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Radical Polymerization of Maleic Acid by Potassium Persulfate in the Presence of Polyvinylpyrrolidone in Water

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ABSTRACT

Maleic acid(MA) was found to polymerize easily by potassium persulfate (KPS) in water in the presence of polyvinylpyrrolidone (PVP), and to form a polymer complex in which the molar ratio of MA to VP monomer unit was approximately unity. The formation of the polymer complex was accelerated by increases in the reaction temperature, in the concentrations of KPS and MA, and in the molecular weight of PVP used. Thermal degradation behavior of the polymer complex was studied thermogravimetrically. The thermagram of the polymer complex was substantially different from those of PVP and the 1:1 mixture of MA and PVP. It was found that the poly-MA portion of the polymer complex decomposed at 100-300° C, while the PVP portion underwent degradation at 350-500°C. In order to separate poly-MA from the polymer complex, the polymer complex was methylated by diazomethane, and 50 ~ 60% of the poly-MA part in the polymer complex was separated as its methyl ester, which was found to be oligomer ($\overline{M}_w = 400 \sim 500$) by GPC. Unseparated part of poly-MA seems to be grafted onto PVP. The polymerization of citraconic acid (CA) was also performed in the same manner. Similar results were obtained, though the polymerization of CA was slower as compared with that of MA.

INTRODUCTION

Radical polymerizations of vinyl monomers in the presence of synthetic polymers have been investigated by many workers, and the effects of the added polymers on polymerization rate, molecular weight, and stereospecificity of the resulting polymers have been discussed [1-5].

Ferguson et al. [2] demonstrated that the radical polymerization of acrylic acid in water was much accelerated by the presence of polyvinylpyrrolidone (PVP), in which a polymer complex formed between PVP and poly(acrylic acid).

In a previous paper [5], polyacrylamide was also found to show a pronounced effect on the radical polymerization of methacrylic acid in water as a result of complex formation of polyacrylamide with the acid monomer or its polymer.

On the other hand, most 1,2-disubstituted olefinic monomers are well known to show little homopolymerizability in the usual radical polymerization. Bengough et al. [6], however, found that the polymerization of diethyl fumarate with azobisisobutyronitrile gave the corresponding polymer with fairly high molecular weight.

Recently, we have found that maleic acid (MA) and citraconic acid (CA) were easily polymerized by potassium persulfate (KPS) in water in the presence of PVP to produce polymer complexes.

The present paper describes the results of the polymerizations of MA and CA by KPS in water in the presence of PVP.

EXPERIMENTAL

Materials

MA was used after recrystallization from an acetone-benzene mixture. Commercially available PVP ($\overline{M}_w = 36 \times 10^4$, 4×10^4, and 1×10^4) and guaranteed grade CA were used without further purifications. KPS was recrystallized from water. Water, as a polymerization solvent, was purified by ion exchange and distillation.

Polymerization

All polymerizations were carried out in sealed tubes which were degassed by the usual freezing and thawing method. The polymer complex formed in the polymerization of MA in the presence of PVP was washed several times with water and finally by acetone, and dried under vacuum. The polymer complex from CA was washed with hot (80°C) water, because the complex was soluble in cold water.

Methylation of the Resulting Polymer Complex by Diazomethane

The polymer complex, about 0.1 g, was dispersed in 20 ml benzene. To this solution, an excess of diazomethane in ether was added. The reaction mixture was allowed to stand for several days at room temperature. Insoluble polymer was separated by filtration and dried under vacuum. The filtrate was concentrated, and the residue was dried under vacuum.

Thermogravimetric (TG) Study

Dynamic TG behavior of the resulting polymer complexes was studied in a nitrogen atmosphere (flow rate 20 ml/min) by using a thermogravimeter (Shimazu TG-20), at a heating rate of 10°C/min. A 1.580 mg portion of polymer complex was employed in each experiment. All runs were terminated at 500°C.

