Solvent Extractive Fractionation of Ziegler Polystyrene

By Akira YAMADA, Yoshio YAMAMURO and Masaya YANAGITA

(Received December 24, 1960)

In the preceding paper[1], one of the authors pointed out the possibility of the extractive fractionation of Alfin Polystyrene with solvents other than acetone[2], ethyl methyl ketone[2,3] and benzene[4]. In the present paper, the authors wish to report that the polystyrene samples polymerized by the Ziegler catalyst were separated into two parts, i. e., crystalline and amorphous, by extractive fractionation with several solvents.

The solvents have been selected on the basis of the results of the solubility-test and the solvent extractive fractionation in the previous work[1]. The densities and the ratios of the intensities of the infrared spectra (D_{984}/D_{1028}) of the extractive residues were measured in order to check the extractive fractional ability; the molecular weights and melting points of the residues were also measured.

One of the authors has reported previously that the infrared intensity (D_{984}) was proportional to the X-ray crystalline content[5]. However, as shown in Fig. 1, the X-ray crystallinity percentage with a vibration of densities between 1.05 to 1.08 did not vary in proportion to the infrared ratio. Accordingly, X-ray diagrams have not been used in the present studies.

The physical properties measured are summarized in Table I.

It is seen that of the densities of the extractive residues resulting from the hot solvent treatment, the lowest is for ethyl methyl ketone. The decreasing order in the case of hot extraction is; tetrahydrofuran, ethyl acetate, dioxane, cyclohexanone and ethyl methyl ketone. In the cold extraction, however, the highest value was obtained by using ethyl methyl ketone, and this was followed by benzene, toluene, ethyl acetate and tetrahydrofuran.

The ratio of the infrared intensities (D_{984}/D_{1028}) is linearly proportional with the density between 1.05 to 1.08, as is shown in Fig. 1. It is considered that these infrared ratios show the difference in crystallinity (or tacticity) of each residue. The decreasing order of the ratio in the hot extraction was as follows: dioxane, tetrahydrofuran, ethyl acetate and cyclohexanone. In the cold extraction, the order was benzene, ethyl methyl ketone, ethyl acetate, toluene, tetrahydrofuran and ether.

The relation of the molecular weight to the fractional weight percentage of residue is shown in Fig. 2.

The dotted line and the curved line (from right to left in Fig. 2) show the over-all process of the extraction. In the initial step, it is observed that the average molecular weight

---

[1] A. Yamada, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 2204 (1961).

[2] G. Natta, *Makromol. Chem.*, **16**, 213 (1955).

[3] F. Danusso and G. Moraglio, *J. Polymer Sci.*, **24**, 161 (1957).

[4] N. Yamazaki, *Chem. High Polymers* (*Kobunshi Kagaku*), **15**, 49 (1958).

[5] M. Takeda, K. Iimura, A. Yamada and Y. Imamura, This Bulletin, **33**, 1219 (1960).

TABLE I. PHYSICAL PROPERTIES OF THE EXTRACTIVE RESIDUES; DENSITY, MOLECULAR WEIGHT (mol. wt.) AND MELTING POINT (m. p.)

Extraction type	Solvent	Extractive hr./g.	Extractive fractional wt. % of residue	Density	IR ratio[a] %	Mol. wt. ×10⁻⁴	M. p. °C
Hot	Ethyl methyl ketone	5	84	1.078	63	204	240
	Cyclohexanone	7	27	1.078	50	176	245
	Tetrahydrofuran	15	17	1.085	64	—	230
	Dioxan	5	61	1.081	66	189	235
	Ethyl acetate	5	91	1.082	57	232	240
Cold	Ethyl methyl ketone	20	93	1.081	55	220	240
	Ether	21	93	?	31	230	240
	Tetrahydrofuran	20	5	1.073	46	—	240
	Ethyl acetate	20	92	1.075	53	214	240
	Benzene	20	40	1.080	56	257	240
	Toluene	20	91	1.078	51	227	240

a) The IR ratio for atactic polystyrene had been presented as 16.

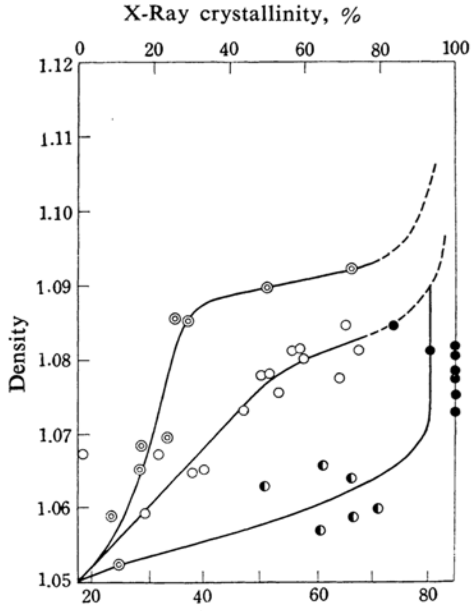

Fig. 1. Relationship between density and X-ray crystallinity, IR ratio and/or melting point.

◎ X-Ray crystallinity previously reported[5].
○ IR ratio in this paper.
● Melting point in this paper.
◐ Melting point of Alfin polystyrene (A. Yamada, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **64**, 2208 (1961).

