

Water-Soluble Polymers. I. Synthesis of *N*-Succinimido (*N*) Thiocarbonyl Acrylamide and Its Polymerization: Grafting of this Monomer and Acrylamide onto Poly(vinyl alcohol)

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SYNOPSIS

A new monomer, *N*-succinimido (*N*) thiocarbonyl acrylamide is formed when succinic anhydride, thiourea, and acryloyl chloride are condensed in mole proportions at low temperatures. The monomer is polymerized and graft copolymerized onto poly(vinyl alcohol) using a potassium bromate–thiourea redox system. Acrylamide is also similarly grafted to poly(vinyl alcohol) using the same initiator system. Grafting efficiencies of the monomers are determined from the elemental analyses data of the graft copolymers. Thermal behavior of the polymers are derived from the DSC thermograms of the polymers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A number of unique properties associated with water-soluble polymers allow them to have wide application in industry and medicine. For instance, poly(vinyl alcohol) (PVA) is used as an emulsifier and protective colloid in suspension polymerization because it has the capacity to reduce the surface tension on the interface, which contributes to the dispersion of the liquid in the form of small drops, and it also acts as a protective colloid by enveloping particles of the dispersed internal phase by a thin surface film preventing coagulation.¹ Its good adhesive properties allow it to be used as an adhesive for paper, veneer, etc. The other set of water-soluble polymers in broad use in various industries is polyamides.

Polyamides, especially aromatic polyamides, possess high thermal stability and acceptable mechanical properties. However, aromatic polyamides show infusibility and limited solubility, restricting their synthesis, characterization, processing, and application. Various approaches like lateral substituents, flexible alkyl side chains, or alkyl spacers have

been adjusted to enhance the solubility of aromatic polyamides.² The processability of these polymers is enhanced by introducing bulky and rigid units in the polymer backbone and there have been concerted efforts to synthesize new polyamides from various types of monomers.^{3,4}

Water-soluble polymers are employed in the photo film industry as binders, covering power agents, sensitizers, viscosity reducers/boosters, etc. A mixture of two or three polymers or a copolymer is required for specific applications as, in the majority of cases, a single water-soluble polymer does not comply with all the properties. Among the different methods of modification of a base polymer (synthetic or natural) like change of functionality, oxidative degradation, inter- and intramolecular gelation, graft copolymerization, etc., the grafting reaction provides a high polymer whose molecule consists of two or more polymeric parts of different compositions chemically united together. Grafting establishes a potential route for significantly altering the physical and mechanical properties of a substrate polymer, thus tailoring the properties of the material for specific end uses.⁵ Recently, we reported a method of converting poly(vinyl pyrrolidone) into a product of lower viscosity.⁶ Now, work is in progress in this laboratory on the preparation and characterization of some water-soluble polymers from water-insoluble/low-soluble and low-processable

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polymers such as silk and alginic acid. An acrylamide monomer embedded with a substituent carrying a sulfur and succinimido moiety is envisaged to provide a homopolymer and graft copolymers with PVA having unique characteristics suitable for processability and applications. The substituent, possessing a thiocarbonyl group as well as a pyrrolinedione ring, is introduced into the acrylamido moiety by condensing thiourea, succinic anhydride, and acryloyl chloride in mole proportions at low temperatures. When polymerized at 60°C using the potassium bromate/thiourea redox system as initiator, this new monomer, *N*-succinimido (*N*) thiocarbonyl acrylamide (STAA) undergoes thermal polymerization very easily. It is also found to polymerize well thermally in the presence of any normal initiator like benzoyl peroxide, azobisisobutyronitrile (AIBN), potassium persulfate, etc.

This monomer has been graft-copolymerized onto PVA ($\bar{M}_n = 14,000$). Graft copolymers of PVA and acrylamide (AA) were also made under identical conditions so as to draw some commonalities between STAA and AA and to comprehend the effect of the long substituent on the AA structure. Poly(*N*-succinimido (*N*) thiocarbonyl acrylamide) (PSTAA) is very soluble in water and both the graft copolymers are more soluble than is the PVA employed in the present work. Thermal characterization of the polymers were derived from the DSC thermograms of the polymers.

EXPERIMENTAL

Materials

Succinic anhydride, thiourea, ethyl acetate, and acetone all were of L.R. grades of BDH India. Potassium bromate, azobisisobutyronitrile, benzoyl peroxide, and potassium persulfate were AnalaR grades of BDH. PVA and AA were of Sigma source.

Methods

Synthesis of STAA

Step 1. Preparation of Thiourea Succinimide. One mole each of succinic anhydride and thiourea were dissolved in 30 mL of distilled ethyl acetate and stirred vigorously at 15°C for 6 h. Thiourea succinimide separated out slowly. The white solid was collected, filtered, washed with a small amount of ethyl acetate, and dried.

Yield = 97%; mp, 160°C; TLC, single spot. IR(KBr): $=C=S$, 1050 cm^{-1} ; $=C=$, 1750 cm^{-1} ;

$-CH_2-$, 1450 cm^{-1} ; $-NH_2$, 3220 cm^{-1} ;
 $\equiv C-N=$, 1200 cm^{-1} .

