Factors affecting the formation of high molecular weight aromatic polyesteramides by solution polycondensation

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Fully aromatic polyesteramides from aminophenols and benzenedicarbonyl chlorides are synthesized by low temperature solution polycondensation. The optimum conditions for the polycondensation reaction are established through systematic study of the factors affecting the molecular weight of the resulting polymers, which are reaction temperature, LiCl concentration, nature and concentration of the tertiary amine catalyst, water content in the solvent, concentration of the monomers, nature of solvent, rate of stirring and state of the acid chloride added.

(Keywords: aromatic polyesteramides; polycondensation; low temperature solution)

INTRODUCTION

Fully aromatic polyesteramides, based on aminophenols and phenylene dicarboxylic acids, are represented by the general formula:

$$(-\mathrm{HN}-\mathrm{Ar}-\mathrm{OOC}-\mathrm{Ar}'-\mathrm{CO}-)_x \quad (-\mathrm{O}-\mathrm{Ar}-\mathrm{NHCO}-\mathrm{Ar}'-\mathrm{CO}-)_y$$

Several members of this class have been synthesized by solution, interfacial and melt polycondensation[1–6]. The first two techniques are the key to the production of infusible polymers having adequately high molecular weights. The most frequently used monomers are diacid chlorides with aminophenols or diphenols and diamines containing preformed amide and ester groups, respectively. However, direct polycondensation of diacids and aminophenols has also been applied successfully, employing several condensing agents, such as thionyl chloride[5], diphenyl chlorophosphate[7], tosyl chloride and N-methyl imidazole[8].

No systematic study has been reported on the factors affecting the formation of high molecular weight polyesteramides produced by low temperature solution polycondensation employing aminophenols and diacid chlorides. Thus, the aim of this work is to reveal their effect on the relative molecular weights, judged by comparison of inherent viscosities, of the resulting polymers.

EXPERIMENTAL

Materials

m- and *p*-aminophenols (BDH) were recrystallized twice from oxygen-free water under nitrogen, in the presence of sodium dithionite. The melting points (Reichert Thermovar hot stage microscope) were *m*-aminophenol (mAP) = 123.5–124.5°C and *p*-aminophenol (pAP) = 184.5–185.5°C.

Iso- and tere-phthaloyl chloride (Aldrich) were recrystallized twice from low boiling point petroleum ether under nitrogen. The melting points were isophthaloyl chloride (IADCl) = 43.0–44.0°C and terephthaloyl chloride (TADCl) = 83.0–84.0°C.

The purification procedures for the solvents used are tabulated in *Table 1*.

Triethylamine (TEA) (Aldrich) was refluxed with benzoyl chloride, followed by distillation over sodium. The collected fraction had b.p. = 89–90°C. The purification procedures for the other tertiary amines used are given in *Table 2*.

Lithium chloride (BDH) was dried under vacuum at 110°C overnight or normal pressure at 240°C for 48 h.

Nitrogen (BOC) was dried by passing through concentrated sulphuric acid, glass wool, calcium chloride and self-indicating silica gel.

Typical polymer preparation

A 100 ml three-necked round-bottomed flask, equipped with a hook-type glass stirrer, nitrogen inlet tube and calcium chloride drying tube, was taken out of the oven and swept out with dry nitrogen for at least 20 min. The flask was charged with 0.0125 mol LiCl and 20 ml NMP:$CHCl_3$ 50:50 v/v. The salt was completely dissolved after 15–20 min stirring. The flask was then placed in an ice-water bath for at least 10 min to cool down the solution. 0.01 mol pAP and 0.026 mol TEA were added. The funnel was rinsed with 3 ml of the solvent. Solid IADCl (0.01 mol) was added all at once; 2 ml of the solvent was used to rinse in the IADCl residues. The speed of stirring was increased to 1300 ± 100 rpm for 10 min and then reduced to 600 ± 100 rpm for the rest of the reaction time (1 h). The viscous, light yellow opaque reaction mixture was poured into 250 ml alcohol, yielding a fibrous precipitate. After stirring the alcohol–polymer mixture for 10 min in a home blender, the polymer was filtered off and washed with 200 ml hot water in the blender twice. Finally, the