RESULTS AND DISCUSSION

Polymerization of MA by KPS in Water in the Presence of PVP

MA was polymerized in water by using KPS as an initiator in the presence of PVP ($\overline{M}_w = 3.6 \times 10^5$). Table 1 shows the results obtained in the temperature range from 50 to 80°C. The polymerization mixture became viscous with time, and then the polymer complex formed precipitated from the system. The time for precipitation of the polymer complex became shorter as temperature increased. After formation of the polymer complex precipitate, the yield was almost independent of the reaction time. Thus, the polymerization came already to an end when the precipitation occurred.

TABLE 1. Polymerization of MA by KPS in Water in the Presence of PVP[a]

No.	Temp. (°C)	Time (hr)	Precipitation	Yield (g)	[MA]/[VP] in polymer complex
1	50	3	No	0.30	-
2	50	6	Yes	0.54	-
3	50	9	Yes	0.59	-
4	50	13.5	Yes	0.58	0.67
5	60	2	No	0.30	-
6	60	4	Yes	0.68	0.77
7	60	6	Yes	0.71	1.25
8	60	10	Yes	0.79	1.0
9	70	0.5	No	0.35	-
10	70	1	Yes	0.61	-
11	70	1.5	Yes	0.62	-
12	70	5	Yes	0.64	-
13	70	8	Yes	0.67	0.71
14	80	0.33	No	0.37	-
15	80	0.75	Yes	0.71	-
16	80	1	Yes	0.71	-
17	80	1.5	Yes	0.72	-
18	80	3	Yes	0.74	-
19	80	6	Yes	0.75	1.25

[a] Polymerization conditions: PVP, 0.5 g; MA, 1 g; [MA]/[VP] (in feed) = 1.86; [KPS] = 1.85×10^{-2} mole/liter; H_2O:10 ml. VP indicates the VP monomer unit.

The formation of the polymer complex was observed only in the presence of both PVP and MA. The KPS/MA and KPS/PVP systems did not give any precipitation in the reactions at 60°C for 10 hr in water.

Figure 1 shows the IR spectrum of the polymer complex (No. 19),

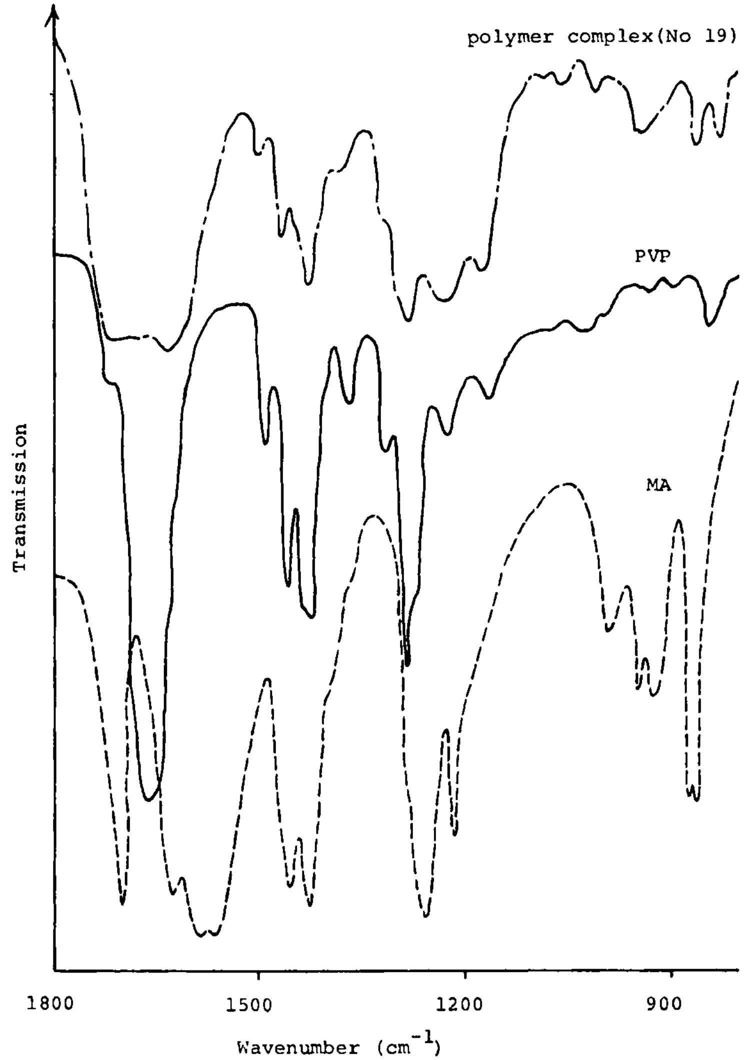
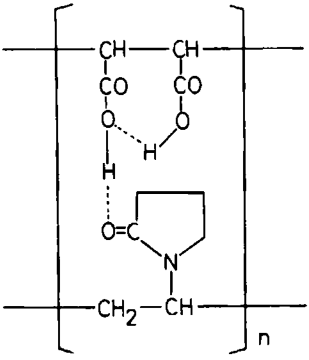


