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Color Reactions of Polyvinyl Acetate and Its Derivatives with Iodine*[1]

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It has been found that the addition of a methanol solution containing polyvinyl acetate (PVAc) and iodine to an aqueous solution of potassium iodide results in a red-violet color without precipitating any polymer. The absorption maximum was located at 510 mμ. The absorbance of the PVAc-iodine complex decreased only slightly with an increase in the degree of the polymerization of PVAc. A linear relationship was obtained between the abosrbance and the PVAc concentration. It was found from these results that the color reaction of PVAc with iodine can be used in a colorimetric determination of PVAc, which is insoluble in water. Further, an attempt was made to investigate the complex formation of the vinyl acetate-vinyl propionate copolymer (PVAc-PVPr) and the vinyl acetate-vinyl formacetal copolymer (PVAc-PVFA) with iodine. Although the absorption maximum of the color complex of PVAc-PVPr with iodine appeared at 510 mμ, independent of the copolymer composition, the absorbance decreased with an increase in the number of vinyl propionate units in the copolymer. The absorption maximum of the complex of PVAc-PVFA with iodine was observed to lie at 620 mμ for highly-acetalyzed polyvinyl alcohol and at 520 mμ for polyvinyl alcohol of a low degree of acetalyzation, while a new absorption maximum appeared in the range from 520 to 620 mμ in the intermediate case. The absorbances at the absorption maxima of the complexes of PVAc-PVFA with iodine were approximately the same as those of PVAc. The effect of an elevated temperature on the absorbance was smaller for PVAc-PVFA than for PVAc-PVPr. From these experiments, it became clear that the glass-transition temperature and the color intensity of the polymer-iodine complex have a simple relation.

It is well known that PVAc yields a red-violet-colored complex with iodine; this reaction has previously been applied to the detection of PVAc.[1] This color development has been carried out in a heterogeneous system which sprays an iodine-potassium iodide solution on the polymer, or immerses the polymer in an iodine-iodide solution. Schweepe[2] has already reported, regarding the detection of PVAc, that when a few drops of iodine in a potassium iodide solution are added to a sample

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*[1] Polyvinyl Acetate and Its Derivatives. VI. Part V: S. Hayashi, M. Takayama and C. Kawamura, *Kogyo Kagaku Zasshi*, **73**, 412 (1970).

[1] F. D. Hartley, *J. Polym. Sci.*, **34**, 397 (1959).

[2] H. Schweepe, *Paint Technol.*, **27**, 14 (1963).

dissolved in some glacial acetic acid and the solution is diluted with water, the solution develops an intensive red-violet color. We[3] have also found that when both PVAc and iodine are dissolved in a solvent which is easy to mix with water such as methanol or acetone, and the solution is poured into an aqueous solution containing potassium iodide, then, immediately after mixing, the solution exhibits a red-violet color. If the color reaction of PVAc with iodine takes place in a homogeneous system, its reaction might be expected to be applicable to the determination of PVAc and the investigation of the properties of PVAc.

The present work was undertaken in order to examine the optimum conditions of the complex formation of PVAc with iodine in an aqueous phase, and to determine PVAc colorimetrically under the optimum conditions thus obtained. The invessigations of the complex formation of the PVAc copolymers, PVAc-PVPr and PVAc-PVFA, with iodine were also made, and the relationships between the absorbances of the complexes of the copolymers with iodine and the temperature at various temperatures were discussed.

Experimental

Preparations of PVAc and Its Derivatives. It may be expected that the color reaction depends on the degree of polymerization and on the branches in the polymer, as in the cases of amylose and amylopectin.[4] Therefore, two kinds of PVAc samples prepared by different processes were investigated.

PVAc samples made from vinyl acetate: Vinyl acetate was purified by distillation under a reduced pressure in a stream of nitrogen. The polymerization of vinyl acetate was carried out at 60—62°C by using benzoyl peroxide as an initiator. After polymerization for a given time, the contents were poured into a large amount of water in order to precipitate the polymer. The resultant polymer was washed five times with boiling water and then dried in a vacuum.

