV detector reading and the weight fraction of components.

The area of the RI curve I_{RI} is expressed in a similar manner.

$$I_{RI} = G_c\left[R_A W_A + R_B(1 - W_B)\right] \cdots\cdots (2)$$

where R is the proportionality constant between the RI detector reading and the weight fraction of components. These relationships hold for each count interval in a chromatogram. The weight fraction $(W_A)_i$ of the component A in the i-th interval is derived from eqs.(1) and (2).

$$(W_A)_i = (D_i R_B - U_B)/(\Delta U - D_i \Delta R) \cdots\cdots (3)$$

where

$$\Delta U = U_A - U_B$$
$$\Delta R = R_A - R_B$$

$$D_i = (I_{UV})_i/(I_{RI})_i$$

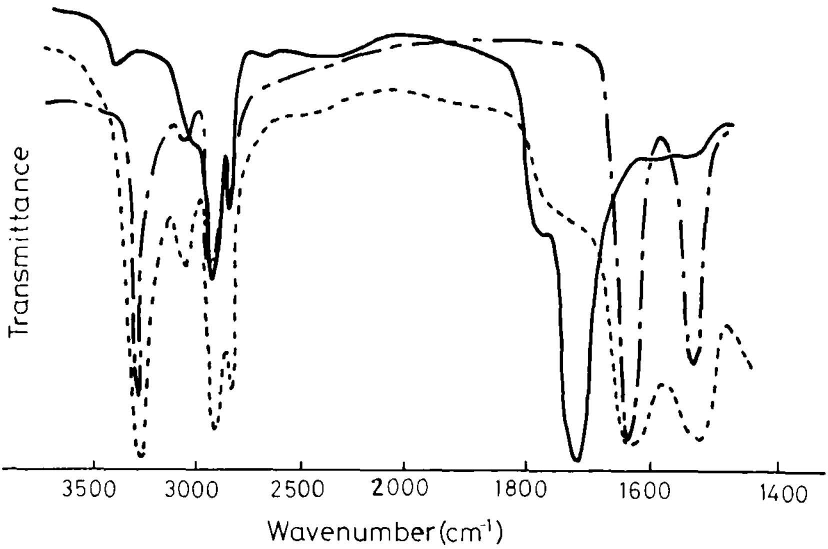

FIGURE 1. Infrared spectra of nylon 6.
——— : N-TFA nylon 6, -----: N-TFA nylon 6 after exposing to air for one hour, —— - : original nylon 6.

Since two detectors were in series, their output did not coincide on the abscissa. This difference was corrected, when the areas for each count interval were taken from a chromatogram.

RESULTS

Copolymer I

The areas of the UV curves were measured as a function of concentration of N-TFA nylon 12 (component A) and the model compound (component B). The area for the component B was not detected, when the UV detector was employed. The areas of the RI curves were also measured. These results are shown in Figure 2. The weight fraction of the component A in the i-th interval is expressed as folloows.

$$(W_A)_i = D_i/(4.134 - 0.182D_i) \cdots\cdots\cdots (4)$$

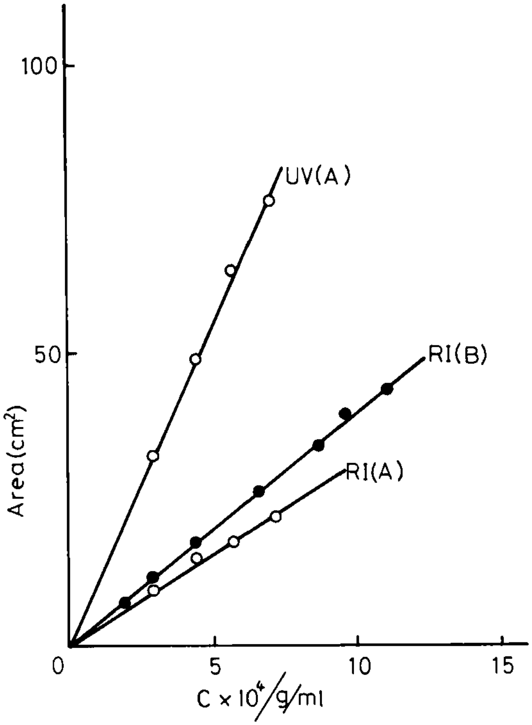

FIGURE 2. Response areas for components A and B in Copolymer I.

