Studies of Reactions with Polymers. II. The Reaction of Maleic Anhydride with Acrylonitrile onto PVA and the Properties of the Resultant

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Synopsis

Graft terpolymers were prepared by graft polymerization of a mixture of acrylonitrile (AN) and maleic anhydride (MA) onto PVA in DMSO solution using KPS as an initiator. Structure and solubility of graft terpolymers varied with the concentrations of KPS and MA. Both lower and upper critical values of KPS concentration varied with MA concentration, and the resulting reaction could be divided into three regions—crosslinked, hydrophobic, and hydrophilic regions. Structures of graft terpolymers were considered to be composed of homopolymer side chain grafted onto PVA while gelation occurred from the surplus radicals in PVA backbone to carry on the coupling reaction. The mechanical properties and viscosities increased with the increase of the wt % of AN in graft terpolymers; however, to increase AN content in PVA by increasing KPS concentration would bring about the oxidation scission and do damage to mechanical properties. Thus it becomes obvious that KPS can only be used at a suitable amount.

INTRODUCTION

Polymer membranes have a wide range of use in industries, such as in the separation, purification, and concentration of substances. Poly(vinyl alcohol) (PVA) is a well-known membrane material with good film-forming ability, toughness, hydro-affinity, and easy availability; therefore, investigation has been reported for its use in the field of medical materials.[1] However, because of its high solubility, it has to be turned into a completely insoluble stable material with good mechanical properties. The most common method is the graft copolymerization of hydrophobic monomers to PVA main chain by chemicals and irradiations.[2]

On the other hand, a polymer containing hydrophilic and hydrophobic microphase separation may improve its anti-clotting characteristics.[3] The purpose of this study is to use maleic anhydride (MA) as a hydrophilic monomer and acrylonitrile (AN) as a hydrophobic monomer through grafting so as to prepare terpolymers, in which both AN and MA were grafted onto PVA. The preparations and the properties of membranes were investigated.

EXPERIMENTAL

Materials

PVA BF-17, a products of Chang Chun Petrochemical Co., Taiwan, DP = 1700, degree of saponification of 98.5–99.2 mol % and viscosity of 25–30 cps was used. Maleic anhydride (MA), acrylonitrile (AN), and DMSO of

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reagent grades were purchased from Wako Pure Chemical Industries. AN was purified by first washing with a 5% aqueous solution of sodium hydroxide and a 5% aqueous solution of phosphoric acid and then with distilled water for several times. Afterwards it was dried with calcium chloride and distilled under an atmosphere of nitrogen. DMF is reagent grade of Shimakyu's Pure Chemicals. Potassium persulfate (KPS) of a reagent grade used as the initiator was purchased from Kanto Chemical Co. Solvents such as acetone, methanol, and chloroform were used without further purification.

Graft Terpolymerization

All grafting terpolymerizations were carried out in a four-necked flask equipped with a magnetic stirrer, thermometer, condenser, and nitrogen inlet. The general experimental procedure as example were as follows: PVA 5 g and MA 2 g were dissolved in 95 g DMSO, which was first stirred in an atmosphere of nitrogen. Then AN 15 g was added and stirred until there was a homogeneous solution. Added afterward with 0.2 g of initiator KPS, the solution was then allowed to react at 60°C for 5 h. The reaction was stopped at the predetermined reaction time by adding a small amount of hydroquinone. The reaction mixture was concentrated to about 20% of its original volume at 60°C under reduced pressure and was then added to chloroform to precipitate the polymer.

Purification of Copolymer

The products precipitated from chloroform were a mixture of grafted terpolymer, unreacted PVA as well as homopolymers of AN and MA. They were separated and purified as shown in Chart 1.
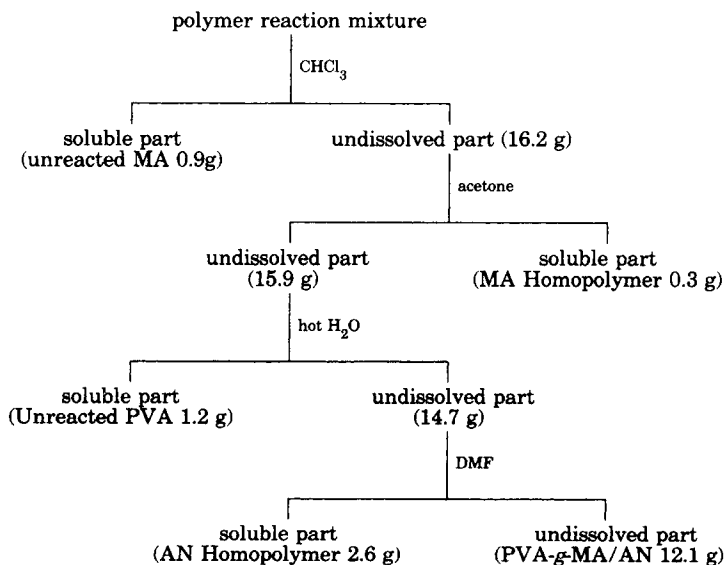