FIG. 1. IR spectra of MA, PVP, and polymer complex (No. 19) formed in the polymerization of MA in the presence of PVP.

together with those of MA and PVP. Comparison of these spectra indicates that the polymer complex stems from PVP and MA.

The composition of the polymer complexes formed was determined from nitrogen content by elementary analysis. Molar ratios of MA to vinylpyrrolidone (VP) monomer unit are considered to be approximately unity in the precipitated polymer complexes, if the difficulty of elementary analysis of such polymers carrying many carboxyl groups is allowed for.

These results suggest the structure of the precipitated polymer complex as envisaged in I.



I

As can be seen from Table 1, the polymer complex yield based on PVP used was 50-70%, though the concentration of MA was 1.86 times that of VP monomer unit. This seems to indicate that PVP of low molecular weight could cause no precipitation of the polymer complex under the present conditions.

Table 2 shows the results obtained at 60°C under various polymerization conditions. An increase in the MA concentration was found to enhance the yield of the polymer complex. When the MA concentration was 2.79 times that of VP unit, the polymer complex was formed in a yield of more than 90% based on PVP used. The yield of the polymer complex highly depended also on the KPS concentration. The use of the high KPS concentration ($\geq 3.7 \times 10^{-2}$ mole/liter) resulted in almost complete complexation of PVP used.

These results suggest that the high concentrations of MA and KPS can cause formation of the polymer complex from low molecular weight PVP.

As shown in Table 2, PVP of low molecular weight ($\overline{M}_w = 1 \times 10^4$ and 4×10^4) gave no precipitation of the polymer complex, though the

TABLE 2. Effect of the Polymerization Conditions on Yield of the Polymer Complex in the Polymerization of MA by KPS at 60°C in Water in the Presence of PVP[a]

No.	M_w PVP $\times 10^{-4}$	MA (g)	[MA]/[VP] in feed[a]	[KPS] $\times 10^2$ (mole/liter)	Time (hr)	Time to precipitation (hr)	Yield of polymer complex (g)	[MA]/[VP] in polymer complex
20	36	0.5	0.93	1.85	12.5	5	0.59	1.0
21	36	1.0	1.86	1.85	12.5	4	0.63	1.0
22	36	1.5	2.79	1.85	12.5	2.5	0.93	1.6
23	36	1.0	1.86	0	3	No precipitation		
24	36	1.0	1.86	0.93	3	No precipitation		
25	36	1.0	1.86	3.70	3	2.7	1.10	1.6
26	36	1.0	1.86	5.56	3	1.7	1.06	1.4
27	1	1.0	1.86	1.85	11.5	No precipitation		
28	4	1.0	1.86	1.85	11.5	No precipitation		
29	4	1.0	1.86	7.41	19	13	0.40	0.7

[a] Polymerization conditions: PVP, 0.5 g; H_2O, 10 ml.

