

Polymerization of 4-Chloroformylphthalic Anhydride with 4,4'-Diaminodiphenylether

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Synopsis

The polymerization of 4-chloroformylphthalic anhydride with 4,4'-diaminodiphenyl ether was investigated under a variety of reaction conditions. Both interfacial and solution techniques were used, with the latter method yielding the highest molecular weight polymer. Synthesis of high molecular weight polyamide-imides requires the use of pure monomers, exclusion of moisture, and proper stoichiometry. Molecular weight control can be achieved by the addition of either aniline or phthalic anhydride. Heating of the resin solution for 1 hr at temperatures $\geq 50^{\circ}\text{C}$ results in a large decrease in inherent viscosity as well as in the polymer properties. Tertiary amines such as triethylamine, when added to the precursor solution, markedly influence the viscosity of the resin.

INTRODUCTION

For some time now we have been engaged in the evaluation and development of high-temperature film-forming polymers. Our work has mainly been directed towards the field of amide-imide polymers. Although the preparation of polyamide-imides is not new,¹⁻⁵ the polymers derived from the use of various monomers possess a good combination of mechanical, electrical, and thermal properties. We have investigated the polymer derived from the reaction of 4-chloroformylphthalic anhydride and 4,4'-diaminodiphenyl ether. Part I of this series deals with some of the reaction variables involved in the synthesis of this polymer and the conversion of the intermediate polyamide acid to its final polyamide-imide form.

EXPERIMENTAL

Reagents

Dimethylacetamide (DMAC). Monsanto Chemical Co. Used as received and after drying over molecular sieve 5A.

4,4'-Diaminodiphenyl Ether (DAPE). Sumitomo Chemical Co. A light tan powder (DTA mp = 190°C). Used as received.

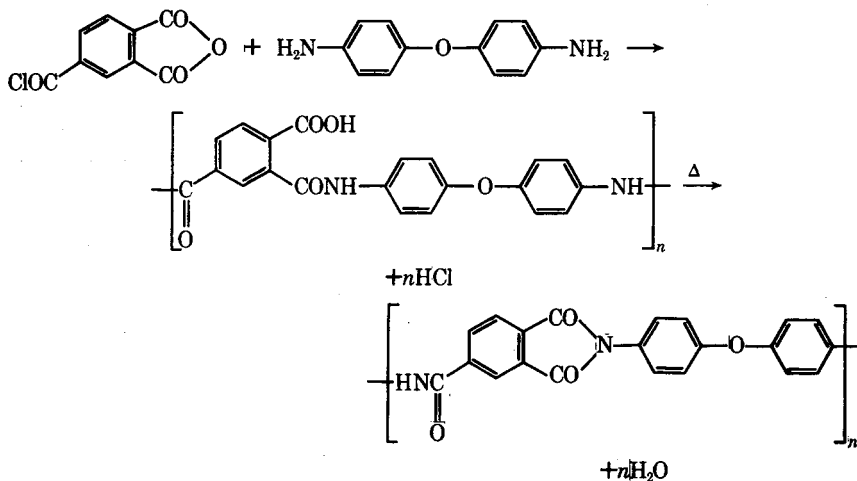
4-Chloroformylphthalic Anhydride (TMAC). Arysenco, Inc. White flakes. Used as received and after purification by distillation (DTA mp = 67°C . Distillation range $170-175^{\circ}\text{C}$ at 5 mm Hg.)

ANAL. Calcd for $\text{C}_8\text{H}_5\text{O}_4\text{Cl}$: C, 51.42%; H, 1.42%; O, 30.47%; Cl, 16.66%. Found: C, 51.24%; H, 1.37%; O, 30.19%; Cl, 16.61%; S, 0.01%; P, <0.01%.

Propylene oxide (PO), triethylamine (TEA), methyl ethyl ketone (MEK), phthalic anhydride (PA), and aniline (AN) were all obtained from Fisher Scientific Co. and used as received.