Chart 1. The Separation Procedure

If the weight of unreacted MA, PVA, and MA homopolymer need not be known, the reacted mixture can directly be dissolved in hot water to eliminate the chloroform and acetone separation procedure.

After the separation, all materials must be dried in a vacuum below 30°C. Data of grafting terpolymerization were calculated as follows:

$$\text{wt \% of MA in terpolymer} = \frac{\text{wt of MA reacted onto PVA (A)}}{\text{wt of PVA-}g\text{-MA/AN}} \times 100$$

$$\text{(A)} = \text{wt of MA fed} - \text{(wt of MA unreacted + MA homopolymer)}$$

wt % of PVA in terpolymer

$$= \frac{\text{wt of PVA reacted with AN and MA (B)}}{\text{wt of PVA-}g\text{-MA/AN}} \times 100$$

$$\text{(B)} = \text{wt of PVA fed} - \text{wt of PVA unreacted}$$

$$\text{wt \% of AN in terpolymer} = \frac{\text{wt of AN reacted onto PVA (C)}}{\text{wt of PVA-}g\text{-MA/AN}} \times 100$$

$$\text{(C)} = \text{(wt of PVA-}g\text{-MA/AN)} - \text{(wt of MA and PVA in terpolymer)}$$

Measurement of Various Properties

Viscosity

The intrinsic viscosities of PVA and grafted terpolymers were determined in distilled water and DMSO in an Ubbelohde viscometer at 30°C by extrapolating of η_{sp}/c to $c = 0$.

IR Spectra

IR spectra were obtained from films or in admixture with KBr on a JASCO Model A-202 Spectrophotometer.

Gel Content

After heat treatment the membranes of grafted terpolymers were extracted with hot water at boiling temperature for 24 h, and residual terpolymers were dried and weighed. Gel content was calculated by the following equation:

$$\text{gel content (\%)} = \frac{\text{wt of terpolymer after Extraction}}{\text{wt of original terpolymer}} \times 100$$

Water Content

Membranes were first immersed in boiling water for 6 h and then taken out. The membranes were superficially dried with filter paper and weighed. Water content was calculated by the following equation:

$$\text{water contents (\%)} = \frac{\text{wt of membrane after absorption water}}{\text{wt of original membrane}} \times 100$$

Mechanical Properties

The tensile strength and elongation at the break of membranes were determined by ASTM D-638 test method by Instron Model 1130.

Thermal Analyses

TGA and DSC measurements were preformed on a DuPont Instruments 1090B Analyzer. TGA was measured on 951 Thermogravimetric Analyzer at a heating rate of 10°C/min in air whose flow rate was at 100 mL/min. DSC was measured on a 910 Differential Scanning Calorimeter at a heating rate of 5°C/min in a nitrogen atmosphere with a flow rate of 30 mL/min. The sample of about 14 mg was cooled at 5°C/min after the initial melt.