PVAc samples derived from polyvinyl alcohol (PVA): The various fractionated PVA samples listed in Table 2 were acetylated with acetic anhydride in pyridine. The pyridine solution was then poured into water to obtain the acetylated polymer. The resultant polymer was washed in boiling water until the odor of pyridine completely disappeared; then it was dried in a vacuum. The degree of acetylation of all the samples obtained was over 98 mol %, judging from the saponification values.

The degree of polymerization of PVAc was measured in a Ubbelohde Viscosimeter at 30°C in acetone by using the following equation:[5]

$$[\eta] = 7.94\times 10^{-4} P^{0.62}$$

The PVAc samples are summarized in Tables 1 and 2.

PVAc-PVPr was prepared by the acetylation of partially-propionated PVA, which had been propionated in a homogeneous system of water and propionic acid by using hydrochloric acid as a catalyst. These samples are listed in Table 3. PVAc-PVFA was also prepared by the acetylation of partially-formacetalyzed PVA, which had been acetalyzed in a homogeneous system of water and formaldehyde by using sulfuric acid as a catalyst. These samples are presented in Table 4.

Reagents. All the chemicals were of a guaranteed grade and were used without further purification. An iodine stock solution was prepared by dissolving iodine (3.2g) in methanol (250 m*l*). The resultant solution was standardized by sodium thiosulfate and was used by diluting it with methanol to the desired concentration just before its use. A 0.1 N solution of potassium iodide was accurately prepared by dissolving potassium iodide (8.3005 g) in distilled water (500 m*l*); it was used by diluting it with distilled water to the desired concentration before use.

Absorbance Measurements. A Shimadzu spectrometer, Model Spectronic 20, was used for the measurement of the absorption spectra. The color development of PVAc-iodine was done as will be described in the following section. The absorption spectra of the PVAc copolymer-iodine complex were recorded under the optimum conditions established by the use of the PVAc-iodine complex. After 1 m*l* of a methanol solution of the polymer (0.1g/d*l*) had been added to 1 m*l* of a methanol solution of iodine (2.5×10^{-3} mol/*l*), 1 m*l* of the mixture was added to 25 m*l* of an aqueous iodide solution (2×10^{-3} mol/*l*) and the mixture was allowed to stand for an hour at 20°C. The absorbance of the color complex was then measured at the absorption maximum by using the iodine-iodide solution as the reference.

The effect of the temperature on the color development of the polymer-iodine complex was discussed under the above-mentioned conditions. After the color solution had been cooled at 3°C for 24 hr, the solution was permitted to stand for an hour at a definite temperature; then the absorbance was measured at the absorption maximum.

Results and Discussion

The Color Reaction of PVAc with Iodine. A methanol solution containing PVAc and iodine was poured into an aqueous solution of potassium iodide. Immediately after the addition, the solution developed an intensive red-violet color without precipitating any polymer. The spectra of the color complex are indicated in Fig. 1, together with those obtained under different color conditions. The absorption maximum was located at 510 mμ. The absorbance of an iodine-potassium iodide solution at 510 mμ was very small. Even if the contents of PVAc, iodine, and iodide were the same, the order in which iodine was added had a significant effect on the absorbance, as is illustrated in Fig. 1. This is considered to be due to the fact that the penetration of iodine into the polymer was insufficient since molecules of both PVAc and iodine are separately

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[3] T. Motoyama, S. Hayashi and T. Nakano, *Report of the Poval Committee*, No. 44, 95 (1964).

[4] R. M. McCready and W. Z. Hassid, *J. Amer. Chem. Soc.*, **65**, 1154 (1943).

[5] A. Nakajima, *Kobunshi Kagaku*, **6**, 451 (1949).

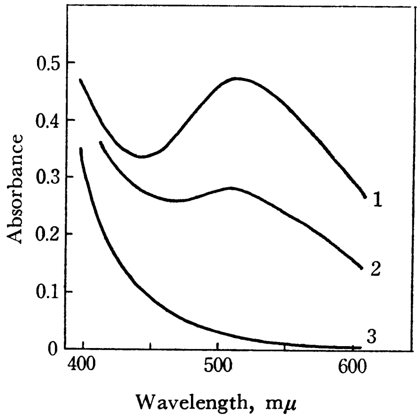

Fig. 1. Absorption spectra of PVAc-iodine complexes. (PVAc : P=980).

