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ABSTRACT

Graft copolymer of poly(phenyl vinyl sulfide) and methyl methacrylate was obtained. The isolation of graft copolymer was carried out by the fractional precipitation method. The isolated polymer was confirmed to be a graft copolymer by IR spectra and T_g determinations. Graft copolymerizations of poly(phenyl vinyl sulfide) with vinyl acetate, acrylonitrile, acrylamide, and acrylic acid were also carried out, but the separation of graft

copolymer in these cases was difficult, and satisfactory results could not be obtained.

INTRODUCTION

There have been numerous investigations of photochemical reactions of organic sulfur compounds [1]. It is also known that the sulfide linkage is easily broken down to thiyl radical [2].

On the basis of this photochemical behavior of sulfur compounds, Okawara [3, 4] has thoroughly investigated poly(vinyldialkyl dithiocarbamates). In the field of graft copolymerization of sulfide compounds, Otsu [5] prepared several polymers by reaction with tetraethylthiuram disulfide and grafting with a second monomer by a photochemical method.

Since 1967, we have been studying the polymerization of phenyl vinyl sulfide (PVS) and its reactivity. The polymerization character of PVS [6, 7] and photochemical behavior [8] of PVS have been clarified: the photochemical reaction of PVS leads to the scission of the carbon-sulfur linkage and formation of vinyl and thiyl radicals.

Therefore, the application of this photochemical reaction of PVS to the graft copolymerization would be expected to yield a new graft-copolymer. For this reason, PVS was polymerized as a base polymer, and the photochemical scission of sulfide linkages in poly-PVS (PPVS) generated carbon and thiyl radicals. Grafting on the carbon radical produced a new polymer, a graft copolymer of PPVS and methyl methacrylate (MMA). This PPVS graft copolymer is expected to have an interesting character, because it has an unchanged sulfide bond which is easily converted to useful sulfonium salts [9] and grafted MMA side chains.

RESULTS AND DISCUSSIONS

Reactions of PPVS with MMA Monomer

The photochemical reaction of PPVS with MMA is summarized in Table 1. It is clear from these data that PPVS has photosensitizing ability and polymerizes MMA.

Separation and Confirmation of Graft Copolymer

From the fractionation curve (Fig. 1), it is apparent that PPVS precipitated at about 0.5-1.5 precipitant/solvent ratio; however, it

TABLE 1. Photochemical Polymerization of MMA in the Presence of PPVS (15 hr, Room Temperature)

Expt. no.	Benzene (ml)	MMA		PPVS		Yield (g) ^a	Conversion of MMA (%)
		(ml)	(mole/liter)	(g)	(%)		
1	2	2	4.68	0.4	9.1	0.75	18.7
2	4	3	5.62	0.4	7.4	1.13	25.8
3	6	3	3.12	0.4	4.3	1.74	47.3
4	8	2	1.87	0.4	3.8	1.34	49.8
5	9	3	2.34	0.4	3.2	1.42	36.1
6	0	5	9.36	0	0	0	0

^aWeights of polymerized MMA.

was reported [10] that the polymer of MMA precipitated at over 1.8 precipitant/solvent ratio.

On the basis of this fractional precipitation behavior of PPVS, each sample was fractionally separated, and the results are shown in Figs. 2-5. After the fractionation, the structure of each fraction was confirmed by IR spectra (characteristic absorption of phenyl group of PPVS, $\nu = 1600 \text{ cm}^{-1}$, and carbonyl group of MMA, $\nu = 1720 \text{ cm}^{-1}$). Characteristic IR spectra of these bands are shown in Fig. 6.

From fractional precipitation curves and IR absorption spectra it is clear that homopolymers of MMA precipitated between PPVS for all runs except No. 1. The second appearance of PPVS in the IR absorption is seen in the precipitant/solvent ratio range of 3.2-3.4 which is beyond the precipitation region of PPVS.

This result indicated the formation of PPVS-MMA graft copolymer. In the case of sample 1, since the percentage of PPVS was large, PPVS-MMA copolymer could not be separated from PPVS; however, the fact that the precipitation curve was similar to those of other samples showed the formation of graft copolymer.