RESULTS AND DISCUSSION

The Graft Terpolymerization of Acrylonitrile and Maleic Anhydride onto PVA

In a free-radical system, the monomer reactivity ratios of acrylonitrile (AN) and maleic anhydride (MA) are $r_1 = 6$ and $r_2 = 0$ [4]; therefore, it was obvious that AN had a higher reactivity than MA. However, in our recent study some unusual results were found. It occurred in a DMSO solvent with potassium persulfate (KPS) was used as an initiator to carry on the graft terpolymerization of AN and MA onto PVA. The reactivity of MA was found to be higher than that of AN. What is especially remarkable is that when the initiator was at low concentration, only MA could reacted onto PVA. Not until the concentration of KPS had reached some level could AN be grafted onto PVA; otherwise, only MA could be grafted onto PVA. This observation was confirmed by IR spectra. However, when AN and MA reacted onto PVA, the IR spectrum of the resultant showed —C=N char-
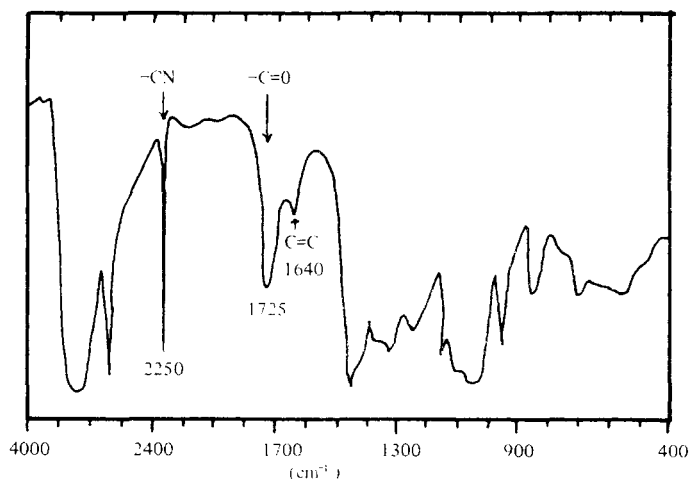

Fig. 1. IR Spectrum of the Resultant of AN and MA Reacted Onto PVA Terpolymer.

acteristic absorption peak at 2250 cm^{-1}, —C=O at 1725 cm^{-1}, and —C=C— at 1640 cm^{-1}, as shown in Figure 1.

In the case of a composition consisting of PVA 5 g, AN 15 g, DMSO 95 g with wt % of MA concentration to comonomers (AN + MA) at 1.7% and weight of KPS concentration to comonomers at 0.16%, it was found that only MA could react to PVA to form a copolymer which contained MA alone. This resultant was water soluble and its IR spectrum was free of —C≡N absorption peak. After using the trial and error method so as to graft AN/MA onto PVA, it was found that at a constant reaction temperature and constant concentration of PVA as well as MA the copolymer was still water soluble if KPS concentration was less than 0.3 wt %. When the KPS concentration was in excess of 0.3 wt %, the resultant obtained was a terpolymer grafted with AN and MA which was insoluble to water but soluble to DMSO. However, in case the concentration was larger than 1 wt %, the terpolymer would gel and could not be dissolved in any solvents. These lower critical point (0.34 wt %) of KPS concentration and the upper one (1 wt %) were dependent on the MA concentration. In other words, the two critical values of KPS concentration rose with the increase of the MA concentration. Figure 2 shows three different regions in the preparation of grafted terpolymers as decided by the different concentrations of MA as well as KPS. The first is the crosslinked region: The prepared grafted terpolymers located in this region would not be dissolved in any solvents. The
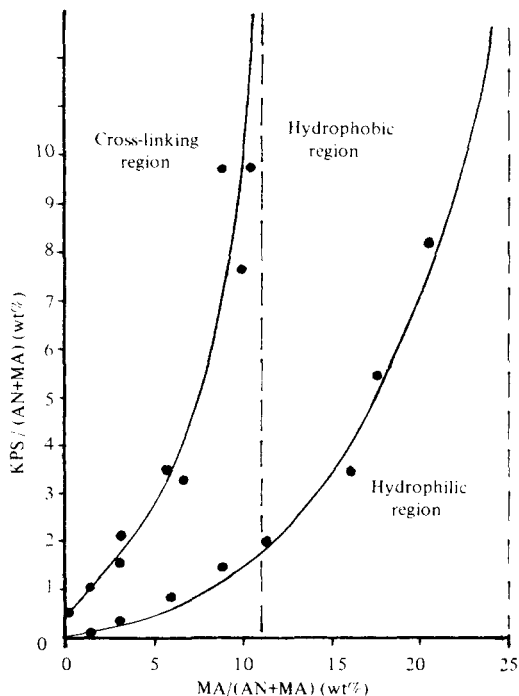

Fig. 2. Effects of the Concentration of KPS and MA on the Solubility of Graft Terpolymers of AN and MA Onto PVA at 60°C.