After trifluoroacetylation of Copolymer I, the compositional variation curve was obtained from the chromatograms according to eq.(4). The result is shown in Figure 3 together with the chromatograms. The average content of N-TFA nylon 12 is 50.7wt%, which was obtained from the above variation curve. This value is in good agreement with the calculated value 49.7wt%. The curve implies that this copolymer has fairly large compositional distribution. The same technique will be generally applicable to the copolymers composed of nylon and polyether in any compositional ratio.

Copolymer II

The main components of this copolymer are natural rubber (component A) and nylon 6 (component B). The effect of the small amount of phenol resin was negligible in the optical density at 260nm. After

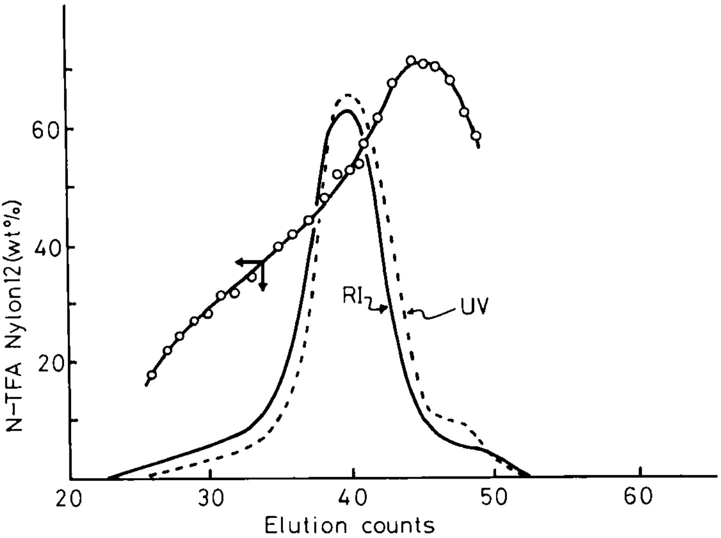

FIGURE 3. Chromatograms obtained by dual detectors and compositional variation curve in Copolymer I.

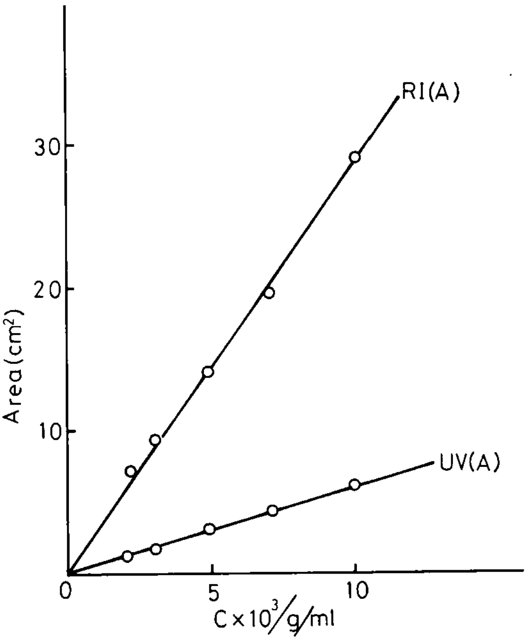

FIGURE 4. Response areas for component A in Copolymer II.

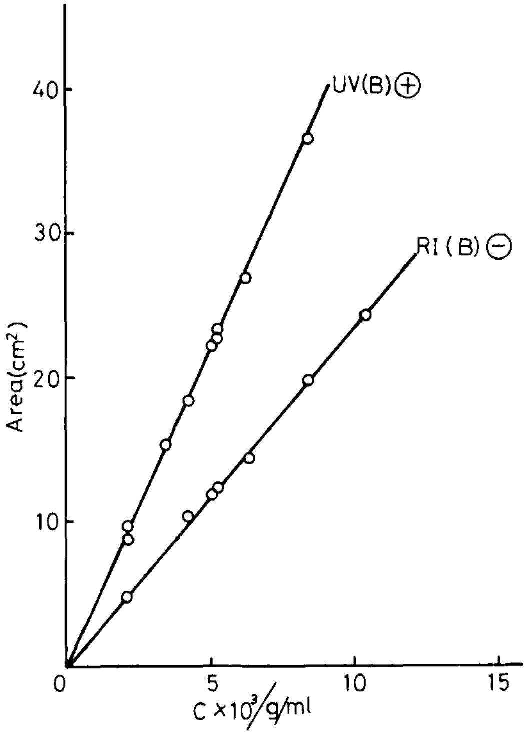

FIGURE 5. Response areas for component B in Copolymer II. The sign of the ordinate is minus when the RI detector is used.