Glass Transition Temperature (T_g) of PPVS-MMA Graft Copolymer

The formation of graft copolymer becomes obvious from the fractional precipitation curves and IR absorption spectra. In order to characterize these graft copolymers, T_g was measured.

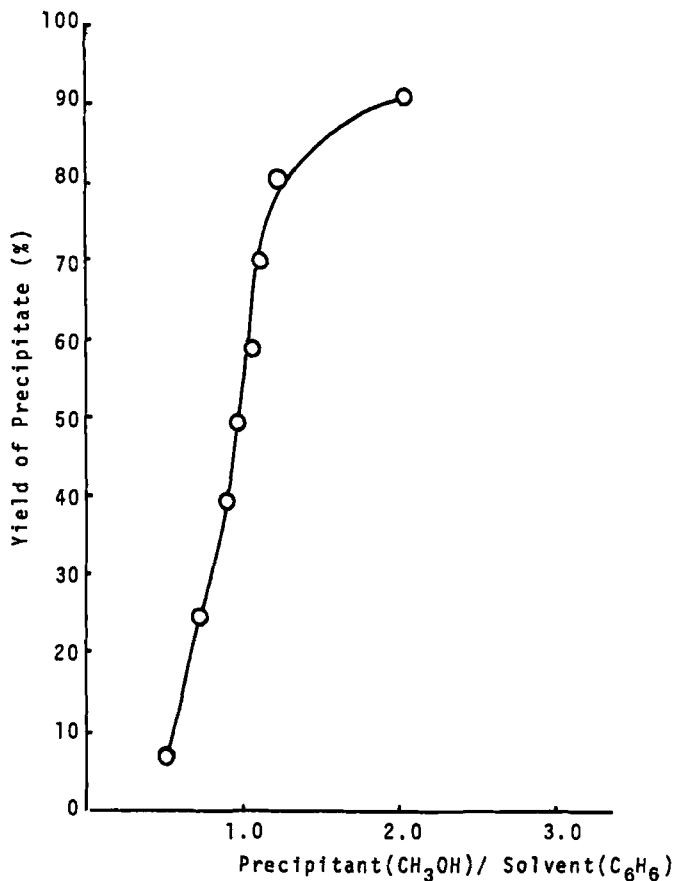


FIG. 1. Fractionation of PPVS.

The T_g of PPVS is 48-49°C, and that of PMMA (prepared by radical polymerization) is 80°C. A mixture of finely powdered PPVS and PMMA shows two T_g 's at the same points as the PPVS and PMMA homopolymers.

In the case of graft copolymer of experiments 4 and 5, the graft copolymer fractions each showed a single T_g at 58.5°C and 59°C, respectively; these values are quite different the T_g of the PPVS and