1: Addition of 1 ml of methanol solution containing PVAc 5×10^{-4} g and iodine 2.5×10^{-6} mol to 25 ml of aqueous solution of potassium iodide 2×10^{-3} mol/l.

2: Addition of 0.5 ml of methanol solution containing PVAc 5×10^{-4} g and then 0.5 ml of methanol solution containing iodine 2.5×10^{-6} mol to 25 ml of aqueous solution of potassium iodide 2×10^{-3} mol/l.

3: Blank.

dispersed in an aqueous solution. Considering the fact that the PVAc-iodine color reaction did not occur in the absence of potassium iodide, it may be concluded that iodide ions are indispensable to the formation of the complex with PVAc, as in the case of amylose.⁶⁾

The standing time for the color development of the PVAc-iodine complex was investigated at 20°C, while the other components were kept constant. The color of the complex reached its maximum within half an hour after mixing; thereafter the absorbance remained almost constant for three days.

In order to study the effects of the concentrations of iodine and potassium iodide, a series of absorbances was measured under various concentrations of iodine and iodide. It was found from these experiments that the absorbance of the complex at 510 mμ, when the concentration of PVAc was kept at (5×10^{-4} g), reached a higher maximum more than iodine (2.5×10^{-6} mol) and potassium iodide (5×10^{-5} mol).

Figure 2 shows the effect of the amount of methanol on the color development, while the other compoments were kept constant. As is shown by the curve in Fig. 2, the absorbance decreased with an increase in the amount of methanol, but the decrease was only slight in the range of small amounts of methanol.

From the experimental results obtained above, the following procedures were selected as the optimum conditions for the measurement of the PVAc-iodine complex. One volume of a methanol solution of iodine (2.5×10^{-3} mol/l) is added to an equal volume of a methanol solution of PVAc, and then 1 ml of the mixture is stirred into 25 ml of an aqueous solution of iodide (2×10^{-3} mol/l). The color solutions are at once transferred into the test tube cells, which are covered with parafilm. The test tube cells are stored for an hour at 20°C, after which the absorbance at 510 mμ is measured with a spectrometer by using an iodine-iodide solution as a reference.

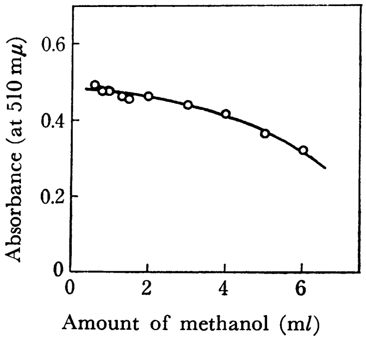

Fig. 2. Effect of amount of methanol on color intensity. (PVAc : P = 980)
PVAc : 5×10^{-4} g, Iodine : 2.5×10^{-6} mol, Potassium iodide : 5×10^{-5} mol

A calibration curve was made under the above-mentioned conditions. A linear relationship was obtained between the absorbance and the PVAc concentration over the range investigated.

The effect of the degree of the polymerization of PVAc on the color development was studied by using the samples shown in Tables 1 and 2. The results are shown in Fig. 3. In both the PVAc obtained from the acetylation of PVA and the PVAc formed by the polymerization of vinyl acetate in methanol, it was found that all the absorption maxima appear at 510 mμ, regardless of the degree of polymerization, while the absorbances of the PVAc-iodine complexes decrease only slightly with an increase in the degree of polymerization.

From the above results, it was found that, if the degree of polymerization of PVAc is known, the color reaction of PVAc with iodine can be used in the colorimetric determination of PVAc, which is itself insoluble in water.

In free-radical polymerization, it is well known that long-chain branches are present in the PVAc molecules.⁷⁾ These branches are released during the hydrolysis of PVAc to PVA. Thus, such long-chain branches do not exist in PVA molecules.⁸⁾ To ascertain the effect of a branch on the color

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6) A. J. Thoma and D. French, *J. Amer. Chem. Soc.*, **82**, 4144 (1960).

7) S. Imoto, J. Ukida and T. Kominami, *Kobunshi Kagaku*, **14**, 101 (1957).