Polymerizations

Both solution condensation and interfacial polymerization were employed to study the reaction between TMAC and DAPE. This reaction is schematically shown below:



A random mixture of head-to-head and head-to-tail linkages is probable. The detailed procedures used are as follows:

Solution Condensation. To 200 g (1.0 mole) of DAPE dissolved in 1640 g DMAC is added 210 g (1.0 mole) TMAC. An exothermic reaction occurred, and the temperature was maintained between 20° and 45°C by means of an ice-water bath. The reaction was carried out under a nitrogen blanket. The reaction was continued until a maximum viscosity was reached, at which time a stoichiometric amount of propylene oxide was added to act as the acid acceptor. A second exotherm was noted, and again the reaction was continued until a maximum viscosity was reached. The viscous resin solution was either refrigerated at this point or diluted with DMAC and poured into a rapidly stirred nonsolvent in a Waring Blendor to precipitate the polymer. The nonsolvent could be water, acetone, methanol, or tetrahydrofuran, preferably methanol. The fibrous polymer thus obtained was washed thoroughly with methanol and dried overnight under vacuum at 80°C.

Interfacial Polymerization. The polymerization was carried out according to the method reported by Imai et al.⁴ In a Waring Blendor there were placed 20 g (0.1 mole) DAPE, 10.2 g (0.1 mole) TEA, 25 cc distilled water, and 150 cc MEK. A cream-colored slurry was obtained. To this rapidly stirred system was added all at once a solution of 21 g (0.1 mole) TMAC in 100 cc MEK. As soon as the TMAC-MEK solution was added, a coarse, brown precipitate separated. The reaction vessel became quite warm, and stirring was continued for 20 min. The brown precipitate was quite sticky because of entrapped solvent and had to be washed many times

TABLE I
Comparison of Interfacial and Solution Polymerization Methods

	Inherent viscosity, dl/g	Physical state of polymer	Film properties	Reaction time	Comments
Interfacial	0.35	coarse powder	brittle	20 min	requires considerable washing to free precipitated polymer of entrained reaction solvents; needs to be redissolved in DMAC prior to film casting
Solution	0.4-2.0	fibrous polymer	flexible	>5 hrs	no washing necessary; resin solution can be used as prepared without precipitating polymer

with large volumes of water. The brown, coarse powder was dried overnight under vacuum at 80°C.

Test Methods

Inherent Viscosity. Measurements were made on 0.5% solutions of the polymers in DMAC at 24°C using a Cannon Fenske viscometer (size 75). Viscosity measurements were made on the precipitated polymer as well as on aliquot samples taken from the reaction mixture. Gardner viscosity was also recorded on the final polymer solution using the Comparative Gardner-Holdt standard viscosity tubes.

Folding Endurance. Flexibility was determined on films made from the synthesized resin solutions according to ASTM D-2176 (MIT folding test under a 1-kg load).

RESULTS AND DISCUSSION

In Table I data are presented comparing the two polymerization methods used for the synthesis of the amide-imide resin derived from TMAC and DAPE. Although only a short reaction time is needed for interfacial polymerization, we were unable to prepare high molecular weight polymer suitable for film casting. In addition, another step is required to prepare the precipitated polymer for solution casting. In the solution method, high molecular weight polymer is obtained which can be used for solution casting directly from the reaction mixture, thus avoiding the long work-up time required in the former method.

POLYMERIZATION CONDITIONS

Monomer Purity

As shown by others⁷⁻⁹ in the preparation of polyimides, the synthesis of high molecular weight polyamide-imides is dependent on the preparation of high molecular weight polyamic acid. Generally, it is preferable to add the solid acyl anhydride to a solution of the diamine in a polar solvent such as dimethylacetamide. It would appear that the rate of reaction is limited

TABLE II
Effect of Monomer Purity and Moisture on Polymerization

Reaction	Inherent viscosity, dl/g	Solids, %	Gardner viscosity	Comments
A	2.16	10	Z6	distilled TMAC stored in dry box
B	1.84	17	Y	flake TMAC stored in dry box
C	0.30	25	I	flake TMAC exposed to lab atmosphere ambient conditions for five days
D	0.64	19	U	TMAC stored in polyethylene bag at ambient conditions for ~ eight months
E	0.51	19		distilled monomers but nondried DMAC
F	1.84	20		distilled monomers and DMAC dried over molecular sieve 5A

by the rate of solution of the acyl anhydride. Powdered anhydride is preferred over chunk material. The preparation of high molecular weight polyamic acid depends on the use of pure monomers, exclusion of moisture, correct stoichiometry, and the utilization of low-to-moderate temperature. We have found that only low molecular weight polymer is obtained if the acyl chloride is either impure or has been left standing for several days in the open at ambient laboratory temperatures.