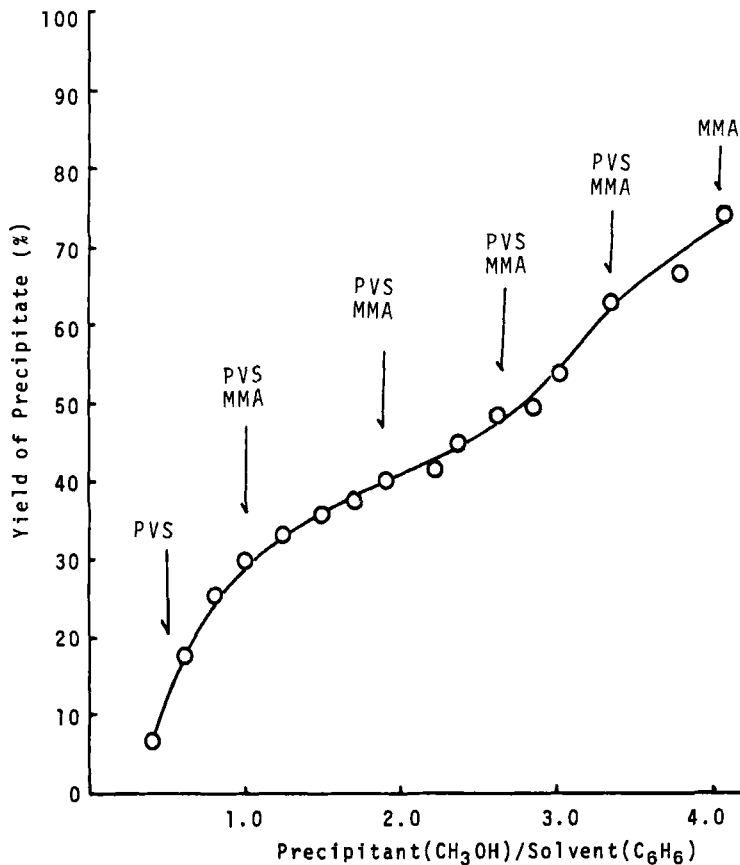


FIG. 2. Fractionation of sample 1 and results of IR spectral characterization.

PMMA homopolymers (Fig. 7). This result shows clearly the formation of graft copolymer rather than a physical mixture of the homopolymers.

The formation of graft copolymers was thus confirmed by fractional precipitation curves, IR spectra, and T_g data.

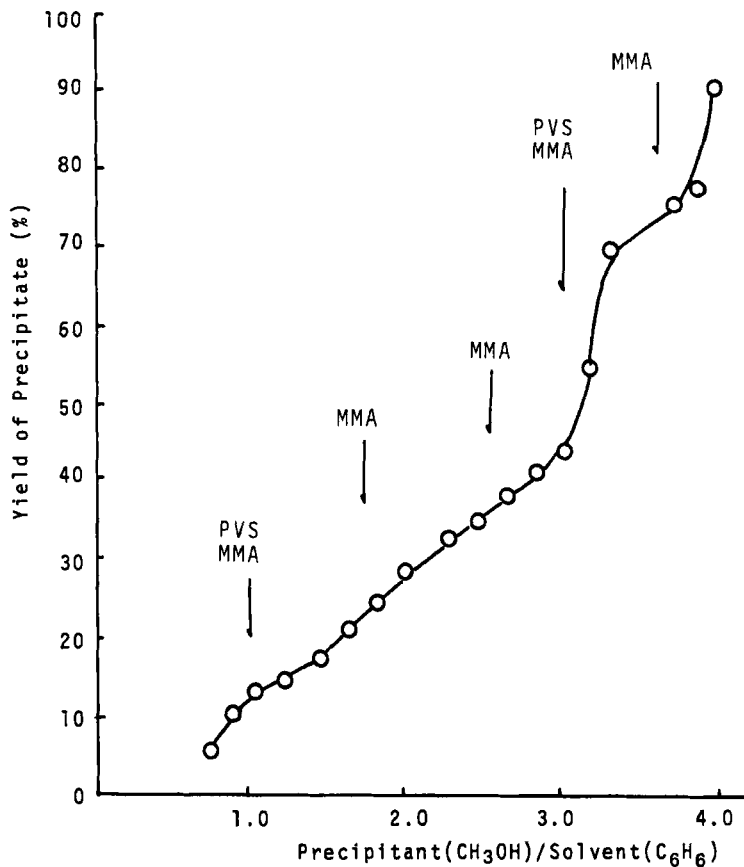


FIG. 3. Fractionation of sample 3 and results of IR spectral characterization.

Calculation of Graft Efficiency

The quantity of graft copolymer was calculated from the graph of fractional precipitation curves. The weight of grafted copolymer was obtained from the difference of the linear part which indicated grafted copolymer (Fig. 8). The results are summarized in Table 2.