Step 2. Preparation of STAA. Each 1 mol of thiourea succinimide (from Step 1) and acryloyl chloride were dissolved in 50 mL of dioxane and stirred well at 15°C for 2 h. Triethylamine, 12.5 mL, was added during the period and stirring was allowed to continue for another 8 h, maintaining the temperature of the reaction vessel at 15°C. A white solid separated along with the amine salt was collected, dissolved in dry acetone (distilled acetone kept over potassium carbonate), and filtered. The amine salt was left in the filter, and the filtrate, on slow evaporation, yielded a lustrous white solid of STAA. The monomer was recovered and recrystallized from acetone.

Yield: 57%; mp, 120°C; TLC, single spot. IR(KBr): $CH_2=CH-$ 15 cm^{-1} ; $-NHCO$ 3220 and 1640 cm^{-1} ; $=N-C-N=$, 1260 cm^{-1} .

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Polymerization Reactions

1. Polymerization of STAA Monomer. Ten grams of the monomer were dissolved in 100 mL of distilled water in a 250 mL three-necked flask. The contents were effectively stirred and pure nitrogen was passed for 10 min. The temperature was raised to 60°C and 0.5 g of potassium bromate and 0.25 g of thiourea were added to the flask with vigorous stirring at 60°C for 3 h. The PSTAA was recovered by adding the polymerized solution to acetone. The polymer was reprecipitated three times, washed well in acetone, and dried. The yield of the polymer was almost quantitative. The PSTAA obtained was a lustrous, glistening, and fluffy white solid, very highly soluble in water. It was observed that an aqueous solution of STAA polymerizes very easily in the presence of any of the normal initiators like ammonium persulfate, azobisisobutyronitrile (AIBN), benzoyl peroxide, etc., besides the thiourea/potassium bromate redox system described earlier.

2. Graft Copolymerization Reactions.

A. Grafting of STAA on to PVA. Five grams of PVA was dissolved at 80°C in 100 mL of water and the solution was cooled. Five grams of STAA was added to the solution and the contents of the flask were purged with nitrogen for 10 min. Raising the temperature of the solution to 50°C, 0.5 g of potassium bromate and 0.25 g of thiourea were added in sequence and the liquid mixture was stirred well. Reaction was allowed to proceed for 0.5 h and the PVA-graft-co-STAA was separated by adding the

Table I Solubility of Polymers

Polymer	Solvent						
	Water	Methanol	Ethanol	Acetic Acid	DMF	Benzene	Hexane
PAA ^a	s	is	is	is	is	is	is
PVA	s	s	s	is	s	is	is
	(35% acetyl)						
PSTAA	vs	vs	vs	vs	vs	is	is
PVA-co-STAA	vs	s	s	s	s	is	is
PVA-co-AA	s	s	s	s	s	is	is

is = insoluble; s = soluble; vs = very soluble.

^a PAA = polyacrylamide.

solution to acetone. The polymer (1 : 1 w/w ratio) was reprecipitated three times in acetone, washed well in acetone, and dried. Similarly, polymers formed in the time intervals of 1, 1.5, 2, 2.5, 3, 6, and 12 h were also recovered.

Graft copolymerization with the w/w ratio 1 : 2, consisting of 5 g of PVA and 10 g of STAA, was performed by adopting identical conditions and fol-

lowing similar procedures for the time intervals mentioned earlier. Polymers formed in this series were also collected.

B. Grafting of AA onto PVA. A typical graft polymerization of AA to the same sample of PVA was repeated under identical conditions for the w/w ratios 1 : 1 and 1 : 2, with respect to PVA and AA, respectively, and for the same durations of time