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Table 1 Purification of solvents

	Drying agent	b.p. (°C)
N-methyl pyrrolidone (NMP) (BDH)	molecular sieves 4A, CaH_2	202–4
Dimethylacetamide (DMA) (BDH)	as NMP	164.5–6
Dimethylformamide (DMF) (BDH)	as NMP	152–3
Chloroform (Aldrich)	conc. H_2SO_4, 10% NaOH, H_2O, $CaH_2+Na_2SO_4$, Na_2CO_3	61–2
Methylene chloride (BDH)	as $CHCl_3$	39.5–40.5
1,2-dichloroethane (BDH)	as $CHCl_3$	83–83.5
Trichloroethylene (BDH)	P_2O_5	86–87.5
Tetramethylurea (TMU) (ICI)	BaO	177–8
Tetramethylene sulphone (TMS) (ICI)	NaOH	150–1/14 mm
Tetrahydrofuran (THF) (Aldrich)	Na	65–7
Acetonitrile (Aldrich)	$CaCl_2$, P_2O_5	80.5–81
Hexamethylphosphoramide (BDH)	CaH_2	67–70/0.12 mm

Table 2 Purification of tertiary amines

Amine	Drying agent	b.p. (°C)
N-ethylmorpholine (BDH)	–	137.5–139.5
N-ethylpiperidine (BDH)	–	129.5–131.5
N,N-dimethylaniline (BDH)	Na	191.5–192.5
Tri-n-butylamine (BDH)	Na	211–213

polymer was dried in an oven, under vacuum, at 110°C, overnight. The yield was quantitative and the inherent viscosity (IV) was 0.86 (in DMA/LiCl 5%).

For several polymerization conditions, repeat experiments were carried out and the IVs obtained were in general reproducible within the range $\pm 2\%$.

All viscosity measurements were performed at 0.5% polymer concentration at 25 ± 0.1°C using an Ostwald type viscometer.

RESULTS AND DISCUSSION

Effect of temperature

The effect of the temperature on the IV of the polymer based on pAP and IADCl [poly(pAPIA)] in NMP/LiCl and NMP/$CHCl_3$/LiCl systems is shown in *Figure 1*. In polyesterification reactions, similar studies usually lead to a curve with a single or double maximum[9,10]. In polyamidation, the data are contradictory[11–13]. In model reactions, on increasing the temperature the ratio of the rates of reaction of acid chlorides with amines and with amide type solvents apparently decreases[14]. The decrease in IV as the temperature increases above 0°C can thus be explained. In addition, it has been suggested[13] that, in the early stages, the viscosity increases more rapidly at the higher temperature, and that this may prevent uniform distribution of the acid chloride throughout the mixture, so encouraging the side reactions. The peak in the NMP/$CHCl_3$/LiCl system is less pronounced because the concentration of the more reactive solvent, NMP, is half that in the pure NMP/LiCl system. The reduction in IV at fixed reaction time as the temperature decreases below about 0°C can be attributed to a lower rate of polycondensation as the temperature falls.

Effect of LiCl concentration

The effect of the LiCl concentration on the MW of poly(pAPIA) was studied in both NMP/$CHCl_3$ and NMP systems and is expressed by curves, each with a single maximum (*Figure 2*).

In polyamide synthesis it is known that the introduction of LiCl increases the solvent power through the formation of a 'bridge' between the amide solvent and the amide bonds of the polymer[12,15], but also accelerates the side reactions[16]. On the other hand, LiCl does not alter the solvent properties of $CHCl_3$ since it is insoluble in it. Additionally, $CHCl_3$ is relatively inert to acid chlorides. The above arguments can be used to explain