trifluoroacetylation of nylon 6, the areas of the UV and the RI curves were plotted against the amount of N-TFA nylon 6. The same plots were performed for natural rubber without any pretreatment. The results are shown in Figure 3. The weight fraction of the component A in the i-th interval is expressed as follows.

$$(W_A)_i = (2.32D_i + 4.44)/(3.34 + 5.20D_i) \cdots\cdots\cdots\cdots (5)$$

After trifluoroacetylation of Copolymer II, the compositional variation curve was obtained from the chromatograms according to eq.(5). The result is shown in Figure 4 together with the chromatogram, which was

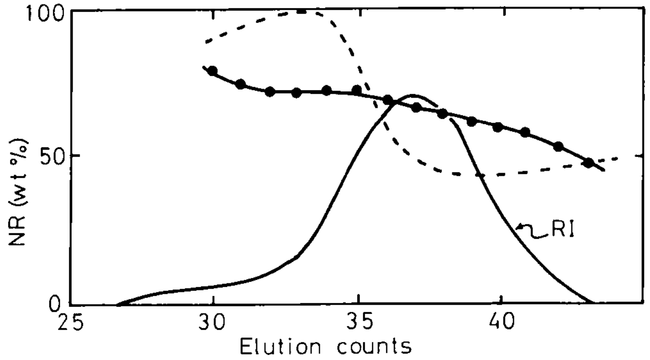

FIGURE 6. Chromatogram obtained by RI detector and compositional variation curves.
——— : compositional variation curve for Copolymer II,
- - - - : that for blend sample of natural rubber and N-TFA nylon 6 (2 : 1 by weight).

obtained by the RI detector. The broken line indicates the compositional variation curve for a blend sample of natural rubber and N-TFA nylon 6 in the same ratio as for Copolymer II.

The compositional variation curve of the grafted copolymer, i.e., Copolymer II, is undoubtedly different from that of the blend sample. The same technique was applied to another sample, which was the residue of Copolymer II by extraction with toluene and hexafluoroisopropanol. The compositional variation curve of the sample was very similar to that shown above. The grafted copolymer is expected to have fairly narrow compositional distribution.

REFERENCES

1. Runyon, J. R., Barne, D. E., Rudd, J. F. and Tung, L. H., J. Appl. Polym. Sci., 13, 2359(1969)

2. Adams, H. E., Separation Sci., 6, 259(1971)

3. Ogawa, T., J. Appl. Polym. Sci., 23, 3515(1979)

4. Tokiwa, Y., Suzuki, T. and Ando, T., J. Appl. Polym. Sci., 24, 1701(1979)

5. Wondraczek, R. H. and Kennedy, J. P., J. Polym. Sci., Polym. Chem. Ed., 20, 173(1982)

6. Drott, E. E., "Liquid Chromatography of Polymers and Related Materials", Cazes, J., Ed., p.41(1977), Marcel Dekker, New York

7. Provder, T., Woodbrey, J. C., Clark, J. H. and Drott, E. E., Adv. Chem. Ser., No.125, 117(1973)

8. Ogawa, T., Sakai, M. and Ishitobi, W., J. Polym. Sci., Polym. Chem. Ed., submitted.

9. Sakai, M. and Ogawa, T., Bunseki Kagaku, 32, 259(1983)

10. Jacobi, E., Schuttenberg, H. and Schulz, R. C., Makromol. Chem., Rapid Commun., 1, 397(1980)

11. Chemische Werke Hüls, Japanese Pat. 57-24808 (May 26, 1982)

12. Chemische Werke Hüls, Japanese Opened Pat. 56-65026 (June 2, 1981)