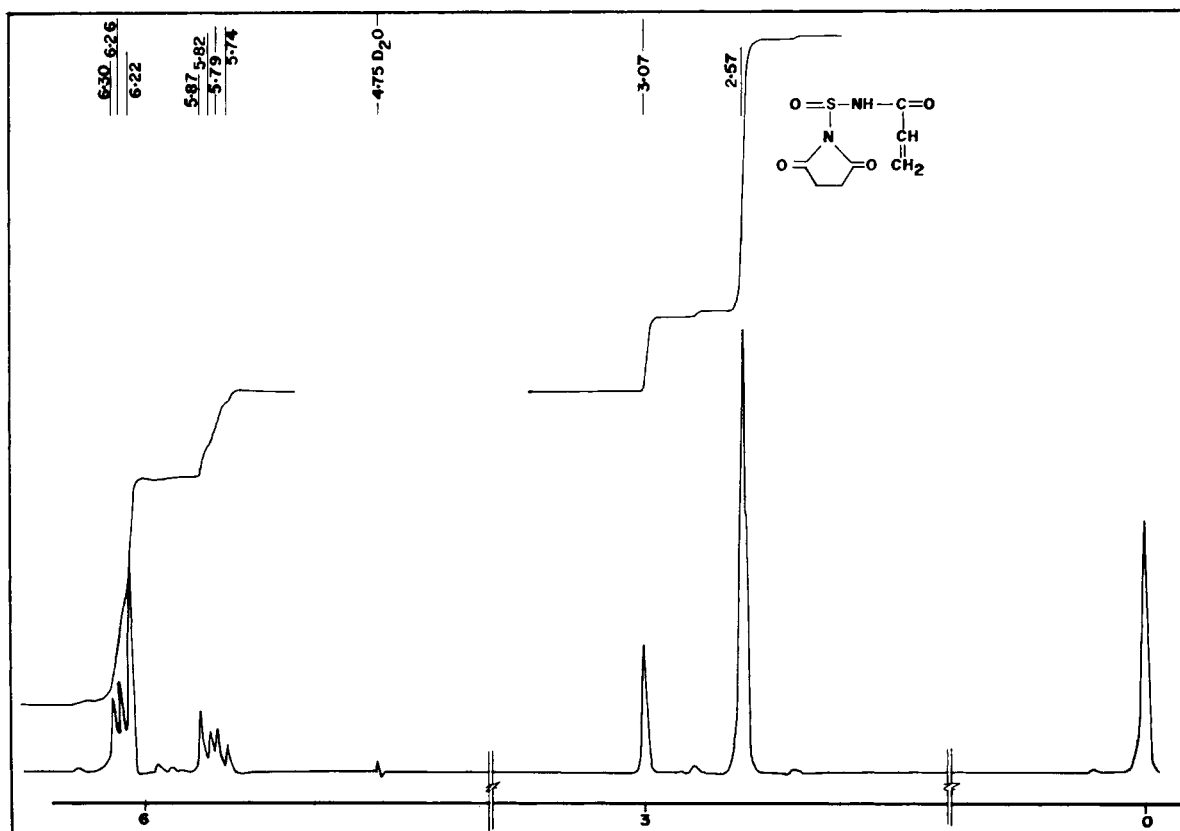


Figure 1 ¹H-NMR spectrum of the monomer, STAA.

as in the grafting of STAA to PVA. The yields of PVA-*graft-co*-acrylamide polymer obtained at the said intervals of time were found to be excellent in this technique. Solubility data of polymers are given in Table I.

Measurements

The IR spectra were taken using a Perkin-Elmer 230 spectrometer, CHN values were recorded using a Perkin-Elmer 240 C analyzer, and NMR spectra in D₂O were imprinted in an H¹ 90 Bruker spectrometer. The glass transition, melting, and decomposition temperatures were determined by differential scanning calorimetry using a Mettler TA 3000 DSC system interfaced through computer controlled software for monitoring the various parameters. Samples for DSC analysis were prepared in appropriate aluminum pans by standard techniques. Prior to each scan, the samples were heated to 85°C for 5 min and suddenly quenched by immersing into an ice-water bath for 2 min and dried to ensure that no acetone was retained. The scanning was made over a temperature range of 40–300°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

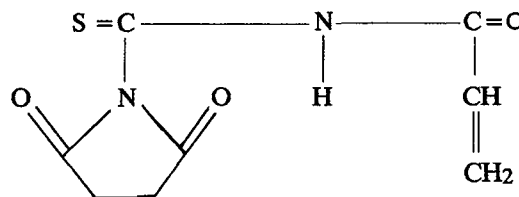
Thiourea undergoes tautomerism and only the isothiourea tautomeric form is taking part in the majority of chemical reactions. However, there are also a few instances in the literature where the thiocarbamido tautomeric form as such is entering into condensation reactions.⁷ Evidence in the literature is also found for the molecular condensation of succinic anhydride as such with the elimination of its anhydric oxygen.⁸

Under the conditions mentioned in the Experimental section, the thiocarbamido form of the thiourea molecule has condensed with the anhydric oxygen of succinic anhydride, and the thiourea succinimide formed thereof has condensed with acryloyl chloride with the elimination of a molecule of hydrogen chloride and the STAA monomer is formed. The IR peak positions obtained for the various linkages, as given in the Experimental section, support the reaction pathway explained. Functional group analyses were also carried out to confirm the presence of certain functions. The evidence for the structure of STAA, an *N*-substituted acrylamide derivative, comes from the NMR data for the eight protons present in the monomer: all prominent signals at 2.57δ for the alicyclic methylene protons, at 3.07δ for the lone N—H proton, and 5.74–5.87 and

6.22–6.30δ for the vinyl protons⁹ (Fig. 1). Finally, the elemental analyses data of the monomer are the following:

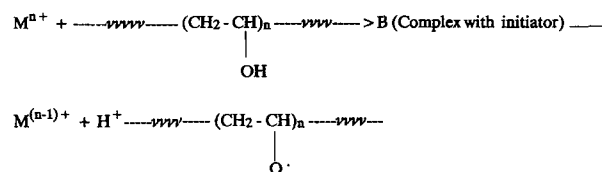
ANAL: Calcd: C, 45.58%; H, 3.92%; N, 13.18%.
Found: C, 45.28%; H, 3.80%; N, 13.20%.

Therefore, the structure of the monomer is concluded to be



Grafting onto PVA

It was reported¹⁰ that PVA forms a complex with the initiator, which subsequently decomposes to provide a radical site on the backbone polymer. The site and mechanism of grafting were given as:



The nonsolvent for PVA-*graft-co*-STAA, like PVA-*graft-co*-AA, is acetone. Unreacted monomers in both cases were removed by repeated precipitations and washings in acetone. The polymers were vacuum-dried for 3 h and NMR spectra were taken for PSTAA and the graft copolymers (Figs. 2–4). The weights of all the graft copolymers were determined gravimetrically. In the time intervals between 0.5 and 12 h, the yields of PVA-*graft-co*-STAA were from 55 to 67.5%, but the range in respect of PVA-*graft-co*-AA in the said time intervals was from 81.6 to 86.6%.