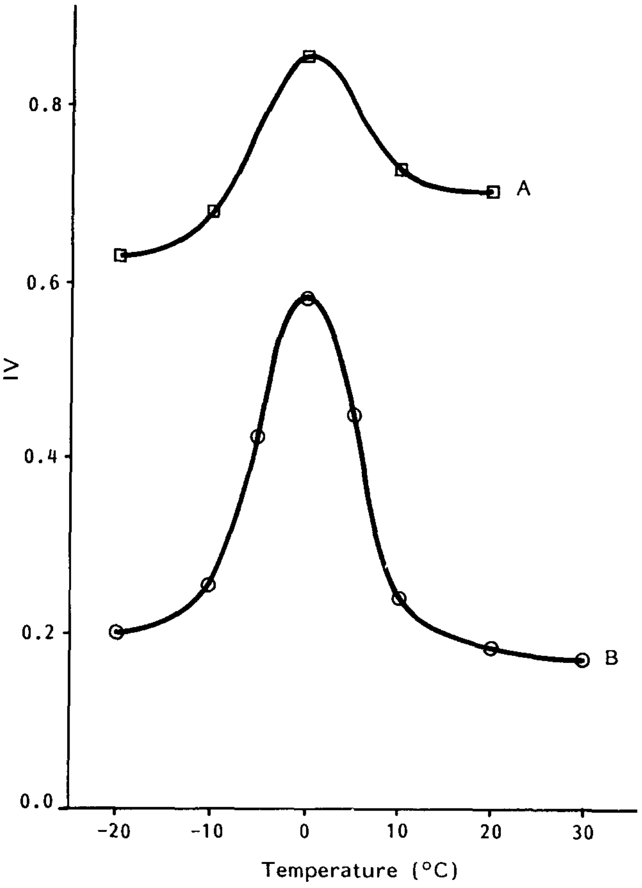

Figure 1 The effect of the temperature on the IV of the poly(pAPIA) in (A) NMP/$CHCl_3$/LiCl and (B) NMP/LiCl

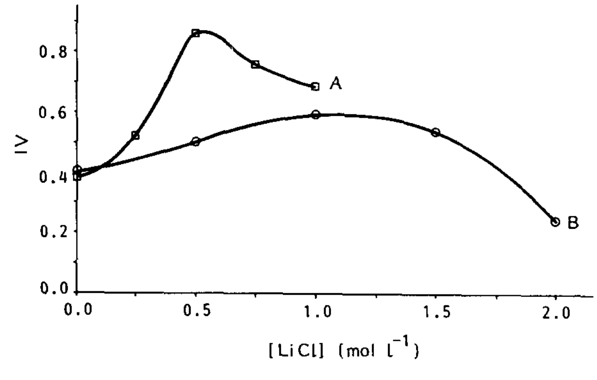

Figure 2 The effect of the concentration of LiCl on the IV of poly(pAPIA) (A) NMP/$CHCl_3$ and (B) NMP

Table 3 Synthesis of poly(pAPIA) under various conditions

Solvent for IADCl	Solvent for pAP	Yield (%)	IV
- (solid)	NMP + 1 mol l^{-1} LiCl	99	0.59
- (solid)	$CHCl_3$	97	0.42
NMP (5 min)	NMP + 2 mol l^{-1} LiCl	92	0.44
$CHCl_3$ (5 min)	$CHCl_3$	97	0.62
NMP (10 min)	NMP + 2 mol l^{-1} LiCl	88	0.20
NMP + 1 mol l^{-1} LiCl (5 min)	NMP + 1 mol l^{-1} LiCl	80	0.12

Table 4 Effect of the nature of acid acceptor on IV of poly(pAPIA)[a]

Base	pKa (in H_2O)	Yield (%)	IV
Triethylamine	10.74	100	0.59
Tri-n-butylamine	10.89	92	0.38
N-ethylpiperidine	10.45	97	0.32
N-ethylmorpholine	7.70	70	0.12
N,N-dimethylaniline	6.50	Polymer not formed	
CaO		41	0.10

[a] Solvent NMP, monomers 0.4 mol l^{-1}, LiCl 1.0 mol l^{-1}, base 1.02 mol l^{-1}, T = 0°C and reaction time 60 min

Table 5 Comparison of the effect of TEA and N-ethylpiperidine on IV of poly(pAPIA) prepared in various solvents

	Solvent			
Acid acceptor	DMA	DMF	$CHCl_3$	Sym. $CHCl_2CHCl_2$
TEA	0.49	-	0.42	0.26
N-ethylpiperidine	0.29	0.14	0.31	0.24

the shapes and the differences of the two curves. The two maxima (*Figure 2*) are at about 0.5 mol l^{-1} and 1.0 mol l^{-1}, respectively, because the concentration of the reactive solvent, NMP, is double in the latter system.