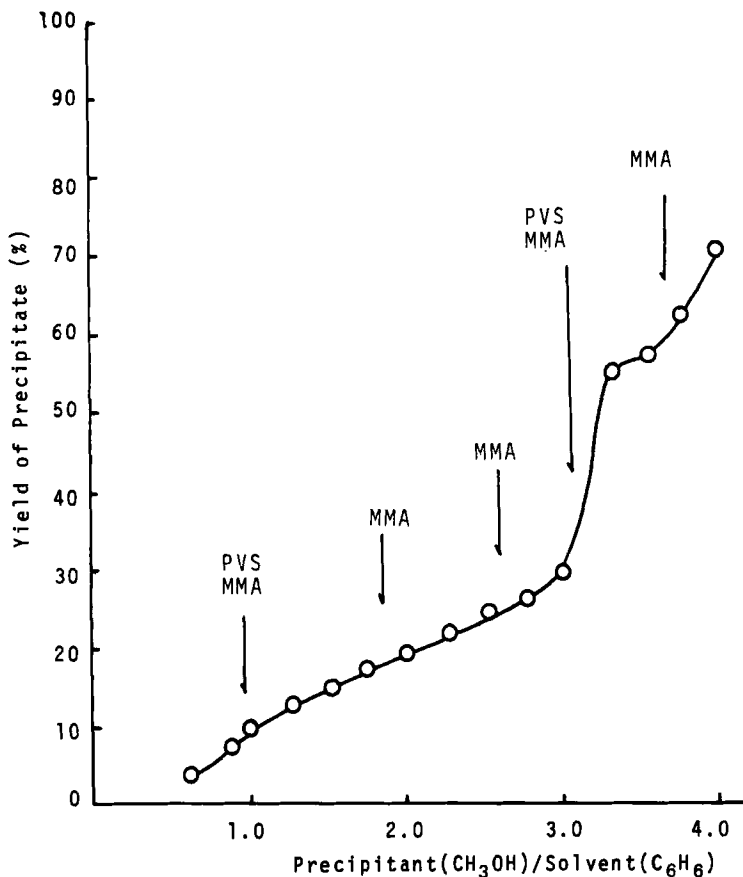


FIG. 4. Fractionation of sample 4 and results of IR spectral characterization.

This small grafting efficiency came from the calculation method. In this case, polymers were fractionated and fractional precipitation curves plotted. After that, graft efficiency was calculated on graphs. Therefore, the weight of pure graft copolymer is easily obtained but the quantity is small, because the weight was obtained only from the linear part of the curves. By the usual method, the residue of the extraction is treated as a graft copolymer, and the quantity of graft copolymer is much larger.

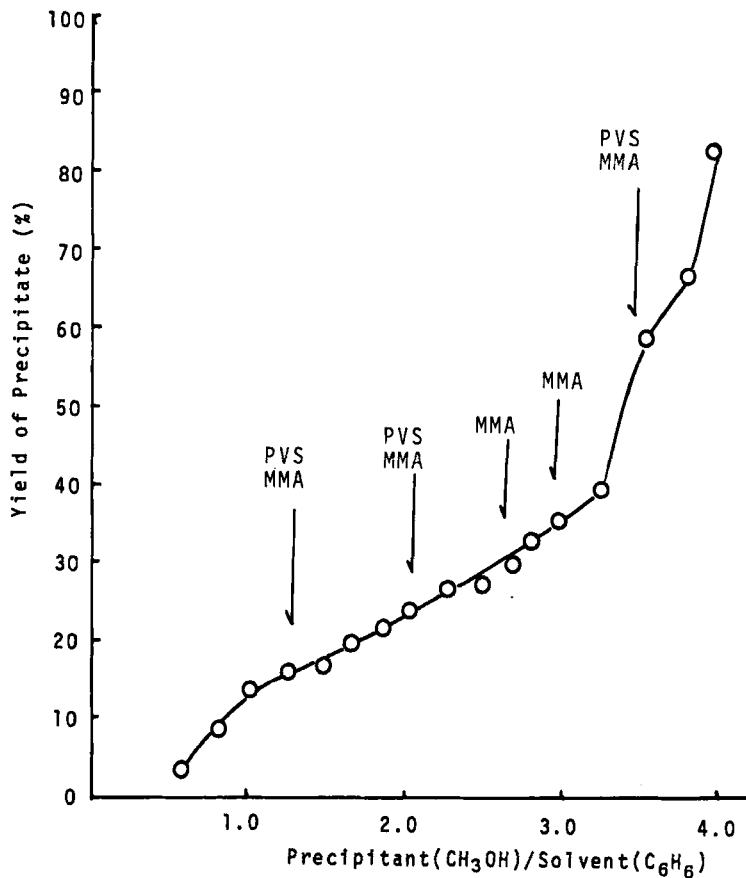


FIG. 5. Fractionation of sample 5 and results of IR spectral characterization.