Weights of grafted monomer in each case of PVA-*graft-co*-STAA and PVA-*graft-co*-AA were determined from elemental analyses data. Prior to introducing the samples into the analyzer, the grafted polymers were vacuum-dried overnight so as to ensure that no moisture was present:

$$\begin{aligned} &\text{The weight of the grafted monomer (AA or STAA)} \\ &= \frac{\text{Molecular weight of monomer}}{\text{Weight of nitrogen present in the monomer}} \\ &\times \text{Percentage of nitrogen present} \\ &\qquad\qquad\qquad \text{in the graft copolymer} \end{aligned}$$

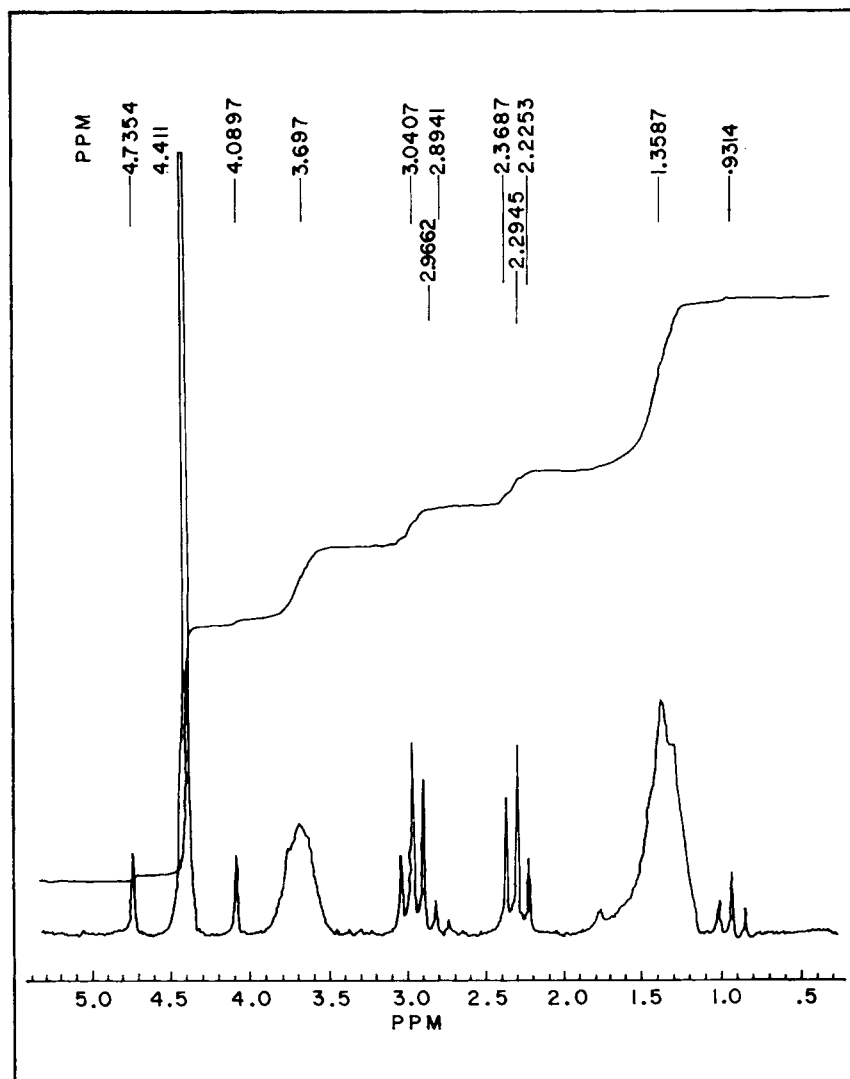


Figure 2 $^1\text{H-NMR}$ spectrum of PSTAA.

The weights of grafted monomers were used to determine the graft efficiency of the monomers in the different samples of the graft copolymers prepared. The equation used to calculate graft efficiency was

Graft efficiency

$$= \frac{\text{Weight of monomer (AA or STAA) grafted on to PVA}}{\text{Weight of PVA}} \times 100$$

The yields obtained and the graft efficiencies calculated are listed in Table II. The graft efficiency of STAA can be seen to be poorer than that of AA.

Thermal Characterization of the Polymers

It is observed that not only PSTAA but all the copolymers prepared in the present work give rise to transparent, homogeneous, thermoplastic materials. DSC thermograms of PVA and PSTAA, and those of some typical graft copolymers of PVA-*graft-co*-AA and PVA-*graft-co*-STAA are given in Figures 5-7 and the different peak temperatures with the respective enthalpy values obtained thereof, and T_g/T_m values calculated for each polymer are given in Table III.

As can be seen in Figure 5(A₁), the PVA sample employed in the present study has a glass transition temperature, T_g , at 156.8°C; the thermogram shows a slight heat distortion range around 185°C and