The presence of the two competitive effects (increase of solvent power and acceleration of side reactions) can also be seen from the data presented in *Table 3*. Dissolution of the acid chloride in NMP before mixing lowers the IV and this effect is time dependent. The decrease of IV is greater in the presence of LiCl. Conversely, if $CHCl_3$ is used as solvent for the acid chloride, the IV increases. Overall, dissolving the acid chloride improves the uniformity of the mixing and hence the IV.

Effect of the nature and the concentration of the tertiary amine

The role of the tertiary amines in the preparation of polyarylates, polyamides and polyesteramides has been studied[17–20]. It has been concluded that this role may be that of simple base and/or nucleophilic catalysis, depending on the reagents used. The presence of side reactions has also been noted[21]. It has been stressed that the higher the basicity and the lower the steric hindrance of the tertiary amine, the higher is the polymer molecular weight.

The effect of several bases on the molecular weight of poly(pAPIA) was examined and the results are given in *Table 4*. It can be seen that, in general, the stronger the base, the higher is the IV. The difference between the first two amines might be attributed to greater steric hindrance of the tri-n-butylamine. Comparing TEA and *N*-ethylpiperidine in other solvents leads to the same conclusions (*Table 5*).

A few studies on the effect of the amount of the tertiary amine on the IV of polyarylates[22], polyamides[23] and polyesteramides[20] have been reported. In the present work, this effect was studied for the synthesis of the polymer, based on m-aminophenol and terephthaloyl chloride, poly(mAPTA), (*Figure 3*). By increasing the amount of TEA to 1.4 equivalents, the concentration of the active intermediate species is greatly increased; beyond this level side reactions, detrimental effects reducing molecular weight, are noted. The latter includes catalysis of side reactions by the excess of the amine, the less effective control of the reaction temperature and the reduction of the solvent power of the media.

Effect of the water content in the solvent

The deleterious effects of the presence of water on these polycondensations have been studied by several researchers[12,24,25]. These include hydrolysis of acid chlorides, ester and amide links and formation of anhydride bonds, which are all accelerated by the presence of strong bases like TEA. In the present study, the effect of water on the molecular weight of the polyesteramides was studied in the synthesis of poly(mAPTA) in NMP/CH_2Cl_2 under the experimental conditions specified (*Table 4*). The results are shown in *Figure 4*.

In order to study further the hydrolysis effect in the presence of TEA, the IV of poly(mAPTA) dissolved in DMA (0.5%) in the presence of LiCl (5%), H_2O (1%) and TEA (7.4%), was measured as a function of time, taking into account the different flow times of the media. For comparison, the same effect was studied in the absence of TEA. The results are given in *Figure 5*. The reduction in molecular weight is presumed to be due to hydrolysis

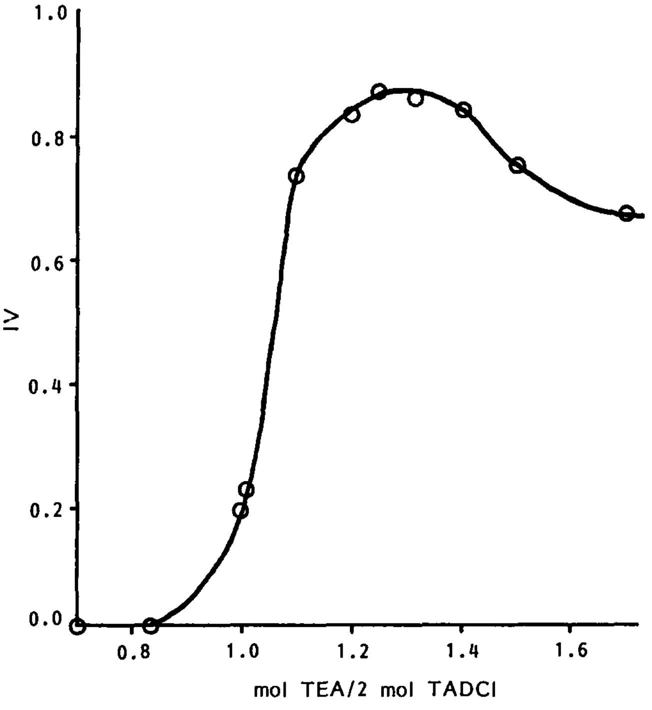

Figure 3 The effect of the mol TEA/2 mol TAD Cl ratio on the IV of poly(mAPTA)