TABLE 3. Polymerization of CA by KPS in Water in the Presence of PVP

No.	CA (g)	[CA]/[VP] in feed[a]	[KPS] × 10^2 (mole/liter)	Temp. (°C)	Time (hr)	Time to precipitation (hr)	Yield of polymer complex (g)	[CA]/[VP] in polymer complex
30	1.0	1.66	1.85	60	30	No precipitation		
31	1.0	1.66	5.56	60	68	29	0.67	0.9
32	1.5	2.49	5.56	60	35	23	0.95	1.0
33	0.5	0.83	7.41	60	37	No precipitation		
34	1.0	1.66	7.69	60	18	11	0.83	0.8
35	1.5	2.49	7.69	60	13	9	0.88	1.0
36	0.5	0.83	5.56	80	12	3	0.49	0.7
37	1.0	1.66	5.56	80	2.3	0.8	0.76	0.8
38	1.5	2.49	5.56	80	2.2	0.7	0.78	0.7

[a] Polymerization conditions: PVP ($\bar{M}_w = 3.6 \times 10^5$), 0.5 g; H_2O, 10 ml.

other polymerization conditions were identical. However, the use of the high KPS concentration was found to lead to formation of the polymer complex from PVP of $\overline{M}_w = 4 \times 10^4$.

Polymerization of CA by KPS in the Presence of PVP

The polymerization of CA by KPS was carried out at 60 and 80°C in water in the presence of PVP ($\overline{M}_w = 3.6 \times 10^5$). The polymerization system became viscous with time and then the polymer complex separated out. The results observed are summarized in Table 3. The polymerization of CA was slower as compared with that of MA. The higher KPS and CA concentrations and the increased polymerization temperature resulted in higher yield of the polymer complex as similarly as in the case of MA.

As shown in Fig. 2, the IR spectrum of the formed polymer complex indicates that the complex results from PVP and CA. Further, the composition of the polymer complex was found to be approximately equimolar CA and VP units. Consequently, the polymer complex is considered to have a structure similar to I.

Interestingly, the polymer complex from CA is soluble in cold water, but insoluble in hot water.

Methylation of Polymer Complexes with Diazomethane

As described above, in the polymer complex, PVP is considered to interact with poly-MA or poly-CA through hydrogen bonding between the carbonyl group of PVP and the carboxyl group of the acid polymers.

Thus, separation of the acid polymers was attempted by methylation of the carboxyl groups in the polymer complexes with diazomethane.

An ether solution of diazomethane was added to polymer complex dispersed in a benzene solution. Nitrogen gas evolved violently. After standing for several days, the insoluble portion was filtered. The filtrate was concentrated and the residue (soluble portion) was dried under vacuum.

As a control experiment, PVP was also allowed to react with diazomethane in the same manner, but unreacted PVP was recovered.

Table 4 shows the results obtained in methylation of the polymer complexes with diazomethane. Figure 3 shows IR spectra of the soluble and the insoluble portions from methylation of a polymer complex (No. 19). The IR spectrum of the soluble portion is apparently