Acid chlorides are extremely susceptible to hydrolysis, and moisture must be rigorously excluded from the reaction medium. High molecular weight polymer can be obtained if pure TMAC (distilled) is used and stored under dry conditions. In Table II data are shown on several reactions illustrating the effect of impure TMAC (caused by hydrolysis) on the polymer molecular weight. These reactions shown in the table were all run under nitrogen and using DMAC which had been dried over molecular sieve 5A for two days prior to its use.

Several reactions were then run using distilled monomers but with DMAC as obtained from a 55-gal storage drum. In all cases, inherent viscosity and Gardner viscosity were low. This same DMAC was dried over molecular sieve 5A and the reaction rerun. High molecular weight polymer was obtained as reflected in the high inherent viscosity (see Table II, E and F). Clearly, high molecular weight polymer can only be obtained if pure monomers are used and dry conditions (exclusion of moisture) are maintained.

Effect of Solids

The procedure used in the polymerizations was the addition of the solid TMAC to a solution of the diamine in DMAC in a 1:1 molar ratio. The concentration of the reactants was varied from 5% to 30% to determine its effect on the process. Propylene oxide (PO) was used as the acid acceptor. The data for these reactions are shown in Table III.

It was observed that a double viscosity increase was obtained during the course of the polymerization; this viscosity increase occurred both before and after the addition of PO. A considerable fluctuation in viscosity oc-

TABLE III
Concentration Effects for TMAC-DAPE Solution Polymerization

Reaction	Solids, %	Reaction temp., °C	η_{inh} Before PO addition, dl/g	η_{inh} After PO addition, dl/g	Gardner viscosity
A	5	10-24	0.39	1.40	B
B	10	13-35	0.64	2.16	Z7
C	15	13-30	0.51	1.46	Z5
D	20	20-45	1.24	1.87	Z6
E	25	19-40	0.53	0.82	Z5 ⁺
F	30	19-32	1.12	1.50	Z6 ⁺

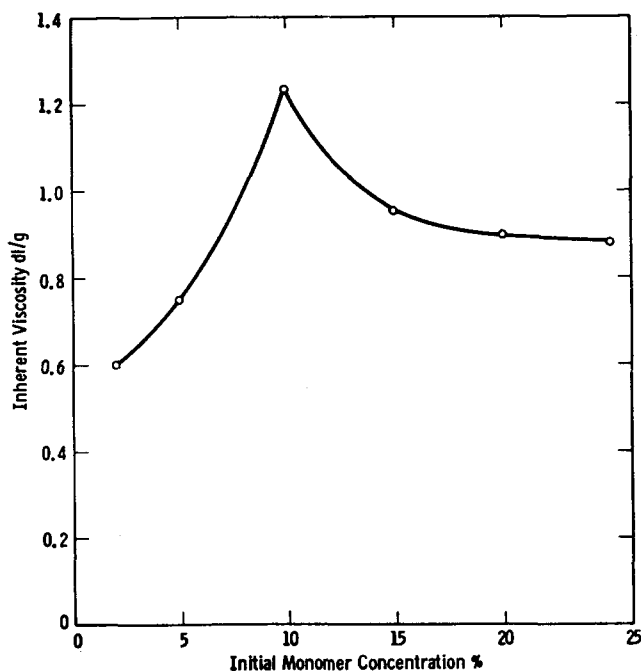


Fig. 1. Viscosity-concentration relationship for TMAC-DAPE solution polymerization with 1 mole-% phthalic anhydride.

curs over the concentration range 5-30%. However, it appears that a maximum viscosity can be reached at around 10% solids.

Another set of reactions were run in the 2% to 25% concentration range but using PA as a chain terminator in order to more carefully control the reaction. These data are shown in Figure 1 and Table IV.