second is the hydrophobic region: Grafted terpolymers situated in this region would not be dissolved in water though was soluble in DMSO or DMAc. The third is the hydrophilic region: Prepared grafted copolymers found in this region would be dissolved in water and DMSO as well as contained MA alone.
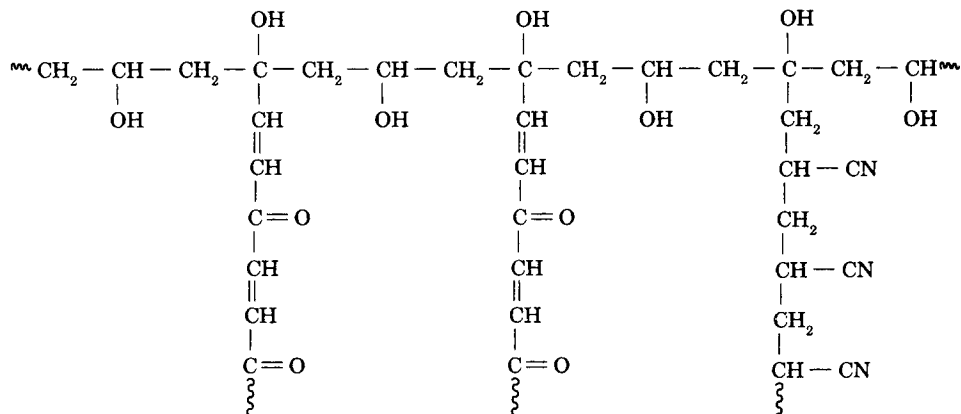
From IR spectra and solubility it appeared that copolymers obtained in the hydrophilic region was PVA-g-MA; however, terpolymers obtained in the hydrophobic region were PVA-g-MA/AN. From Figure 2, there are two special wt % point of MA/(AN + MA): that is, when wt % is lower than 11.8, an increase in the concentration of KPS will bring about a gelation; when wt % is higher than 25%, no reaction of AN will occur. Therefore, controlling of the wt % of MA/(AN + MA) in the range of 11.8–25% and of wt % of KPS/(AN + MA) in the range of 3–10% will facilitate the preparation and enable one to obtain the useful grafted terpolymers. In other words, when the two conditions mentioned above are met, both MA and AN can be grafted onto PVA, with the grafted AN being at the highest possible amount.

Proposed Structure of Grafted Terpolymer

As mentioned above, at two critical points will bring about gelation and be free from the reaction of AN. The reactivities of MA appeared to be higher than AN, even it r_2 was 0 in the copolymerization with AN whose r_1 was 6. Therefore, the structure of grafted terpolymer shown in the following was considered impossible.
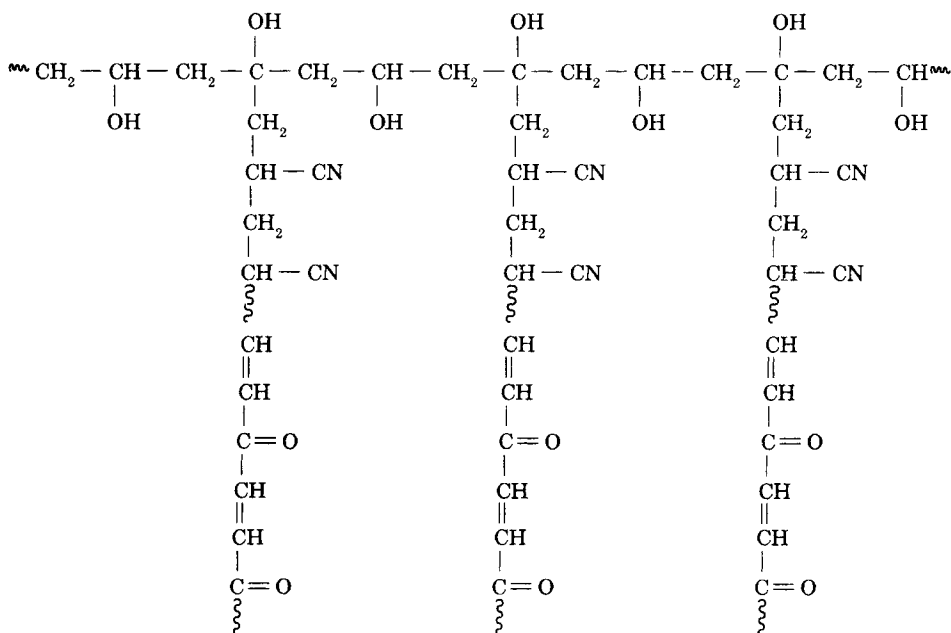
Instead, the structure may be considered as follows:

$$\text{\small{} CH}_2 - \underset{\underset{\text{OH}}{|}}{\text{CH}} - \text{CH}_2 - \underset{\overset{\text{OH}}{|}}{\text{C}} - \text{CH}_2 - \underset{\underset{\text{OH}}{|}}{\text{CH}} - \text{CH}_2 - \underset{\overset{\text{OH}}{|}}{\text{C}} - \text{CH}_2 - \underset{\underset{\text{OH}}{|}}{\text{CH}} - \text{CH}_2 - \underset{\overset{\text{OH}}{|}}{\text{C}} - \text{CH}_2 - \underset{\underset{\text{OH}}{|}}{\text{CH}}$$