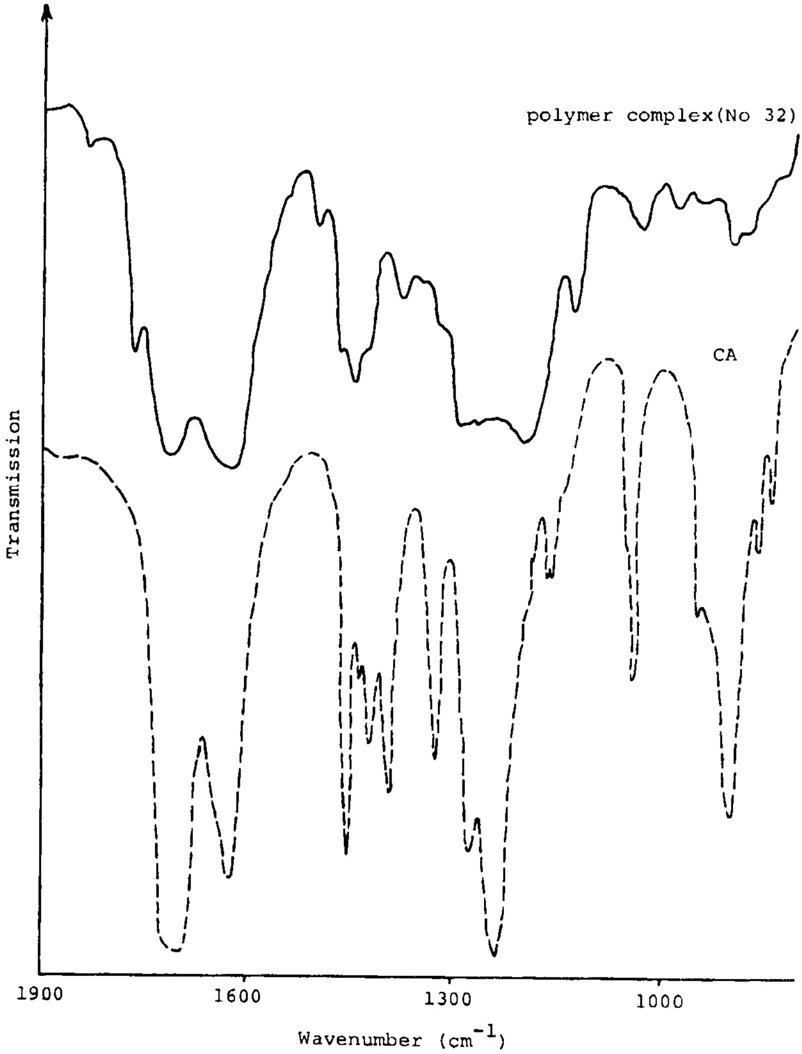


FIG. 2. IR spectra of CA and polymer complex (No. 32) formed in the polymerization of CA in the presence of PVP.

TABLE 4. Methylation of the Polymer Complexes with Diazomethane in Benzene

Polymerization conditions				Weight of polymer complex (g)	Weight of insoluble part (g)	Weight of soluble part (g)
Acid	[Acid]/[VP]	[KPS] × 10^2 (mole/liter)	Temp. (°C)			
MA	0.93	1.85	60	0.1	0.07	0.04
MA	2.79	1.85	60	0.1	0.06	0.07
MA	1.86	3.70	60	0.1	0.06	0.06
MA	1.86	5.56	60	0.1	0.07	0.05
MA	1.86	1.85	60	0.09	0.05	0.05
MA	1.86	1.85	70	0.1	0.09	0.03
MA	1.86	1.85	80	0.09	0.07	0.05
CA	1.66	7.41	60	0.35	0.24	0.20
CA	2.49	7.41	60	0.40	0.28	0.16