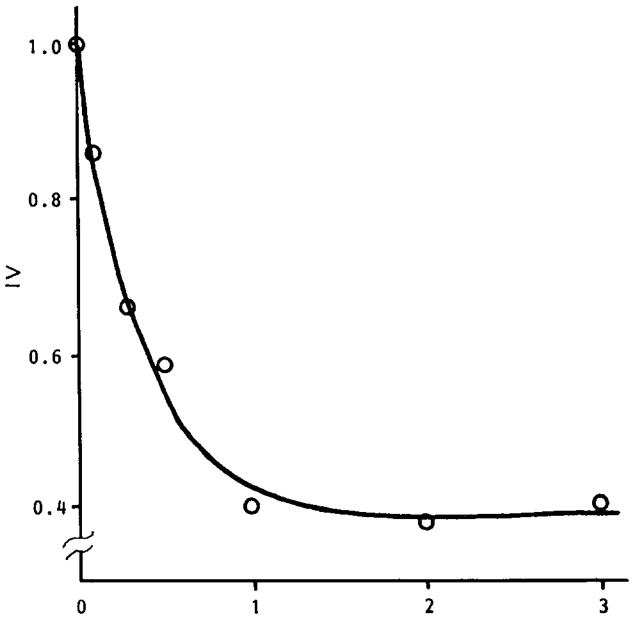

Figure 4 The effect of the concentration of the water in NMP/CH_2Cl_2 on the IV of poly(mAPTA)

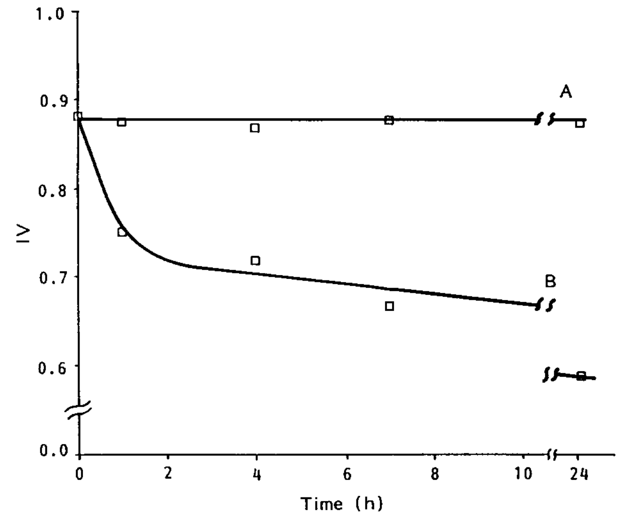

Figure 5 The dependence of the IV of poly(mAPTA) upon time of storage at 25°C in DMA/LiCl/H_2O system (A) without TEA and (B) with TEA

mainly of ester and anhydride and to a lesser extent of amide bonds, as the former are more sensitive to hydrolysis.

Effect of the concentration of the monomers

The effect of the monomer concentration in the synthesis of poly(mAPIA) was studied in NMP/LiCl and NMP/$CHCl_3$/LiCl systems under the usual conditions. The results are given in *Figure 6*.

This pattern seems to be a general one[27–29]. The factors affecting the shape of the curve include the role of side reactions, the viscosity of the media and any changes in the reaction temperature due to the exothermicity of the reaction.

The reduction of the IV in NMP/$CHCl_3$/LiCl is less pronounced than in NMP/LiCl, indicating the different effect of the above factors in different reaction media. As was expected, the effect of side reactions is greater in the latter system.

Effect of rate of stirring and rate and form of addition of the acid chloride

The effect of the side reactions on the molecular weight is likely to be dependent on such factors as the rate of stirring and the uniformity of distribution and state of the acid chloride added. The uniformity of distribution of the active end groups of the growing polymer chains is increased by increasing the rate of stirring, leading to an increase in the molecular weight. This can be seen in *Figure 7*.