First C branch (from second C):
CH
‖
CH
|
C=O
|
CH
‖
CH
|
C=O
⌇

Second branch (from fourth C):
CH
‖
CH
|
C=O
|
CH
‖
CH
|
C=O
⌇

Third branch (from fifth C):
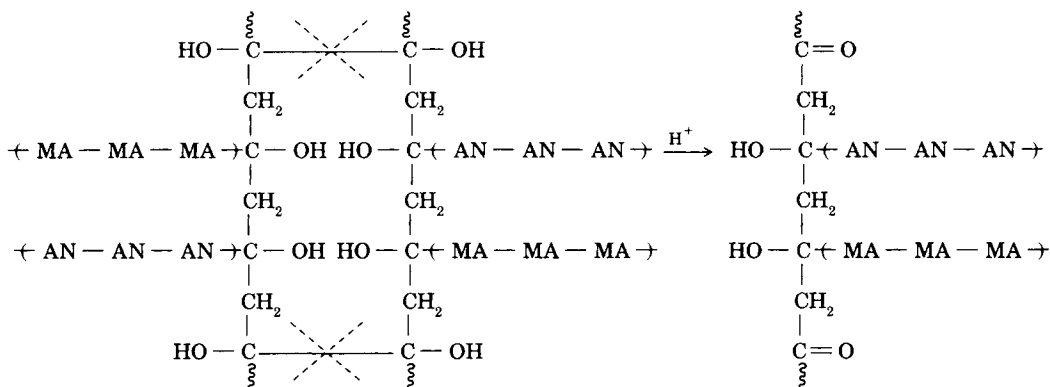CH₂
|
CH—CN
|
CH₂
|
CH—CN
|
CH₂
|
CH—CN
⌇

This supposition was confirmed by the following examinations. First, if we confined the KPS to a low concentration, (below 0.025 wt %), which would limit the radicals on the PVA main chains, then we could clearly learn how the grafted side chain came into being. Then MA was grafted onto PVA before AN monomer was added. The result was that AN did not react onto PVA—what was more, even AN homopolymer did not occur. Conversely, AN was grafted onto PVA before MA monomer was added. The result was that MA did not react onto PVA, either. So, if both MA and AN were to be grafted, KPS should be high concentration, in this way structure of graft terpolymer was considered as separate homopolymer side chains grafted onto PVA.

The higher reactivities of MA can be explained away as follows. As MA was considered to have higher affinities with PVA, so the produced free radicals in PVA backbone were surrounded by MA monomers because there was a strong tendency for hydrogen bonding to occur between MA and the OH group in PVA. As a result, MA had a higher local concentration at the vicinity of the radicals than AN did. Consequently, in the case of terpolymerization, the grafting of MA onto PVA was found to be much easier than that of AN onto PVA.

Gelation of the Graft Terpolymers

The procedure of Danelyan and Livshita[5] was used to treat terpolymers by mixing them with 30% of nitric acid at 70°C for 5 h before boiling the mixture in water for 40 min. Terpolymers were degradated into small fragments. The IR spectra of these fragments show that the absorption peaks are similar to the original terpolymers except the 3350 cm^{-1} of hydroxyl group disappears because of the oxidation by nitric acid. On the other hand, KPS was reported[6] to be able to abstract a proton from tertiary carbons of PVA to form a free radical on PVA main chain. Therefore, gelatin was considered to come from the residuals of radicals after reaction for grafting and brought about a coupling reaction among the radicals in PVA backbone at high KPS concentration. It might also occur as a result of intermolecular

reaction of growing chains with other PVA chains. It was apparent as
mentioned above that the grafted side chains remained unchanged during
the degradation. In addition, gelation probably occurred from the surplus
radicals in PVA backbone to carry on the coupling reaction, but not from
the grafted side chain shown as follows:

$$
\begin{array}{l}
\mathrm{HO-\overset{\displaystyle\xi}{C}\!-\!\!\!\overset{\diagdown\;\;\diagup}{\underset{\diagup\;\;\diagdown}{\times}}\!\!\!-\!\overset{\displaystyle\xi}{C}-OH} \qquad\qquad \overset{\displaystyle\xi}{C}=O \\[4pt]
\qquad\;\; |\qquad\qquad\quad | \qquad\qquad\qquad\qquad\;\; | \\
\qquad CH_2 \qquad\quad CH_2 \qquad\qquad\qquad\quad CH_2 \\
\qquad\;\; |\qquad\qquad\quad | \qquad\qquad\qquad\qquad\;\; | \\
+\!MA\!-\!MA\!-\!MA\!+\!C-OH\;\; HO-C\!+\!AN\!-\!AN\!-\!AN\!+\;\;\xrightarrow{\;H^+\;}\;\; HO-C\!+\!AN\!-\!AN\!-\!AN\!+ \\
\qquad\qquad\qquad\;\; |\qquad\qquad\quad | \qquad\qquad\qquad\qquad\;\; | \\
\qquad\qquad\qquad CH_2 \qquad\quad CH_2 \qquad\qquad\qquad\quad CH_2 \\
\qquad\qquad\qquad\;\; |\qquad\qquad\quad | \qquad\qquad\qquad\qquad\;\; | \\
+\!AN\!-\!AN\!-\!AN\!+\!C-OH\;\; HO-C\!+\!MA\!-\!MA\!-\!MA\!+\;\;\;\; HO-C\!+\!MA\!-\!MA\!-\!MA\!+ \\
\qquad\qquad\qquad\;\; |\qquad\qquad\quad | \qquad\qquad\qquad\qquad\;\; | \\
\qquad\qquad\qquad CH_2 \qquad\quad CH_2 \qquad\qquad\qquad\quad CH_2 \\
\qquad\qquad\qquad\;\; |\qquad\qquad\quad | \qquad\qquad\qquad\qquad\;\; | \\
\qquad\qquad HO-\overset{}{C}\!-\!\!\!\overset{\diagdown\;\;\diagup}{\underset{\diagup\;\;\diagdown}{\times}}\!\!\!-\!C-OH \qquad\qquad\quad C=O \\[4pt]
\qquad\qquad\qquad\;\; \displaystyle\xi \qquad\qquad \displaystyle\xi \qquad\qquad\qquad\qquad \displaystyle\xi
\end{array}
$$

Graft terpolymerization of the mixture of AN and MA onto PVA might
entangle the processes described as follows: first, free radicals produced in
PVA backbone were induced by initiator KPS; second, highly reactive mono-
mer MA reacted onto PVA; third, after MA reacted and still had some
residual free radicals in PVA backbone, then AN reacted onto PVA; fourth,
after MA and AN reacted onto PVA, the remaining, if any, free radicals
of PVA would bring about a coupling reaction among PVA backbone rad-
icals, thus causing crosslinking; fifth, the excess initiator brought about
oxidation scission of PVA backbone[6]; sixth, free radicals are oxidized to
ketone. It may be pointed out that the six processes could take place more
or less concurrently.

From Figure 2 given above, when MA/(AN + MA) is less than 11.8%,
gelation could occur at very high concentration of KPS; however, when it
reaches 11.8%, no matter how high the KPS concentration may be, it is
free from gelation. This phenomenon was considered to result from the fact
that the number of grafted branches of AN and MA side chains was large
at very high concentration of KPS, and for the steric hindrance of grafted
side chains it is difficult to bring about the coupling reaction. As a result,
the residual free radicals will only bring about the oxidation scission and
keto-formation reaction. Therefore, with the increasing concentration of
KPS, there will be a rather sharp increase in the weight % of AN in grafted
terpolymer before the wt % levelled off. On the other hand, the tensile
strength in the dry and wet state is also first increased and then decreased.
This change tends to indicate that the oxidative degradation seems to have
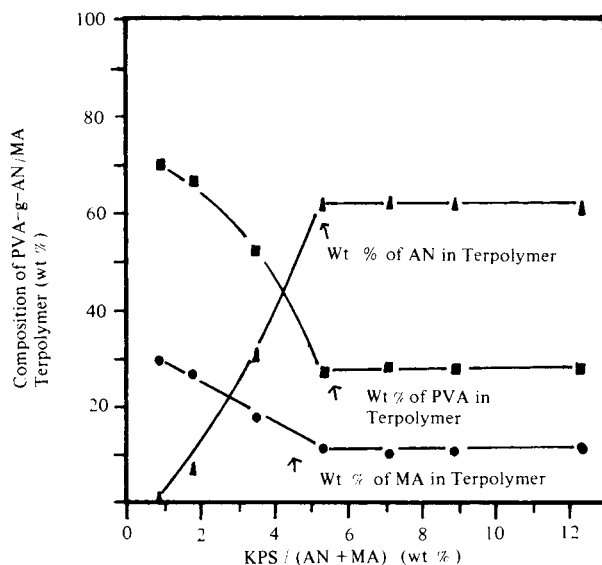taken place. The results are shown in Figures 3 and 4.