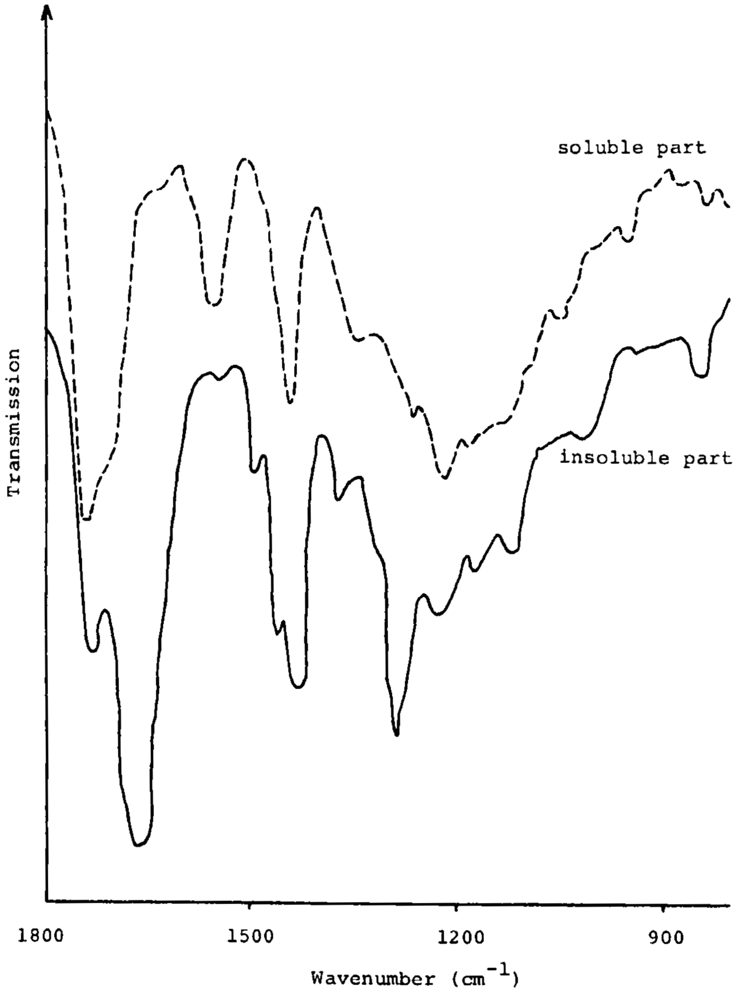


FIG. 3. IR spectra of soluble and insoluble parts from methylation of polymer complex (No. 19) with diazomethane.

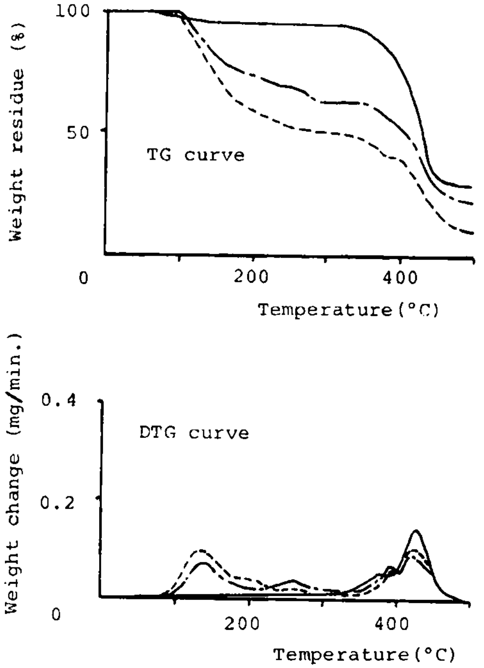


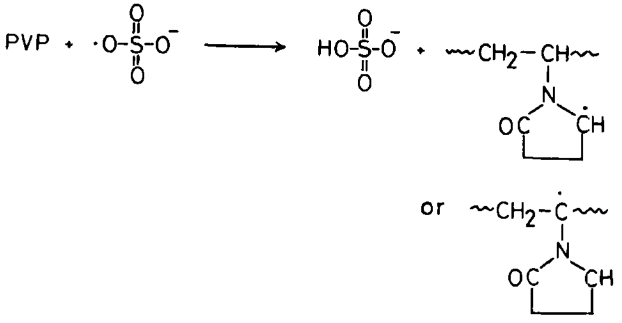
FIG. 4. TG and DTG curves of (– - –) polymer complex (No. 7), (—) PVP, and (--) the mixture of MA and PVP.

different from those of the insoluble portion and of PVP. The soluble portion shows an absorption band due to the ester carbonyl group but no band due to amide group. This suggests that a part of the polymer from MA was separated as its methyl ester from the polymer complex by methylation of carboxyl groups with diazomethane. Further, the soluble part was found to be an oligomer of molecular weight of 400-500 by GPC.