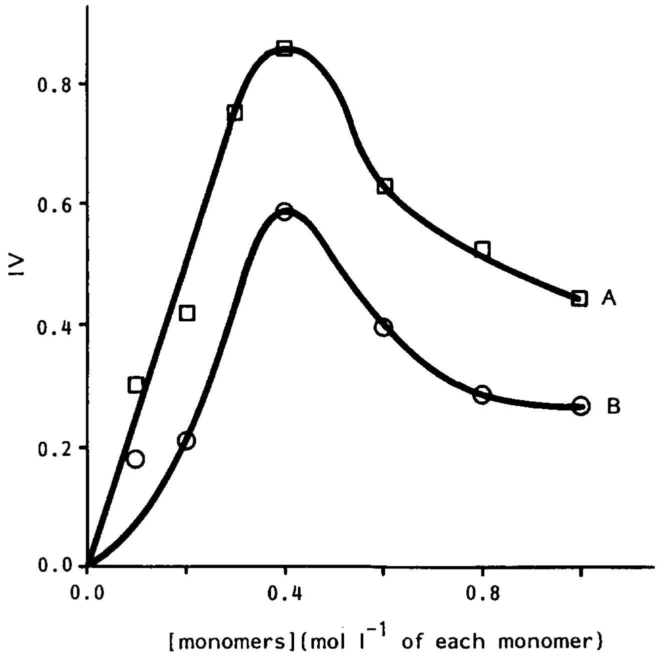

Figure 6 The effect of the concentration of the monomers on the IV of poly(pAPIA) in (A) NMP/$CHCl_3$/LiCl and (B) NMP/LiCl

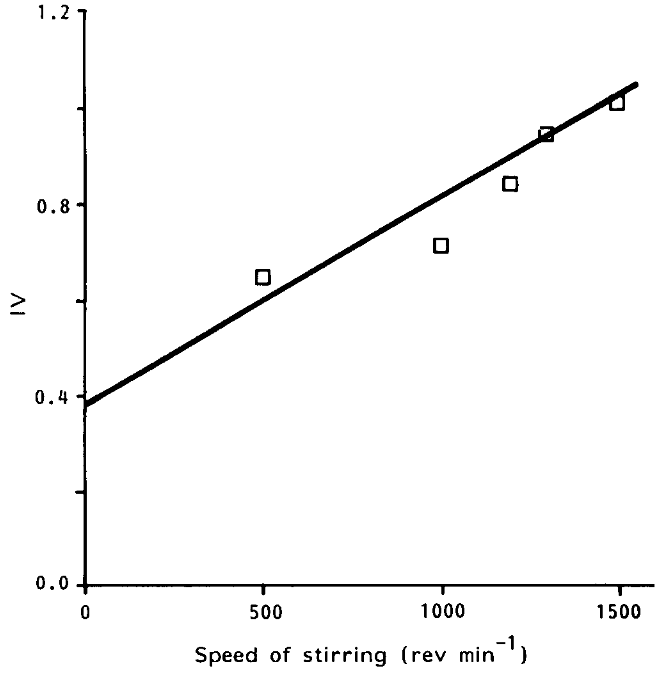

Figure 7 The dependence of the IV of poly(pAPIA) upon the rate of stirring

Table 6 Effect of the state and the rate of feeding of IADCl on the IV of poly(pAPIA)

State of IADCl	Duration of addition	IV
IADCl in $CHCl_3$	over 30 s	0.96
IADCl in $CHCl_3$	over 20 min	0.72
Solid	over 30 s	0.86
Solid	over 20 min	0.74

Table 7 Synthesis of poly(pAPIA) in polar aprotic solvents

Solvent	LiCl (mol l^{-1})	IV	Dipole moment	Dielectric constant
NMP	–	0.40	4.09	32.2
NMP	1	0.59		
DMA	–	0.33	3.8	37.8
DMA	1	0.49		
NMP/DMA 50:50 v/v	1	0.54		
TMU	–	0.18	3.28–3.66	
TMU	1	0.24		
TMS[a]	–	0.39	4.69	4.2