The inherent viscosity goes through a maximum and levels off at about 20% solids. Other workers⁹⁻¹¹ have reported that the inherent viscosity increases, as our results indicate, and reaches a maximum at 10% solids. At concentrations >20%, without the use of a molecular weight control agent, the reaction solution becomes extremely viscous and difficult to stir and soon begins to gel.

TABLE IV
Concentration Study for TMAC-DAPE Solution Polymerization^a

Reaction	Solids, wt-%	Reaction temp., °C	η_{inh} After PO addition	Gardner viscosity
A	2	27-30	0.60	<A
B	5	27-31	0.75	<A
C	10	27-33	1.23	T
D	15	27-43	0.95	X
E	20	27-43	0.90	Z4
F	25	27-43	0.88	Z7-

^a Contains 1 mole-% phthalic anhydride.

Effect of Acid Acceptor

The effect of the propylene oxide addition on the molecular weight of the polymer is very interesting. The polymerization proceeds as if two reactions were taking place. Apparently a limiting molecular weight can only be obtained initially due to the presence of free HCl which could be reacting with the free amino groups on the growing chain, thus decreasing their reactivity or inhibiting their growth to high molecular weight polymer. When PO is added to the reaction after the maximum viscosity is reached, an exothermic reaction occurs and a second viscosity increase occurs. The PO reacts with the HCl, thus releasing the amino groups for further reaction to build up molecular weight. The chlorohydrin formed by the reaction of propylene oxide and the HCl is a volatile liquid which can be evaporated during subsequent processing of the precursor solution. When PO is used, it must be added after the reaction is complete (maximum viscosity is reached); if it was added at the beginning of the reaction, then the PO could react with the diamine monomer making the monomer unavailable for reaction with TMAC to form high molecular weight polymer. In a similar fashion, if PO was added to the reaction solution at some finite time before maximum viscosity was reached, then the amino groups on the growing polymer chain could compete with the liberated HCl for reaction with PO. These competition reactions would provide a source of chain termination, thus limiting the polymer molecular weight.

In another reaction, triethylamine (Et_3N) was used as the acid acceptor. In this case, the Et_3N can be added at the start of the reaction to react with the HCl formed after the TMAC addition. Only a single viscosity rise is observed in this instance, and crystals of triethylamine hydrochloride are dispersed throughout the reaction mixture. The viscosity of the reaction mixture increases more rapidly when using Et_3N compared to PO as the acid acceptor. The inherent viscosity of the resin was not followed during the course of the reaction when Et_3N was employed so it is not known whether the viscosity increase is due to a faster molecular weight rise or to ionization of the free carboxyl groups due to salt formation with Et_3N imparting polyelectrolyte behavior to the growing polymer chain.

In a separate experiment, triethylamine was added to an aliquot of polyamic acid solution derived from the reaction of TMAC-DAPE. The effect of this addition on the viscosity of the resin is quite interesting and

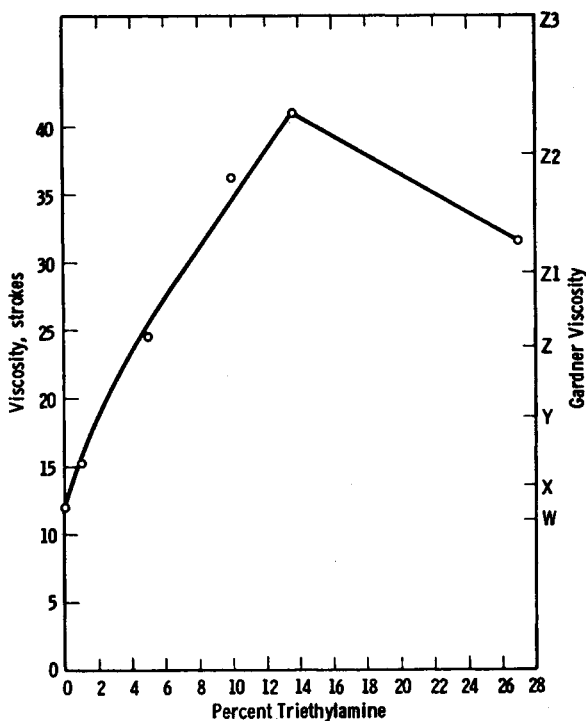


Fig. 2. Effect of triethylamine on the viscosity of TMAC-DAPE resin solution.