Attempts at Graft Copolymerization with Other Monomers

Attempts at graft copolymerization with other monomers, such as vinyl acetate (VAc), acrylonitrile (AN), acrylic acid (Acid), and acrylamide (AA), were made.

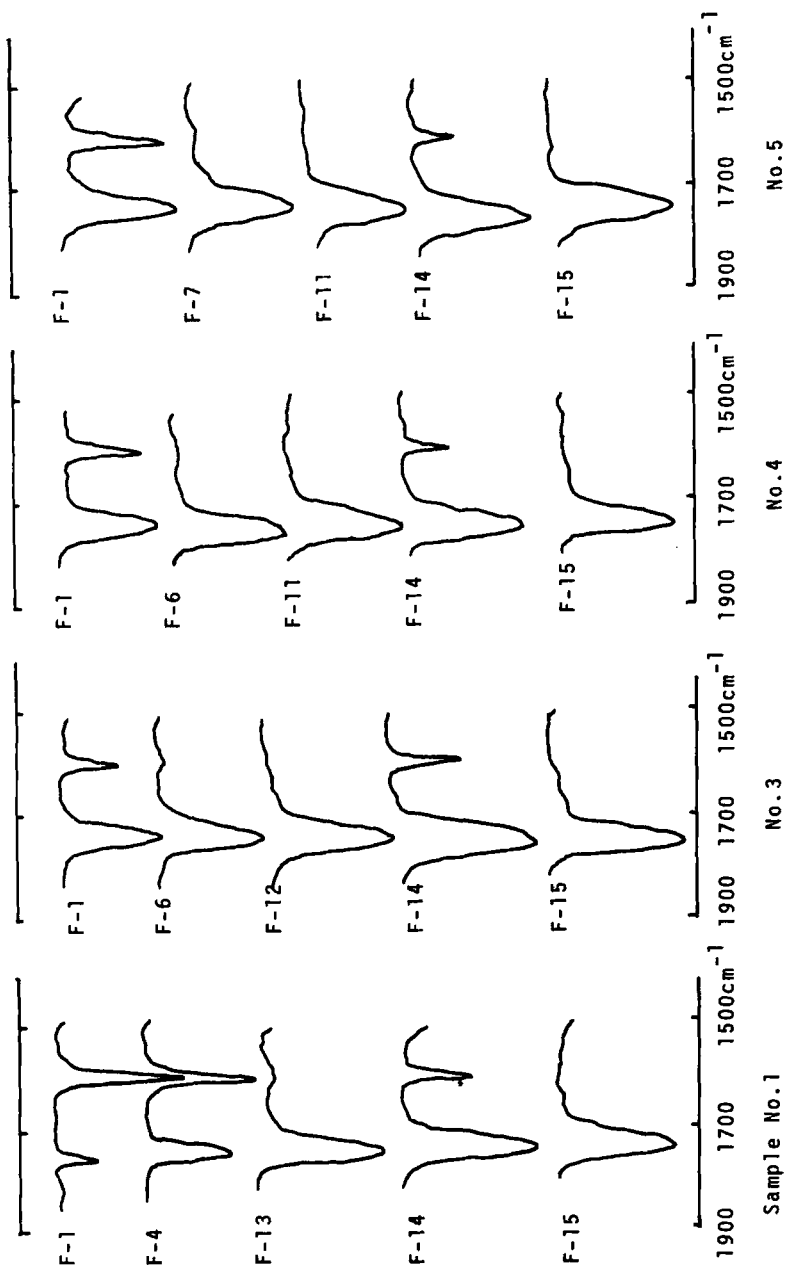


FIG. 6. Characteristic IR spectra of PPVS-MMA graft copolymer (F denotes fraction number).