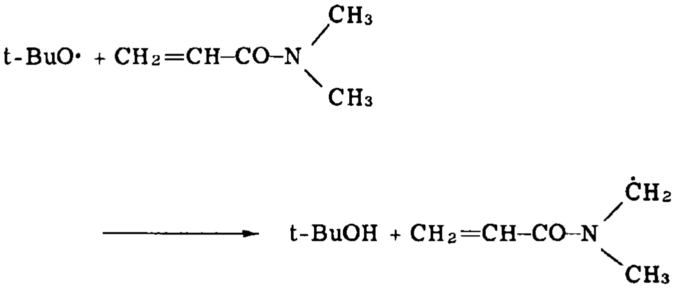
On the other hand, the IR spectrum of the insoluble portion shows the presence of amide and ester groups, indicating that this part consists of PVP and the MA polymer.

As shown in Table 4, the insoluble portions contain 30-40% of the polymers from CA and MA, which might be grafted on PVP.

The initiation of grafting is considered to be derived from hydrogen abstraction by the persulfate radical from N-methylene or N-methine group of PVP [Eq. (1)]. Recently it was found that the tert-butoxy radical, an oxygen-centered radical, can easily abstract



(1)



$$t\text{-BuO}\cdot + CH_2{=}CH{-}CO{-}N(CH_3)_2 \longrightarrow t\text{-BuOH} + CH_2{=}CH{-}CO{-}N(\dot{C}H_2)(CH_3) \qquad (2)$$

hydrogen from N,N-dimethylacrylamide [Eq. (2)], in competition with addition to the double bond of the monomer [7].

Thermogravimetric (TG) Study of the Polymer Complexes

The thermal degradation behavior of the polymer complexes formed in the polymerizations of MA and CA was studied thermogravimetrically. As an example, TG and differential thermogravimetric (DTG) curves of a polymer complex (No. 7) from MA are shown in Fig. 4, together with those of PVP and a 1:1 mixture of PVP and MA prepared by pouring an ethanol solution of the mixture into benzene.

The TG behavior of the polymer complex was found to be substantially different from those of PVP and the mixture of MA and PVP. The part from MA in the polymer complex decomposed at 100-300°C, while that from PVP degraded at 350-500°C. Decomposition of the MA portion was slower for the polymer complex formed at higher temperature and for that obtained in the lower MA and the higher KPS concentrations.

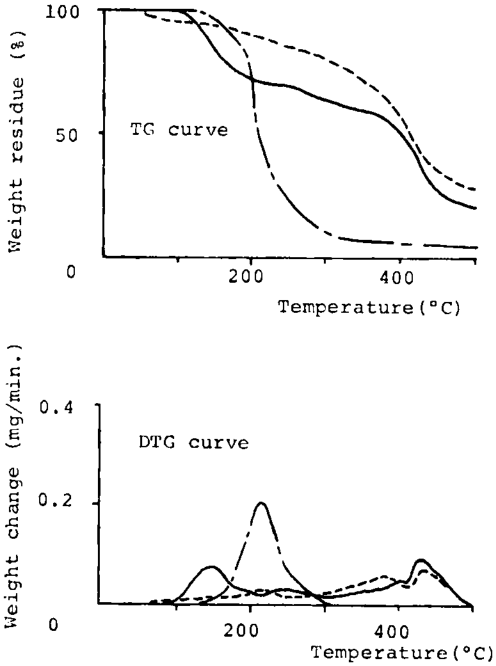


FIG. 5. TG and DTG curves of (—) polymer complex (No. 20) and (– - –) soluble portion and (- -) insoluble portion from its methylation with diazomethane.

The polymer complex from CA showed a similar thermal behavior to that from MA.

Figure 5 shows thermograms of the methylated polymer complex and the separated oligomer, together with that of the original polymer complex (No. 20). The separated oligomer almost decomposed at 150-300°C. The methylated polymer complex was thermally more stable than the original polymer complex.

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