is shown in Figure 2. A significant increase in viscosity occurs by the addition of up to 13% TEA (based on the solids content of the polyamic acid solution) after which further addition causes a decline in viscosity. Apparently, the maximum in Figure 2 corresponds to the carboxyl equivalent of the polyamic acid solution because further addition results in a viscosity decrease. Reynolds and Seddon¹² found a similar decrease in viscosity if more than the stoichiometric amount of TEA required to neutralize the carboxyl groups was added to a PMDA-DAPE polyamic acid solution.

Effect of Temperature

Although the polymerization reaction between TMAC-DAPE is usually run at temperatures not exceeding 50°C, it was of interest to determine the effect of heating on the properties of the polyamic acid solution and on film prepared from this solution. From Figures 3 and 4, it is clearly evident that heating the resin above 60°C for greater than 1 hr results in a sharp decrease in molecular weight as well as in mechanical properties of the film. In addition, the light amber color of the resin solution gradually darkens as the temperature is increased. Although polymerization temperatures ranged from 10° to 45°C, no analysis was made concerning its effect on the reactivity of the functional groups present in the monomer.

Precipitation of Polymer

In earlier, unpublished work, we found that a large decrease in molecular weight occurred when polyimide-type polymers were precipitated into

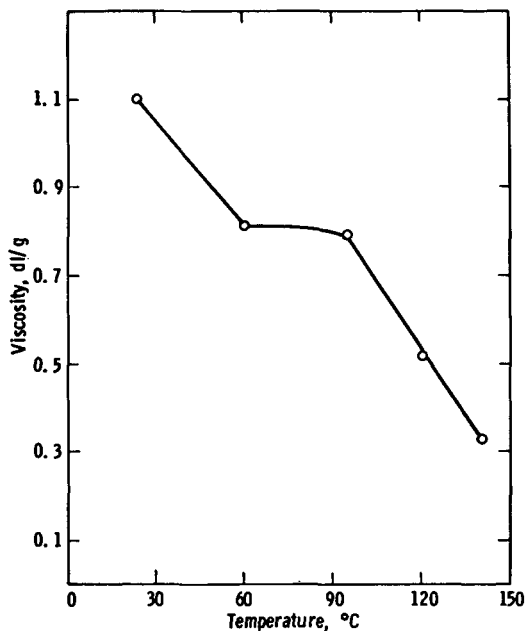


Fig. 3. Effect of heating 1 hr at temperature on inherent viscosity of TMAC-DAPE solution.

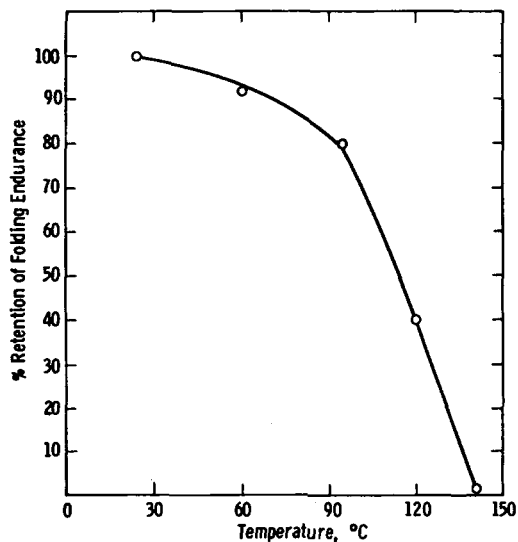


Fig. 4. Effect of heating TMAC-DAPE resin solution 1 hr at temperature on the folding endurance of film cast from heated solution.

water. Similar results were obtained with the TMAC-DAPE system. In fact, inherent viscosities decreased by a factor of 4 when the polymer was precipitated in this medium.