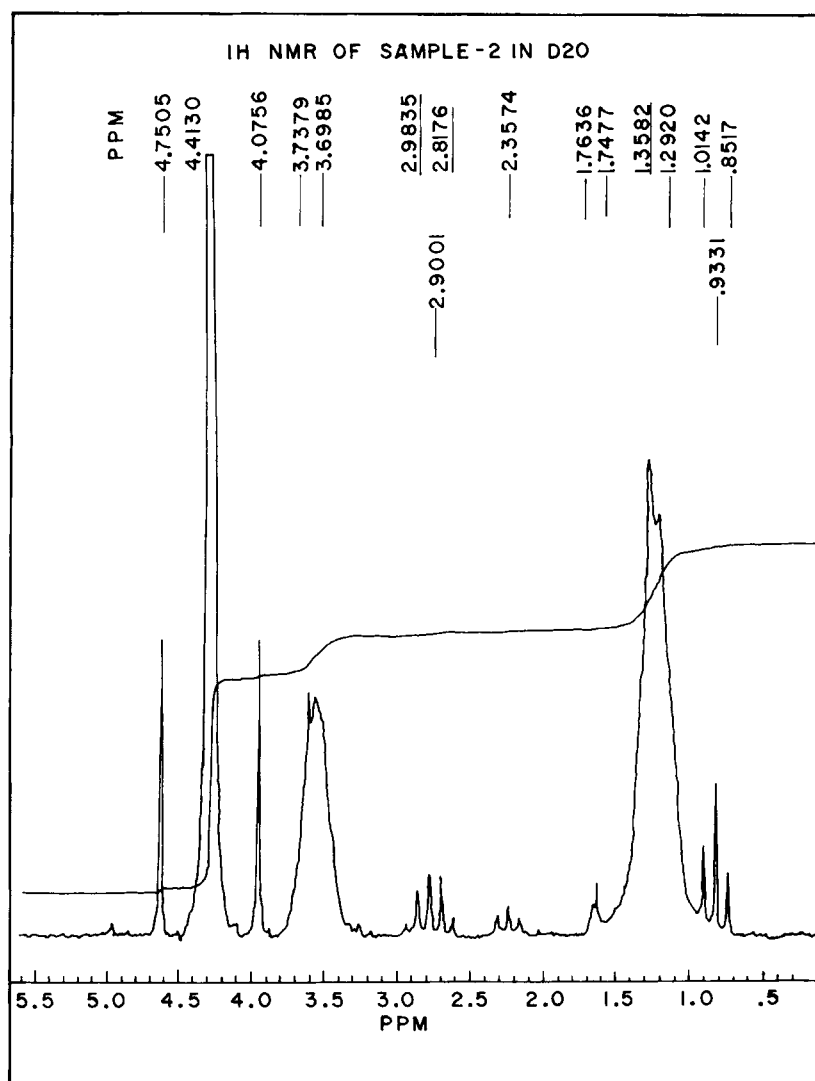


Figure 3 $^1\text{H-NMR}$ spectrum of PVA-graft-co-STAA.

crystalline melting temperature T_m at 211.3°C . The polymer decomposes above 230°C . PSTAA, on the other hand, gives [Fig. 5(A₂)] three relatively narrow peaks that may, respectively, be assigned to T_g , T_m , and T_d (decomposition temperature) of the polymer. T_g of PSTAA is very much lower than the T_g of poly(acrylamide) (PAA) (165°C). The literature catalogs the T_g values of *N*-substituted acrylamides¹¹ as follows:

	T_g (K)
Poly(<i>N</i> -normal butyl acrylamide)	319
Poly(<i>N</i> -octyl acrylamide)	220
Poly(<i>N</i> -octadecylacrylamide)	162
Poly(<i>N</i> -piperidyl acrylamide)	381

This clearly shows a descending trend in the T_g when the substituent is a ring or a hydrocarbon moiety. The greater the length of the hydrocarbon chain, the lower will be the T_g . The substituent in the polymer side chain of PSTAA consists of polar groups and a pyrrolinedione ring. Hence, the T_g of PSTAA (344.6 K) is lower than the T_g of PAA (438 K).

The literature documents well the thermal behavior of individual graft copolymers. Still, the complexity and peculiarity associated with the nature of each graft copolymer make it difficult to draw any generalized conclusion. For example, in the graft and block copolymers, the size of phases is reported to be ranging between less than 100 to several hundred angstrom units.¹² These are called microphases and a two-component microphase system is