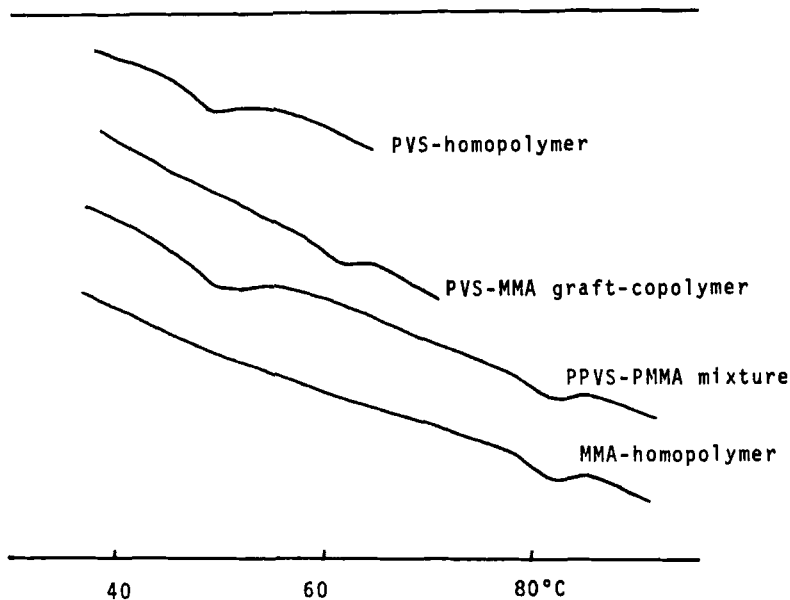


FIG. 7. Glass transition temperature (measured by DSC) of polymers.

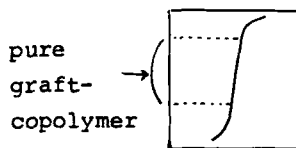


FIG. 8. Graft polymerization curve for calculating graft efficiency.

VAc and AN, have an electron-withdrawing group. Since they are likely to show low reactivity toward electrophilic thiyl radical, they were expected to graft on the carbon radical. In the case of Acd and AA, water-soluble graft copolymers was anticipated.

However, VAc did not graft at all, and in the case of AN and AA, the fractionation was very difficult and clean separation of graft

TABLE 2. Grafting Efficiencies of PPVS-MMA Copolymers

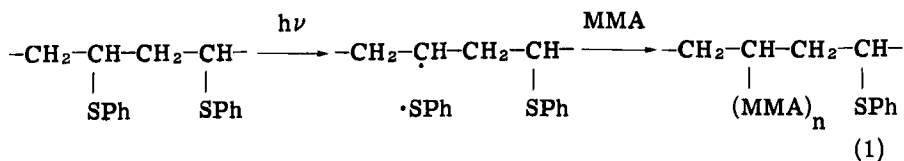
Expt. no.	Graft efficiency (%)
3	10.1
4	13.5
5	15.7

copolymer from homopolymer could not be done. In the case of AN, the graft copolymer could not be separated by any method.

Although the presence of graft copolymer is recognized in the case of Acd, the separation is not satisfactory. When PPVS was extracted with benzene and the graft copolymer was extracted by ethanol, a milky emulsified graft copolymer was obtained. This phenomenon is understood as showing that a kind of surface-active agent had been produced, because the graft copolymer was composed of the hydrophobic PPVS backbone and hydrophilic acrylic acid branch. Therefore, when a large quantity of nonsolvent for one component was added to the solution of graft copolymers, polymolecular micelles are formed and diffused in solvent [11, 12]. The physical properties, such as apparent molecular weight, viscosity, and/or refractive index, should be changed by these micelles. For this reason, the change in viscosity with concentration was studied, as such a case is known in styrene-dimethylsiloxane copolymer [13].