Table V presents a summary of these results. If, however, a different nonsolvent is used, the decrease in inherent viscosity is not as drastic but the effects of precipitation are still dramatic. It seems probable that

TABLE V
Precipitation of TMAC-DAPE in Various Nonsolvents

Polymer	η_{inh} Before precipitation, dl/g	η_{inh} After ppt into H ₂ O, dl/g	η_{inh} After ppt into MeOH, dl/g	η_{inh} After ppt into THF, dl/g	η_{inh} After ppt into acetone, dl/g
A	1.40	0.40	0.80		
B	2.16	0.50	0.86	0.84	0.84
C	1.46	0.50	0.76		
D	1.50	0.52	0.79		

hydrolysis of the polymer could occur upon precipitation into the non-solvent, especially water. If, indeed, this is the case, then the change in viscosity would be a reflection of a decreased molecular weight. Some evidence to support this is obtained by redissolving the precipitated polymer in DMAC and measuring the inherent and Gardner viscosity and solids. In the case of polymer B in Table V, the redissolved polymer gave a Gardner viscosity of Z at 25% solids and an inherent viscosity of 0.50 dl/g. This is compared to a Gardner viscosity of Z6 at 10% solids before precipitation and an inherent of 2.16 dl/g. This fact tends to suggest that precipitation of these amide-imide polymers causes a decrease in molecular weight.

Molecular Weight Control

Although polymerization of TMAC-DAPE in a 1:1 molar ratio produces high molecular weight polymer, the solution properties of the poly-

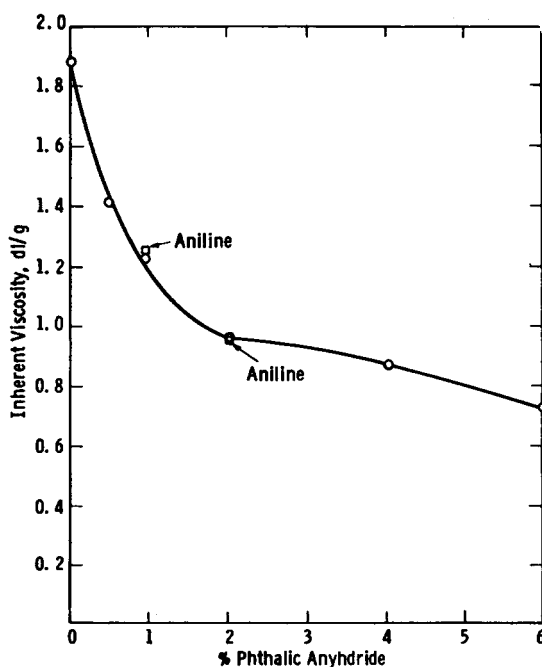


Fig. 5. Effect of addition of phthalic anhydride on the molecular weight of TMAC-DAPE resin.

TABLE VI
Aniline and Phthalic Anhydride as a Molecular Weight Control Agent

No.	Ingredient	Moles of reactant	Solids, %	Reaction temp., °C	η_{inh} , dl/g	Gardner viscosity	Stokes
A	TMAC	1.0	20	20	1.87	Z5 ⁺	123
	DAPE	1.0	to 11	to 40			
B	TMAC	0.99	19.5	25	0.95	Z5	98
	DAPE	1.00		to 46			
	PA	0.02					
C	TMAC	0.98	19.5	23	0.86	Z5	42
	DAPE	1.0		to 39			
	PA	0.027					
D	TMAC	0.98	19.5	26	0.88	Z3 ⁺	54
	DAPE	1.0		to 43			
	PA	0.04					
E	TMAC	0.97	19.5	29	0.73	P	4
	DAPE	1.0		to 42			
	PA	0.06					
F	TMAC	0.995	19.5	24	1.23	Z7 ⁻	370
	DAPE	1.0		to 37			
	PA	0.01					
G	TMAC	0.9975	19.5	20	1.40	Z9	855
	DAPE	1.0		to 37			
	PA	0.0050					
H	TMAC	100	19.5	25	0.90	Z4	
	DAPE	99		to 39			
	Aniline	0.02					
I	TMAC	100	19.5	25	1.24	Z7 ⁻	
	DAPE	0.995		to 39			
	Aniline	0.01					