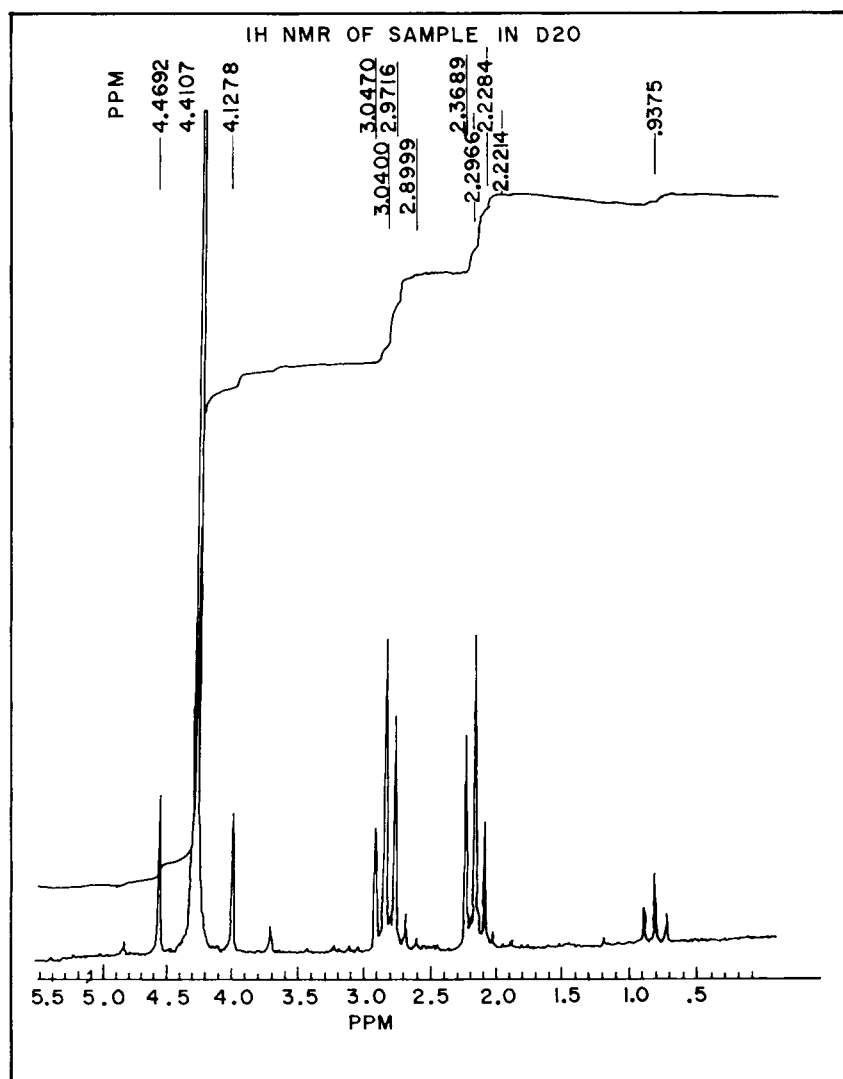


Figure 4 ^1H -NMR spectrum of PVA-graft-co-AA.

Table II Comparative Data of Graft Efficiencies

Time (h)	PVA-STAA				PVA-AA			
	1 : 1		1 : 2		1 : 1		1 : 2	
	Yield (%)	G.E. (%)	Yield (%)	G.E. (%)	Yield (%)	G.E. (%)	Yield (%)	G.E. (%)
0.5	55.0	3.4	43.3	5.5	81.6	72.1	80.0	68.8
1	57.5	17.6	46.6	7.5	86.6	73.6	88.8	74.2
1.5	62.5	—	53.3	—	86.6	65.6	91.1	64.9
2	60.0	27.1	56.6	6.5	85.0	64.2	88.9	68.8
2.5	64.0	—	53.3	—	85.0	79.6	91.1	78.4
3	62.5	31.5	63.3	14.9	91.6	61.3	82.2	61.9
6	65.0	37.6	70.0	25.6	83.3	60.3	77.8	63.7
12	67.5	39.5	80.0	45.4	86.6	63.1	97.8	61.0

G.E. = graft efficiency.

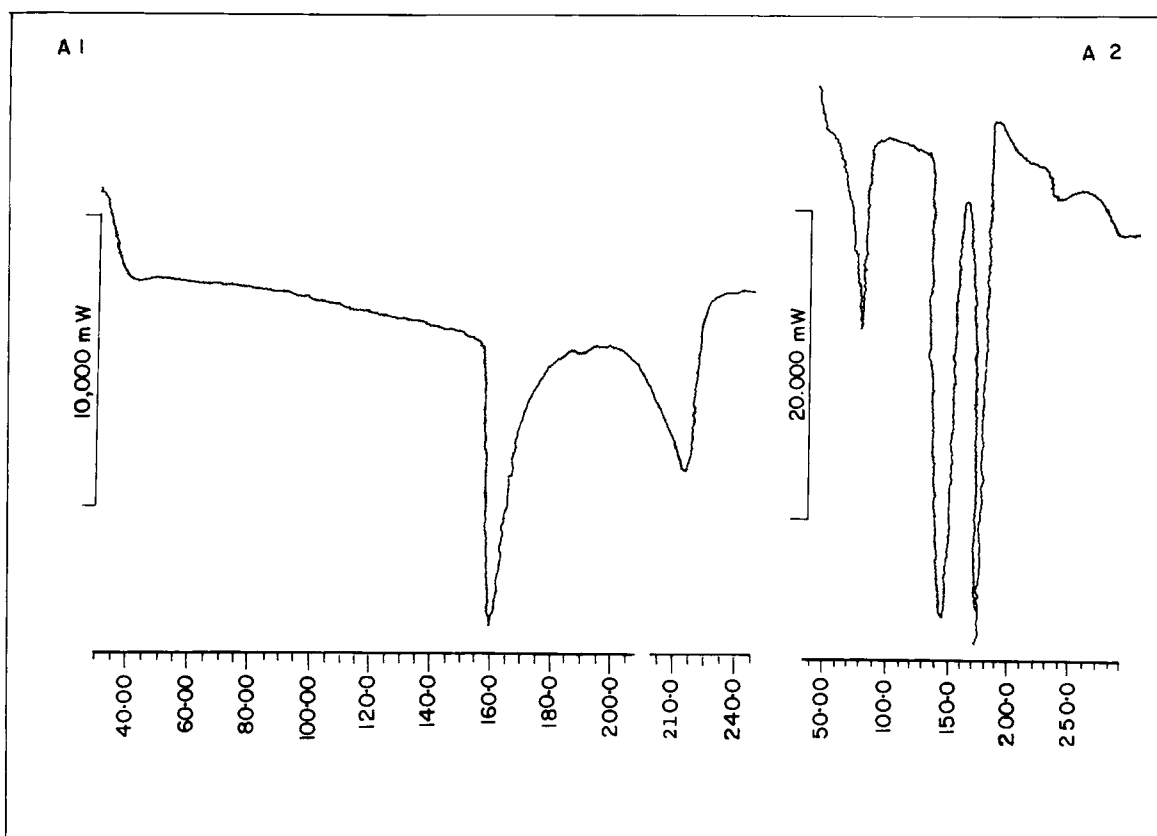


Figure 5 (A₁) DSC thermograms of PVA and (A₂) poly(*N*-succinimido (*N*) thiocarbonyl succinimide).