[a] Polymerized at 25°C

Table 8 Synthesis of poly(pAPIA) in halogenated hydrocarbons

Solvent	$Et_3N.HCl$	IV	Remarks
CH_2Cl_2	—	0.26	Precipitation at once
CH_2Cl_2	0.4	0.45	Gradual precipitation
$CHCl_3$	—	0.42	Precipitation at the beginning, clear solution at the end
$CHCl_3$	0.4	0.40	Clear solution
CH_2ClCH_2Cl	—	0.33	Precipitation at once
CH_2ClCH_2Cl	0.4	0.37	Gradual precipitation
$CHCl_2CHCl_2$	—	0.26	Clear solution
$CHCl_2CHCl_2$	0.4	0.24	Clear solution

Table 9 Synthesis of poly(pAPIA) in mixed solvents (50:50 v/v NMP/named solvent)

Solvent	CH_2Cl_2	$CHCl_3$	CH_2Cl | CH_2Cl	$CHCl$ ‖ CCl_2	THF	CH_3CN	$CHCl_2$ | $CHCl_2$
IV	1.01	0.96	0.86	0.82	0.82	0.81	0.75

The effect of the state and the rate of feeding of IADCl on the molecular weight of poly(pAPIA) has already been mentioned (*Table 3*). Additional results are given in *Table 6*. Fast addition of IADCl in inert solvent ($CHCl_3$) favours the uniformity of distribution of monomers more than addition in the solid form. Slow addition to $CHCl_3$ lowers molecular weight because the polycondensation takes place in an amide-rich medium with consequently more rapid side reactions, leading to an imbalance in the functional group concentrations.

Effect of the solvent

A great number of research workers have studied the effect of the nature of the solvent on the molecular weight of several classes of polymerization. Their common practice is to carry out the polycondensation under identical conditions and to classify the solvents according to the molecular weight obtained.

Most of the solvents used for the preparation of polyamides, polyarylates and polyesteramides by low temperature solution polycondensation can be divided into two main groups, i.e. halogenated hydrocarbons and polar aprotic solvents, such as the N,N-di-substituted amide type. In the present study both classes and mixtures of them were employed for the preparation of poly(pAPIA) under the usual experimental conditions. The acid chloride was added as a solid all at once in the experiments shown in *Tables 7* and *8* and as a solution in those detailed in *Table 9*.

With respect to the IV of poly(pAPIA), the polar aprotic solvents can be arranged in the order

$$\mathrm{NMP} \sim \mathrm{TMS} > \mathrm{DMA} > \mathrm{TMU}$$

which parallels the solvent polarity. Addition of LiCl increases the molecular weight of polymer by increasing the solvent power of the media, as discussed earlier. The halogenated hydrocarbons can be arranged in the order

$$CHCl_3 > CH_2Cl\ CH_2Cl > CH_2Cl_2 \sim CH\ Cl_2CH\ Cl_2$$

This order altered when $Et_3N.HCl$ was added, becoming

$$CH_2Cl_2 > CHCl_3 > CH_2Cl\ CH_2Cl > CHCl_2\ CHCl_2$$

probably due to enhanced polymer solubility in the presence of the salt. This hypothesis is supported from the results in *Table 9*, because the solubility factor has been overcome due to the presence of NMP which is a good solvent for the polymer.

The increase of the molecular weight in the mixed solvents is due, in general, to a more uniform distribution of the monomers, a reduction of the extent of the side reactions and an improved solubility in comparison with the halogenated solvents.

CONCLUSIONS

Fully aromatic polyesteramides, based on aminophenols and phenylenedicarbonyl chlorides, have been prepared by low temperature solution polycondensation.

The dependence of the molecular weight upon concentration of monomers and temperature is expressed by curves with a maximum. Additions of salts improve the solvent power of the media, but also accelerate side reactions. The higher the basicity and the lower the steric hindrance of the acid acceptor, the higher is the molecular weight. The optimum concentration is 1.25–1.30 times the equivalent amount. The presence of water leads to lower molecular weight.

Fast stirring with fast addition of solution of acid chloride in halogenated solvent, to a solution of aminophenol in amide solvent, increases the molecular weight. Amide type solvents are more powerful than the halogenated, although the former promote side reactions. Mixtures of these two classes improve the control of mixing of the monomers and reduce side reactions, leading to increases in molecular weight.

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