8) R. Inoue and I. Sakurada, *ibid.*, **7**, 221 (1950).

Table 1. Polymerization condition of vinyl acetate and degree of polmerization of PVAc

Vinyl acetate (%)	Methanol (%)	Benzoyl peroxide *vs.* vinyl acetate (%)	Conversion (%)	Degree of polymerization
30	70	1.667	10.7	280
30	70	0.333	10.6	380
40	60	0.020	3.1	920
60	40	0.017	4.5	980
75	25	0.013	6.8	1830
80	20	0.013	5.4	2380

Table 2. Fraction of PVA and degree of polymerization of acetylated PVA

Fractionation number	*n*-Propanol (g)	Fractionated PVA (g)	Degree of polymerization of acetylated PVA
1	391	—	—
2	6	3.5592	1660
3	6	1.9106	1640
4	14	4.9394	1390
5	20	2.6024	1110
6	42	2.6262	760
7	60	1.2595	410
8	—	1.5023	210

Used PVA: 500 g of 5% PVA (P=1090) aqueous solution.
Fractionation temperature: at 30°C.

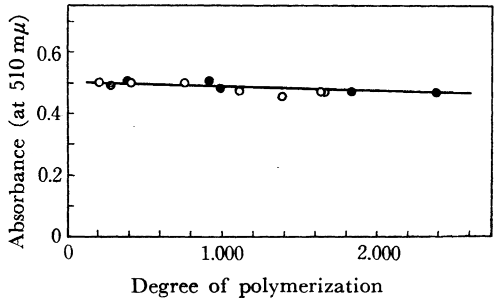

Fig. 3. Degree of polymerization of PVAc and color intensity.
●: PVAc obtained by polymerization of vinyl acetate
○: PVAc derived from acetylation of PVA

reaction, the color reaction was attempted, but the color intensity of the PVAc samples obtained from vinyl acetate was almost identical with that of the PVAc samples derived from PVA, as is indicated in Fig. 3. The long-chain branches in the PVAc molecules may be so small as to be negligible at the low conversion[9] shown in Table 1. However, the effects of nonhydrolyzable long-chain branches formed by the abstration of an α-proton and those of the short-chain branches made by an intramolecular-chain transfer mechanism,[10] as in the case of the free-radical polymerization of ethylene,[11] can not be considered on the basis of the experimental results obtained here. Such discussion must await a detailed investigation of many samples synthesized under various conditions.

The Color Reactions of PVAc Copolymers with Iodine. On the basis of the results obtained above, we then proceeded to examine the absorption spectrum and the temperature dependence of the PVAc copolymer-iodine complex.

Although the color complex of PVAc-PVPr with iodine had its absorption maximum at 510 mμ, as in PVAc, regardless of the copolymer composition, the absorbance decreased with an increase in the number of vinyl propionate units in the copolymer, as is summarized in Table 3.

Table 3. Dependence of degree of propionylation on absorbance of PVAc-PVPr-iodine complex

Degree of propionylation (mol%)	Absorption maximum (mμ)	Absorbance (at 20°C)	T_g (°C)
0	510	0.475	28
5.72	510	0.460	25
11.04	510	0.450	23
16.28	510	0.430	21
22.18	510	0.360	19
27.97	510	0.320	16
30.46	510	0.295	15
32.04	510	0.284	15
33.93	510	0.239	14

Degree of polymerization of PVA used: 1090.

The absorption spectra of the color complex of PVAc-PVFA with iodine are illustrated in Fig. 4. A change in the color from red-violet to green-blue was observed with an increase in the number of vinyl formacetal units in the copolymer. The absorption maximum was observed at 620 mμ for highly-acetalyzed PVA and at 520 mμ for PVA of a low degree of acetalyzation, while a new absorption maximum appeared in the region

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[9] M. Matsumoto and Y. Ohyanagi, *J. Polym. Sci.*, **46**, 520 (1960).

[10] H. N. Fridlandar, H. E. Harris and J. G. Pritchard, *ibid.*, *A-1*, **4**, 649 (1966).

[11] M. J. Roedel, *J. Amer. Chem. Soc.*, **75**, 6110 (1953).