The reduced viscosity in methanol was obtained PPVS-Acd graft copolymer and plotted against the concentration in Fig. 9. An inflection point appeared at 2.1-2.2 g/dl which is supposed to reflect some changes in higher structure; this finding supports the formation of graft copolymer, and it is understandable that the graft copolymer would change into a polymer micelle.

We do not have unambiguous evidence for the structure of these graft copolymers at present time. However, the results of our earlier report [8] suggest that the graft copolymerization starts at the carbon radicals on the polymer main chain which are produced by the photochemical homolysis of PPVS at the carbon-sulfur bond as shown in Eq. (1).



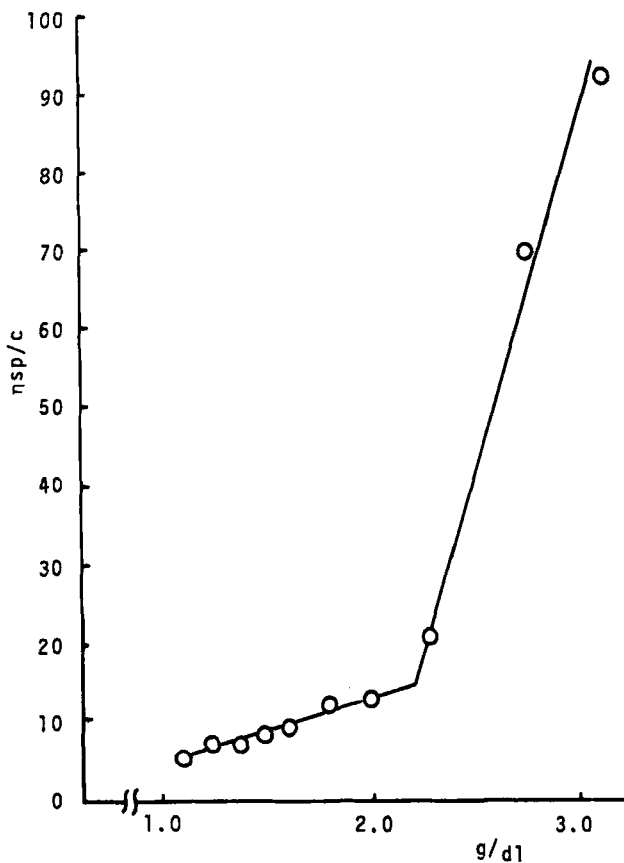


FIG. 9. Change of reduced viscosity by dilution (PPVS-AA).

MMA grafts to this carbon radical and PPVS-MMA graft copolymer is formed.

EXPERIMENTAL

Preparation of PPVS

PVS was prepared as described in the previous papers [6, 7] and polymerized radically by the usual method.

Graft Copolymerization

Graft copolymerization was carried out by a sealed tube method. PPVS and monomer were charged in a Pyrex tube, degassed, and sealed in vacuo by the usual method. Reaction tubes were irradiated 10 cm from a 100-W high-pressure mercury lamp.

After the reactions, polymers were precipitated with a large quantity of nonsolvent (methanol in the case of MMA and AN, petroleum ether in VAc) and dried.

Isolation and Fractionation of Graft Copolymer

A fractional precipitation method was adopted for isolation of the graft copolymers. First, a 0.2-g portion of PPVS was dissolved in 10 ml benzene and adjusted to 1% solution by the addition of 10 ml of acetone. Then 2-ml methanol were added. After every addition, polymers were separated by centrifugation and dried. Yields of each fraction were obtained by weighing the dried polymer. By this method, a fractionation curve of the type shown in Fig. 1 was obtained.

Fractionations of samples 1-5 were carried out by the same method.

Measurement of Glass Transition Temperature (T_g)

The glass transition temperature (T_g) was measured by a differential scanning calorimeter (Rigaku-Standard TG-DSC).

IR and Viscosity Measurements

Infrared spectra were obtained by the JASCO IRA-2 instrument, and viscosities were determined in methanol with an Ubbelohde viscometer at 30°C.

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