Fig. 3.   Effects of the KPS Concentration on the Compositions of PVA-g-AN MA in Weight (PVA 5g, AN 15g, MA 2g, DMSO 95g at 60°C).

Properties of Graft Terpolymers

As mentioned above, the unit content of AN in grafted terpolymers varies with the amount of KPS and MA. AN content in grafted terpolymer increases with the increase of KPS and MA, so the intrinsic viscosity and tensile strength in the dry and wet state increase with the increase of the
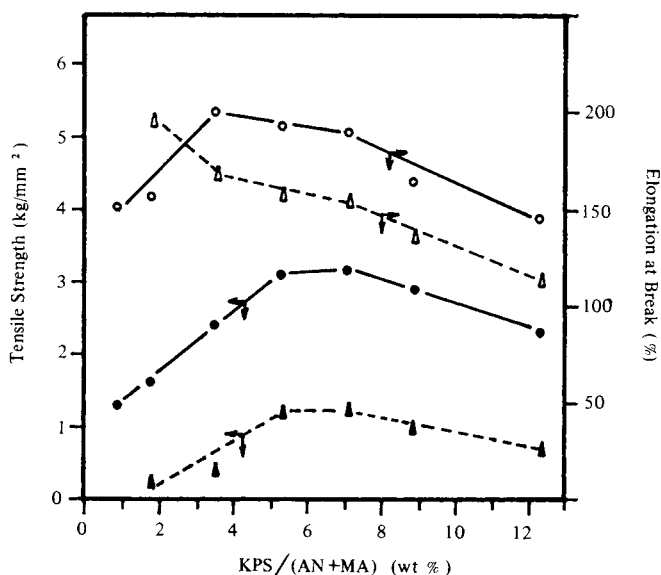

Fig. 4.   Effects of The KPS Concentration on Mechanical Properties of Terpolymers Prepared (PVA 5g, AN 15g, MA 2g, DMSO 95g at 60°C): (—) Dry State; (- - -) Wet State.

TABLE I
The Properties of Graft Terpolymers

Graft ter-polymer[a] no.	Feed MA (g)	Feed MA (wt %)[b]	Feed KPS (g)	Feed KPS (wt %)[c]	AN in Ter-polymer[d] (wt %)	$[\eta]$[e] (dL/g)	Mechanical properties						Water content (%)	
							Tensile strength (kg/mm²)			Elongation (%)			Heat treatment[f]	
							Dry	Wet	Heat[f]	Dry	Wet	Heat[f]	Before	After
PVA	0	0	0	0	0	0.88	3.51	0	7.4	258	0	33	0	0
I	0.5	3.2	0.23	1.5	7.5	1.65	3.75	0.63	—	206	194	—	200	—
II	1.0	6.25	0.48	3.0	31.5	2.42	4.21	1.72	—	154	127	—	151	—
III	1.5	9.1	1.17	7.1	62.6	3.80	4.53	1.93	7.82	140	89	15	147	10
IV	2.0	11.8	1.53	9.0	63.0	2.35	2.98	0.92	3.3	175	160	47	150	12

[a] Terpolymerization was carried on the conditions shown as follows: PVA 5 g, AN 15 g, MA varied from 0.5 to 2.0 g at 60°C.
[b] Based on MA/AN + MA.
[c] Based on KPS/AN + MA.
[d] Calculated on the equations given in the section on Experimental.
[e] In DMSO at 30°C.
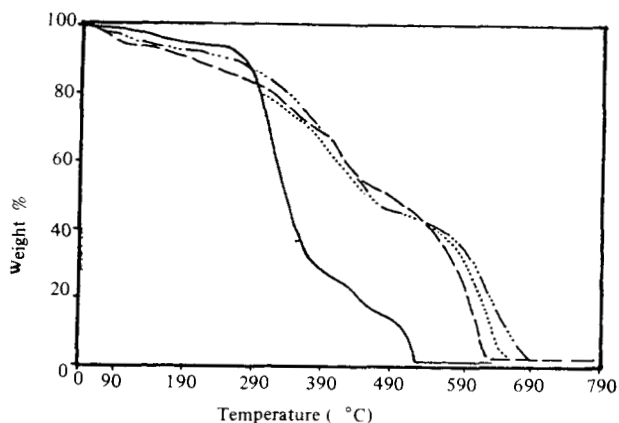[f] Heat treatment was carried out at 150°C for 2 h.