amic acid solution are such that it is difficult to process. The properties of prime interest are inherent viscosity for molecular weight control and Gardner viscosity for rheological control. Phthalic anhydride was used as the molecular weight control agent, using it to replace part of the TMAC. The polymer thus produced would be end capped with a phthalimide group in its final cured form. The PA was added to the reaction mixture after a maximum viscosity was reached. The effect of this addition of PA is shown in Table VI and in Figures 5 and 6. As can be seen from these data, only a few mole % of PA has a striking effect on reducing the molecular weight of the polymer. Samples F and G in Table VI indicate that even at low concentrations of phthalic anhydride, a considerable reduction in inherent viscosity is obtained amounting to 34% and 25%, respectively. Despite almost a 50% reduction in inherent viscosity by the addition of 2 mole-% of PA (compare A and B in Table VI), the resulting polymer is still sufficiently high in molecular weight that a satisfactory film can be obtained. Within the range of 2 to 4 mole % of PA, the resulting solution properties of the polymer are quite acceptable in terms of molecular weight

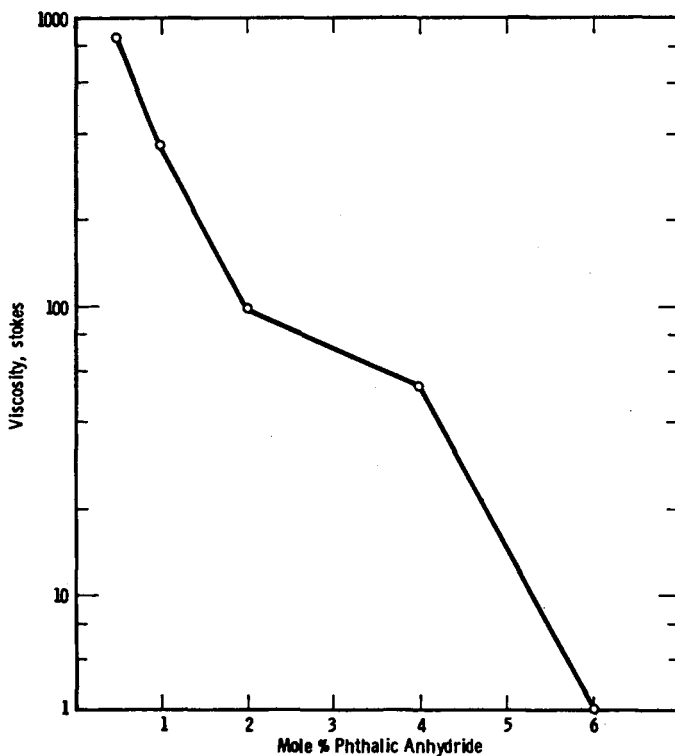


Fig. 6. Effect of phthalic anhydride addition on the viscosity of TMAC-DAPE resin.

and rheological control. In addition to phthalic anhydride, aniline was also used to control molecular weight at the 1 and 2 mole-% level. It gave results similar to the phthalic anhydride system.

CONVERSION TO POLYAMIDE-IMIDE

The polyamic acid can be converted to polyamide-imide by heating a thin film of the precursor solution from 100° to 300°C at a controlled rate. As conversion to polyamide-imide takes place, the polyamide-acid film darkens from pale amber to a moderate amber color. This conversion was followed spectrophotometrically by depositing a thin film of the amide-acid solution on a salt crystal and curing to 300°C. These spectra are shown in Figure 7. The spectra are labeled A through D and represent cumulative cure times of 40 min at 100°C, + 30 min at 150°C, + 15 min at 210°C, and 20 min at 210-310°C, respectively. At the lower cure temperatures, the spectra are masked a little by the absorption of the solvent dimethylacetamide. The characteristic amide and imide absorptions are listed in Table VII.