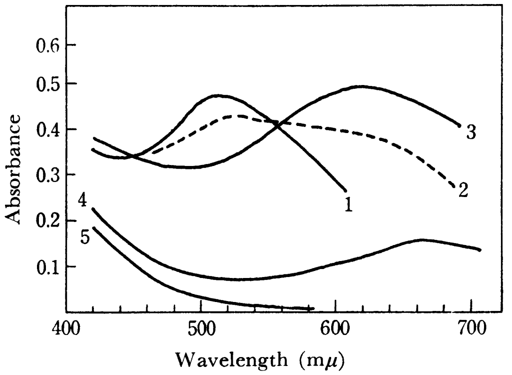

Fig. 4. Absorption spectra of complexes of PVAc, PVc-PVFA and partially formacetalyzed PVA with iodine.
1: PVAc
2: PVAc-PVFA having degree of acetalyzation of 17.11 mol%.
3: PVAc-PVFA having degree of acetalyzation of 31.27 mol%.
4: Partially formacetalyzed PVA having degree of acetalyzation of 31.27 mol%.
5: Blank

TABLE 4. DEPENDENCE OF DEGREE OF ACETALYZATION ON ABSORBANCE OF PVAc-PVFA-IODINE COMPLEX

Degree of acetalyzation (mol%)	Absorption maximum (mμ)	Absorbance (at 20°C)	T_g (°C)
0	510	0.475	28
10.02	520	0.438	32
17.11	520	0.424	35
19.43	600	0.415	36
22.84	620	0.450	38
29.28	620	0.481	42
31.27	620	0.490	43

Degree of polymerization of PVA used: 1090.

between 520 and 620 mμ in the intermediate case. These results are tabulated in Table 4.

Although the PVA used in our experiments did not give the color reaction in a dilute aqueous solution with iodine, partially-formacetalyzed PVA, which had been prepared by the acetalyzation of PVA in a homogeneous system of water and formaldehyde in the presence of sulfuric acid, developed a green-blue color with an increase in the degree of acetalyzation.[12] Since partially-formacetalyzed PVA was insoluble in methanol, the color reaction of the PVA derivatives with iodine was carried out in the aqueous phase, in which methanol as the polymer solvent was replaced by water. The results for formacetalyzed PVA, which had about a 30 mol% degree of acetalyzation, as a representative example are indicated in Fig. 4, together with those of the other PVAc copolymer. The absorption maximum was located at the longer wavelength of 670 mμ, and the absorbance was remarkably lower compared with that of PVAc-PVFA, but with the same degree of acetalyzation. These results clearly suggest that the higher green-blue color development of the copolymer-iodine complex depends not only on the acetal units, but on the vinyl acetate units, and that the red-violet color reaction of PVAc-iodine is based on the long sequence lenght of the vinyl acetate unit in the polymer chain.

Figures 5 and 6 show the results of the temperature dependence of the absorbance at the absorption maximum for the PVAc homopolymer and the PVAc copolymer. In the case of the PVAc homopolymer, it was found that the color intensity is slightly decreased up to about 30°C as the temperature is raised, and that color-fading takes

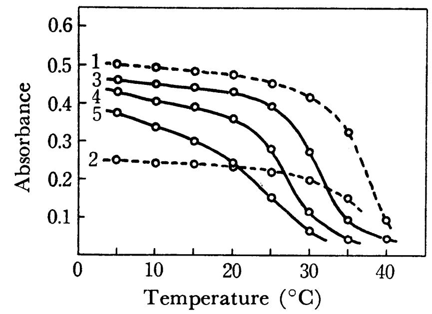

Fig. 5. Effect of temperature on color intensity of complexes of PVAc and PVAc-PVPr with iodine.
PVAc: 1: 5×10^{-4} g, 2: 2.5×10^{-4} g.
PVAc-PVPr, degree of propionylation: 3: 16.28 mol%, 4: 22.18 mol%, 5: 33.93 mol%.