reported to consist of a uniformly dispersed phase or domain and matrix, which, however, cannot be expected in all graft polymers. Second, block and graft copolymers frequently have been reported to have two (or more sometimes) separate T_g 's, each one closer to the T_g of the parent homopolymer or T_g values at intermediate temperatures. Phase mixing on the T_g , mutual solubility, and mutual incompatibility all make the situation unpredictable for graft copolymers to be assigned single T_g 's. Still, as in random copolymers where single T_g 's are possible with specific and well-adjusted copolymer compositions, single T_g 's in many graft copolymers have been observed.¹²

It is also reported that in random copolymers, owing to the irregularity in structure, crystallization is more difficult than for each of the pure homopolymers and so the melting point is depressed and the T_g has a normal value between those for the homopolymers.¹³ This results in very high values for T_g/T_m .

The values of T_g/T_m ranging from 0.76 to 0.93, both for PVA-*graft-co-AA* and PVA-*graft-co-STAA* suggest that the polymers are amorphous. The thermograms of PVA-*graft-co-AA* (Fig. 6) have heat-distortion regions below 100°C, due to secondary transitions of the graft copolymers. They also have single T_g 's and depressed melting points. The single T_g situation is well exhibited in PVA-*graft-co-STAA*, as shown in the thermograms (Fig. 7).

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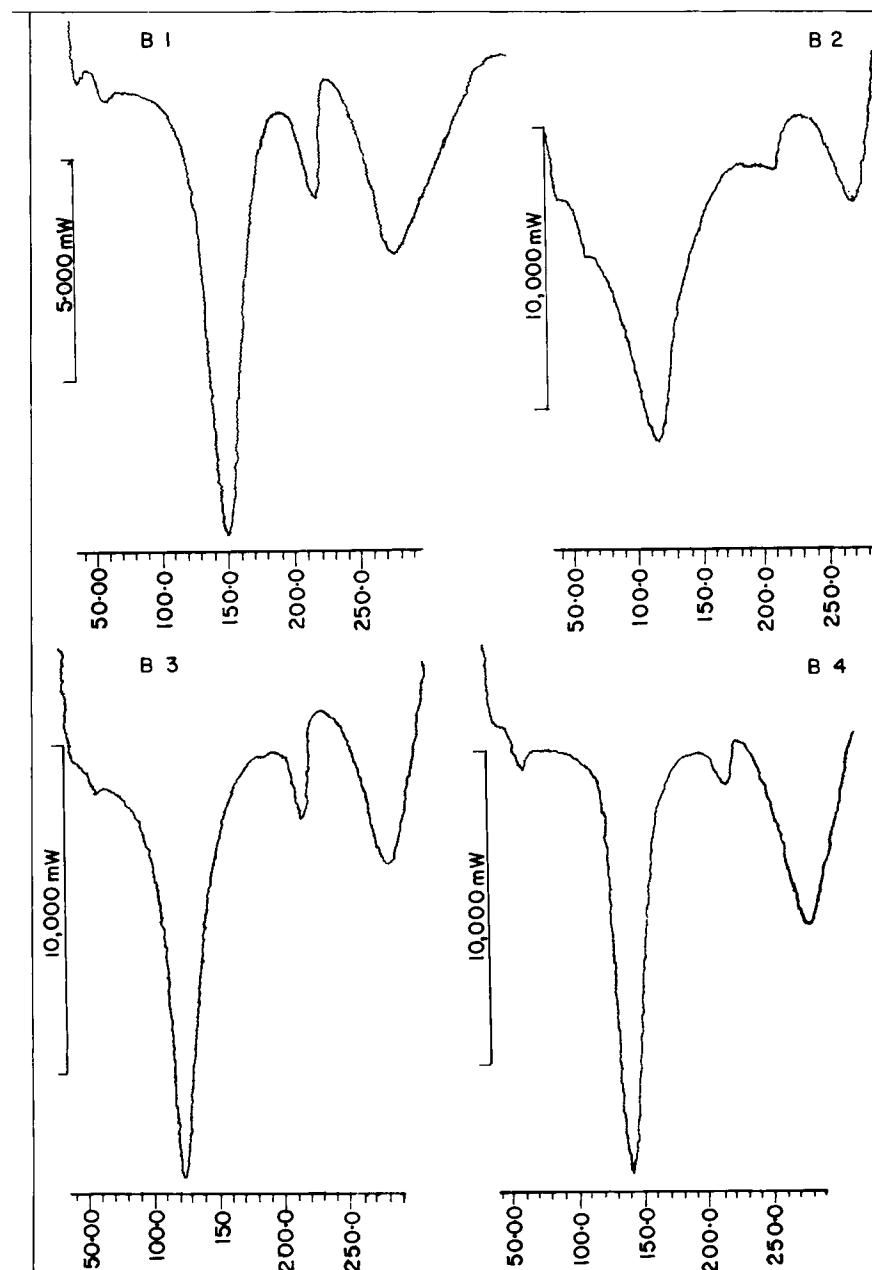


Figure 6 DSC thermograms of PVA-*graft-co-AA*: (B₁) 1 : 1, 0.5 h; (B₂) 1 : 1, 2 h; (B₃) 1 : 2, 0.5 h; (B₄) 1 : 2, 2 h.