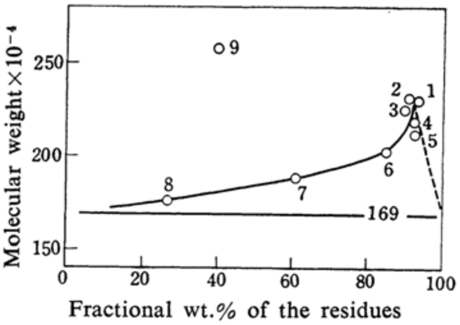

Fig. 2. Relationship between molecular weights and extractive fractional wt. % of residues. Molecular weight of the original sample is 169×10⁴. The number in the figure shows hot(h) or cold(c) solvent extraction respectively;

1 c-ether
2 h-ethyl acetate
3 c-toluene
4 c-ethyl methyl ketone
5 c-ethyl acetate
6 h-ethyl methyl ketone
7 h-dioxan
8 h-cyclohexanone
9 c-benzene

of the residue increases because the lower molecular weight portion was extracted, but thereafter the molecular weight gradually decreases on account of the atactic, higher molecular weight portion that is subsequently extracted. The several extractive types 1 to 6 in Fig. 2 seem to resemble closely those of the hot or cold ethyl methyl ketone extraction. Cold benzene extraction especially, as is seen in Fig. 2, differs from the other in respect to the dependency of the molecular weight on the solvent extractive fractionation.

The residues have a higher melting point, and no information is offered to account for the differences in residues (see Table I).

From the above-described results, it may be considered that the solvent extractive ability in hot extraction decreases in the order: tetrahydrofuran dioxan, ethyl methyl ketone and ethyl acetate. In the cold extraction the order is: benzene, ethyl methyl ketone, ethyl acetate and toluene. Cold benzene extraction, however, was an exception case.

Experimental

Ziegler Polystyrene. — A four-necked flask with a mechanical stirrer was filled with dried nitrogen. Then 200 ml. of dried isooctane, 13 ml. of titanium tetrachloride and 25 ml. of triethyl aluminum ($Al/Ti=3.1$) were poured through medical syringes. While the temperature was maintained at 80°C, 500 ml. of freshly distilled styrene monomer diluted with 500 ml. of dried benzene was added dropwise over a six-hour period. After heating the mixture for 18 hr. at 80°C while stirring it, ethanolic hydrogen chloride was poured into the flask at 0°C. The dried crude polymer was obtained in a yield of 88%. The lower molecular weight portion was discarded by hot acetone extraction. After filtration of the small amount of residue, the filtrate was reprecipitated with methanol. The fine polymer was obtained in a yield of 11%.

Treatment with *n*-Heptane[6].—Before extraction, the sample was treated with boiling *n*-heptane for five hours and then cooled gradually to room temperature.

Extraction.—In the hot extraction, a Soxhlet apparatus was used at a temperature several degrees below the boiling point of the solvent. In the cold extraction, a Soxhlet-type apparatus equipped with a drying tower was used at room temperature (15~20°C).

Density. — A floatation method with a sodium chloride aqueous solution was used for the measurement of the density at 25°C. The measurement error is ±0.0005. The sample used was the same as that used for infrared measurement.

Measurement of Infrared Spectra.—Film specimen 0.05 mm. in thickness were prepared by casting on a mercury surface a chloroform solution that had been prepared by heating it in a sealed tube at 100°C. Before the measurement, the films were annealed at 200°C. The infrared spectra were measured in the region of 3500~700 cm^{-1} using a Nippon Bunko DS-201 spectrophotometer.

Molecular Weight. — The molecular weight was determined from viscosity measurements in benzene solution (concentration (C); 0.4 g./100 ml.) at 25°C. The molecular weight (M); was computed using the two following equations, 1[7] and 2[8]:

$$[\eta]=3(\eta_r^{1/3}-1)/C \qquad (1)$$

$$[\eta]=1.06\times10^{-4}M^{0.735} \qquad (2)$$

where η_r is the relative viscosity and $[\eta]$ is the intrinsic viscosity.

Melting Point.—Determined as the point of clearance or initial flow using a Shimadzu melting point apparatus.

Materials.—The solvents were purified by the usual methods. The boiling points are shown in parentheses: ethyl methyl ketone (79.6~79.8), cyclohexanone (154.5~156.2), tetrahydrofurane (66), dioxane (100.5~101.2), ethyl acetate (76.9~77.1), ether (34.5), benzene (79.5~79.8) and toluene (110.2~110.5).

Summary

The solvent extractive fractional ability has been described, using Ziegler polystyrene as sample. The order in hot extraction is tetrahydrofuran > dioxane > ethyl methyl ketone ≥ ethyl acetate, while that in cold extraction is benzene ≫ ethyl methyl ketone ≥ ethyl acetate = toluene.

The authors wish to express their sincere thanks to Mr. Toshihide Ishikawa for his help in this experiment and also to Mitsui Chemical Ind. Co. for the supply for triethyl aluminum.

Department of Polymer Chemistry
The Institute of Physical and
Chemical Research
Komagome, Bunkyo-ku, Tokyo

---

[6] J. L. R. Williams, W. J. Dunkam, J. V. DenBergh and K. Dulmage, *J. Am. Chem. Soc.*, **78**, 1260 (1956).

[7] I. Sakurada, *Chem. High Polymers* (*Kobunshi Kagaku*), **2**, 260 (1945).

[8] F. Danusso and G. Moraglio, *J. Polymer Sci.*, **24**, 161 (1957).