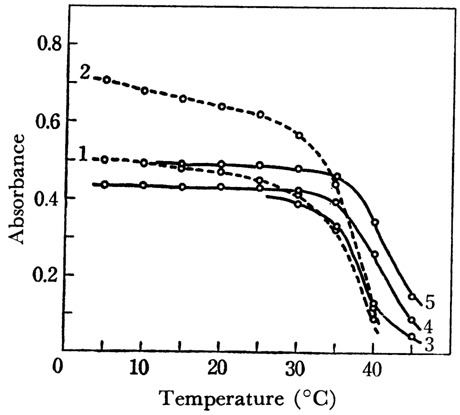

Fig. 6. Effect of temperatue on color intensity of complexes of PVAc and PVAc-PVFA with iodine.
PVAc: 1: 5×10^{-4} g, 2: 7×10^{-4} g.
PVAc-PVFA, degree of formacetalyzation: 3: 10.02 mol%, 4: 23.84 mol%, 5: 31.27 mol%.

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12) S. Hayashi, C. Kawamura and M. Takayama, *Preprints for Annual Meeting of Soc. Polymer Sci. Japan*, **19**, 339 (1969).

place in the vicinity of 30°C. This temperature agrees with the glass-transition temperature (T_g) of PVAc. In order to examine this phenomenon more exactly, the effects of the various PVAc concentrations were investigated. These results are given by the broken lines in Figs. 5 and 6, which show that all the color-fadings of PVAc-iodine complexes are in the vicinity of 30°C, independent of the PVAc concentration. For the temperature dependence of the copolymer-iodine complexes, it is of interest to compare these data with the results of PVAc. The difference between the type of curve obtained with the PVAc copolymer and that obtained with the PVAc homopolymer is striking, as Figs. 5 and 6 show. For the copolymer with vinyl propionate, the magnitude of the decrease in the color intensity with the temperature increased with an increase in the number of vinyl propionate units. On the other hand, the absorbances of the complexes of PVAc-PVFA with iodine at the absorption maximum were approximately the same as that of PVAc, and the effect of the elevated temperature on the absorbance appeared to be smaller for PVAc-PVFA than the PVAc, as the vinyl formacetal units as comonomer are introduced into the PVAc chain.

The polymer-iodine complexes generally lose their color intensities at elevated temperatures. The extent of the loss depends on the kind of polymer12) and on the degree of steric regularity.13) However, these differences have been difficult to explain satifactorily in the absence of mechanistic studies of polymer-iodine complexes. If it is assumed that the source of the color reaction of polymer with iodine is based on the formation of polyiodine chains in the polymer,14) the degree of mobility of the polymer molecule at a given temperature at which the color intensity is measured seems to be one of the important causes of the color development. For example, the color-fading temperature of PVAc agreed with the T_g of PVAc. This probably means that the molecular motion of the PVAc polymer over the T_g is so vigorous that the iodine molecules can not be oriented in polyiodine chains in the PVAc polymer. The reason that the effect of the temperature on the color intensity was greater for PVAc-PVPr than for PVAc-PVFA may be also attributed to the T_g of the copolymer. The T_g values of copolymers tabulated in Tables 3 and 4 were calculated by means of the following equation:15)

$$\frac{1}{T_g}=\frac{W_1}{T_{g_1}}+\frac{W_1}{T_{g_2}}$$

where T_g, T_{g_1}, and T_{g_2} are the glass-transition temperatures of the copolymer, the homopolymer 1, and the homopolymer 2, and where W_1 and W_2 are the weight fractions of the homopolymer 1 and the homopolymer 2 respectively.

On comparing these values with the results of the temperature dependence of the absorbance, it is evident that the T_g and the absorbance have a simple relation, that is, the higher the T_g value, the lower the temperature dependence of the absorbance. Therefore, the curves in Figs. 5 and 6 can be explained as follows. As the temperature rises, the color intensity is gradually lowered up to the extent of the T_g of the polymer; then the rate of lowering becames rapid in the vicinity of the T_g. This can be taken as indicating that the polymer in which iodine molecules form the polyiodine chains can not be held in a definite conformation at elevated temperatures.

The authors are grateful to Professor Nobumasa Hojo of Shinshu University for his valuable discussions.

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13) M. M. Zwick, *J. Appl. Polym. Sci.*, **9**, 2393 (1965).

14) M. Haisa and H. Itami, *J. Phys. Chem.*, **61**, 817 (1957).

15) W. H. Howard, *J. Appl. Polym. Sci.*, **5**, 303 (1961).