Table III Thermal Data of Polymers

Sample	I Peak			II Peak			III Peak			T_g/T_m
	Temp (°C)	ΔH_{endo} (mJ)	ΔH (J/G)	Temp (°C)	ΔH_{endo} (mJ)	ΔH (J/G)	Temp (°C)	ΔH_{endo} (mJ)	ΔH (J/G)	
A1	156.8	541.9	54.1	221.3	414.7	41.4	—	—	—	0.87
A2	71.6	887.4	44.3	138.0	2656.4	132.8	168.9	1284.5	64.2	0.84
B1	148.4	1783.0	118.8	219.3	192.8	12.8	275.0	—	—	0.86
B2	123.1	2297.3	229.7	218.4	199.7	19.9	282.0	—	—	0.81
B3	115.1	2168.6	216.8	215.0	—	—	276.0	744.9	74.4	0.80
B4	139.0	2057.0	205.7	219.2	95.4	9.5	281.0	—	—	0.84
C1	91.0	—	—	205.3	1144.2	57.2	256.0	—	—	0.76
C2	149.5	194.76	32.4	181.8	32.2	5.3	209.4	92.9	15.4	0.93
C3	138.2	1784.5	118.9	213.9	542.5	36.1	257.7	1427.6	95.1	0.85
C4	145.9	161.18	26.4	181.6	144.1	23.6	—	—	—	0.92

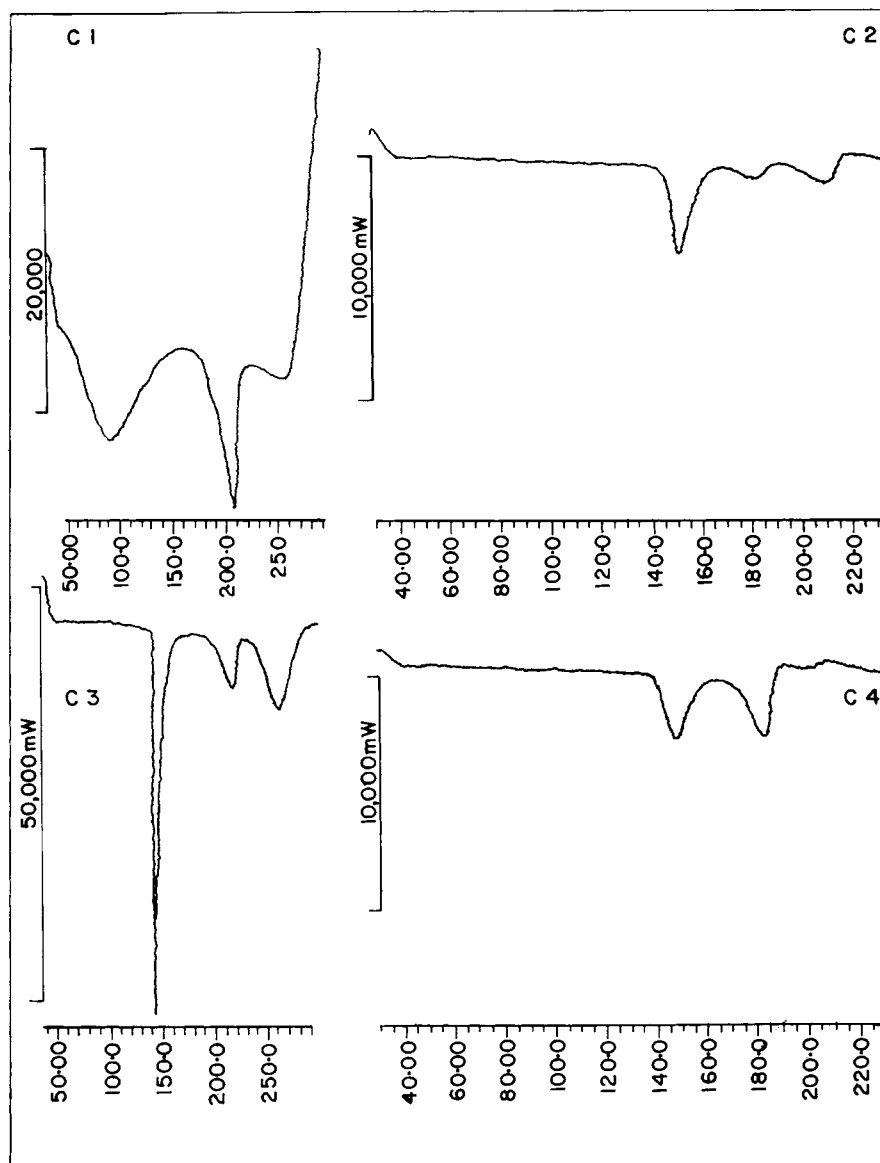


Figure 7 DSC thermograms of PVA-graft-co-STAA: (C₁) 1 : 1, 0.5 h; (C₂) 1 : 1, 2 h; (C₃) 1 : 2, 0.5 h; (C₄) 1 : 2, 2 h.

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