CONCLUSIONS

For the polymerization of TMAC with DAPE, major effects on polymer molecular weight were noted depending on polymerization process (solution

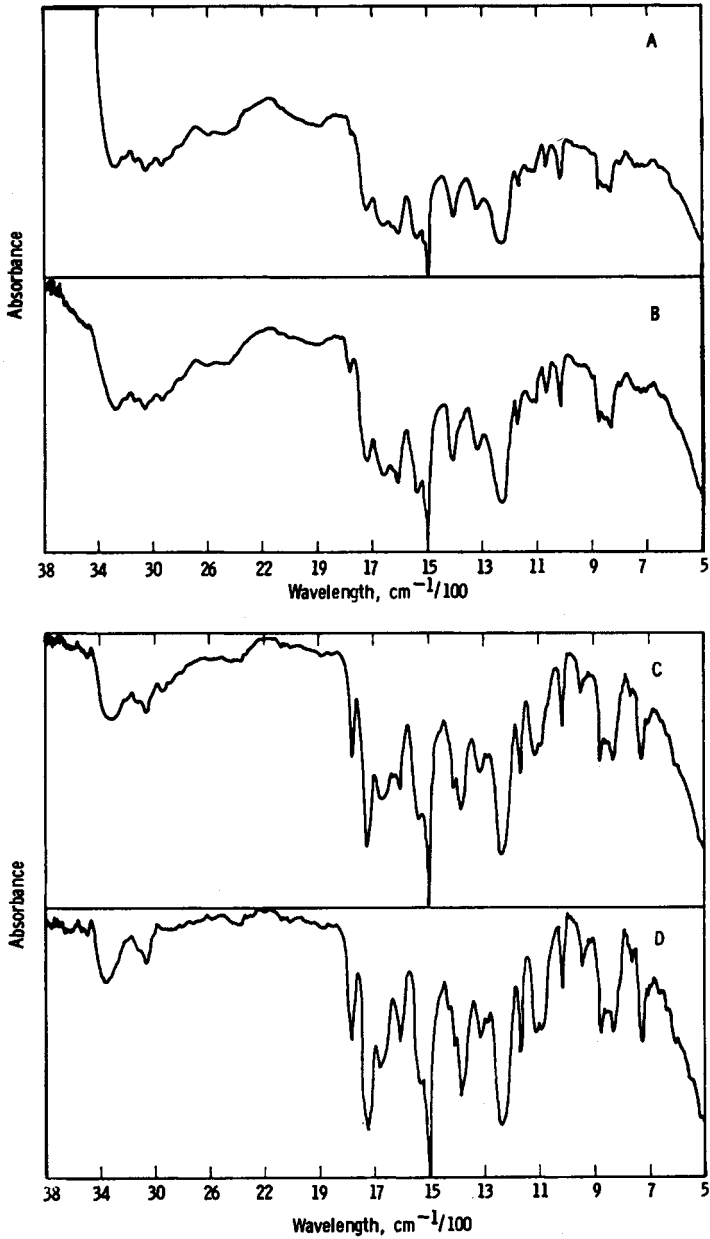


Fig. 7. Infrared spectra of TMAC-DAPE polymer at various stages of cure.

and interfacial), monomer concentration, purity, temperature, and stoichiometry, etc.

Solution polymerization yields higher molecular weight polymers. Propylene oxide is an excellent acid acceptor because the chlorohydrin reaction product is miscible in the reaction medium and is sufficiently volatile to be easily removed from the precursor solution during subsequent processing.

TABLE VII
Infrared Absorption Frequencies for TMAC-DAPE Polymer

Frequency, cm ⁻¹	Assignment	Comment
3340-3400	NH stretch of amide	shift to higher frequency with conversion of amic acid to imide
1780-1710	C=O of imide ring	increase to intensity with conversion to imide
1660-1680	C=O of amide	
1410-1380	C-N	band split to lower frequency and increase in intensity with conversion to imide
1230	ϕ -O- ϕ	
830-880	aryl C-H	
710	C-N imide ring	increase in intensity with conversion to imide

Heating of the resin solution should be avoided since it causes a deterioration in polymer properties.

Precipitation of this polymer into a nonsolvent, particularly water, results in a lower molecular weight resin.

The concentration at which the polymerization is carried out affects the final molecular weight and solution properties of the polymer. Inherent viscosity goes through a maximum at about 10% solute concentration.

Both aniline and phthalic anhydride can be used as molecular weight control agents.

The addition of TEA to the precursor solution markedly increases the viscosity of the resin until an amount equivalent to the carboxyl content is reached. Further addition results in a decrease in viscosity.

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