Fig. 5. TGA Thermogram of PVA and Terpolymers: (—) PVA; (- -) No. I Terpolymer; (— $\cdots$ —) No. II Terpolymer; ($\cdots$) No. III Terpolymer.

amount of AN content. On the other hand, water contents decrease with the increase of AN content. (This experiment indicates that the most desirable effects are achieved when AN in terpolymer is at 62.6 wt %). The decline in mechanical properties is considered to be a side reaction as pointed out by Ikada et al.,[6] who maintained that KPS will bring about the oxidation scission of main chain to form an acetal end group. Therefore, the increase in the amount of KPS will not increase the grafting of AN onto PVA but will bring about oxidation scission and degradation, thus resulting in the decline of mechanical properties. The results are shown in Table I.

Thermograms of TGA and DSC are shown in Figures 5 and 6, respectively. The former shows that the weight loss of grafted terpolymers decreases
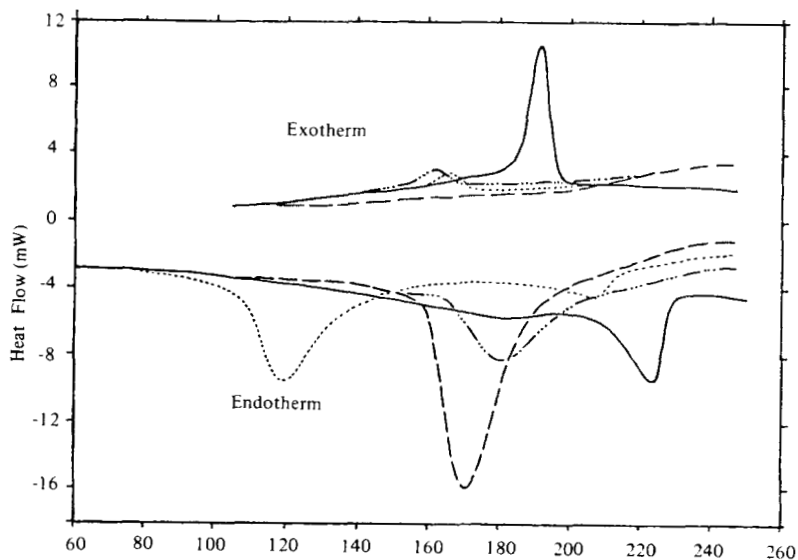

Fig. 6. DSC Thermogram of PVA and Terpolymers: (—) PVA; (- - - -) No. I Terpolymer; (— $\cdots$ —) No. II Terpolymer; ($\cdots$) No. III Terpolymer.

TABLE II
Some Thermal Analyses of TGA and DSC

Graft terpolymer no.	TGA			DSC, crystallization	
	Initial degradation temperature (°C)	% Weight loss at 500°C (%)	Temperature of weight loss at last (°C)	Exotherm (°C)	Endotherm (°C)
PVA	270	98	500	192	224
I	170	51	630	—	170
II	310	55	690	164	182
III	260	55	650	167	120, 208

slowly from 300°C and has a better thermal resistance as well as a higher residual weight than PVA. As compared with Table II, it appears that terpolymer of no. II (i.e., 31.5 wt % of AN in terpolymers) shows the best thermal properties because its weight los is somewhat better to the others. The heat of transitions refers to polymers crystalline exotherm and a melting endotherm temperatures. As shown in Figure 6, terpolymer of no. II manifests a higher endotherm temperature than the others. The results are shown in Table II.

CONCLUSION

In the graft terpolymerization of AN and MA onto PVA in the presence of KPS, it was found that the reactivity of MA was higher than that of AN. Therefore, various amounts of KPS and MA to the comonomer (AN + MA) will produce graft terpolymers of different structure and solubility. Copolymers free of AN were water-soluble: terpolymers with AN and MA were water-insoluble but DMSO soluble. If KPS or MA/(AN + MA) was in excess of a critical value, then the terpolymers obtained were crosslinked. Mechanical properties would increase with the increase of AN content in terpolymers before levelling off. Structure of the graft terpolymer was presented.

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