

Further Studies on Polyamides from Bisacid A2

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Synopsis

Earlier work on the low temperature solution polyamidation of bisacid A2 has raised a number of structural problems. Work carried out more recently showed that the problem of apparent nonstoichiometry could be reasonably satisfactorily explained. The present paper reports the synthesis and investigates the properties of a further series of polyamides based upon Bisacid A2. More importantly, however, a detailed characterization and evaluation of the new polymers with respect to their structures is presented. This enabled us to compare the various structures in the light of the experimental evidence provided by a number of analytical and spectroscopic techniques, solution behavior, molecular weight, and thermal, morphological, and mechanical properties. Some work was also done on the effect of incorporating a small amount of a trifunctional monomer into the polyamide system.

INTRODUCTION

This paper is concerned with an in-depth assessment of structure/property relationships of polycondensation products involving bisacid A2 (or, more precisely, its acid chloride, bischloride A2). The structure of the monomers is familiar from earlier publications and is clearly indicated, by implication, in the early parts of the experimental section which follows. The structural investigations were carried out on polyamides which, although based upon bisacid A2, have never been reported before since they are based on fresh diamines.

In order to avoid fragmentation the implications and discussion of the evidence is included under the appropriate sections and subsections which present the experimental evidence.

The conclusions are summarized in six points. Further work which is presently under way is indicated. This seeks to establish whether bischloride A2 and monofunctional analogs thereof can form (i) amides with secondary and (ii) imides with primary amines under suitable conditions. This in turn may lead to interesting possibilities of ensuring linearity and avoiding branching during polyamidation reactions.

EXPERIMENTAL

Preparation of the Polymers

Polyamides and polyhydrazides were prepared according to Lenk's method,¹⁻³ which involved a modified low temperature solution technique.

Three series of polymers were prepared:

(i) M series. Here bischloride A2 was reacted with a single diamine in a 1:1 molar ratio.

(ii) C series. Here half the diamine was replaced by the equivalent amount of bishydrazide A2 so that the resulting molar ratios of bischloride A2:diamine:bishydrazide A2 was 2:1:1.

The structures of bishydrazide A2 and the diamines are illustrated in Figure 1. Bishydrazide A2 was included because it is known to furnish reasonable polymers with Bischloride A2 and because its high molecular weight as a monomer would ensure high molecular weight polymers, even at relatively low degrees of polymerization.

(iii) A third (T) series is represented by just one polymer with the intended aim of investigating the effect of incorporating varying amounts of tri-functional monomer on the mechanical properties of the resulting polymer. The polymers were numbered according to the diamines incorporated: thus M2 is the polymer formed from a 1:1 combination of bischloride A2 and 4,4'-diaminodiphenyl methane, C1/2 is formed from a 2:1:1 combination of bischloride A2, bishydrazide A2, and 4,4'-diaminodiphenyl methane.

Characterization and Evaluation of the Polymers

The following techniques were used to elucidate the chemical structure and physicochemical properties of the polymers. Shortage of space preclude a quantitative presentation in tabular form, but these are available on request from the second named author.

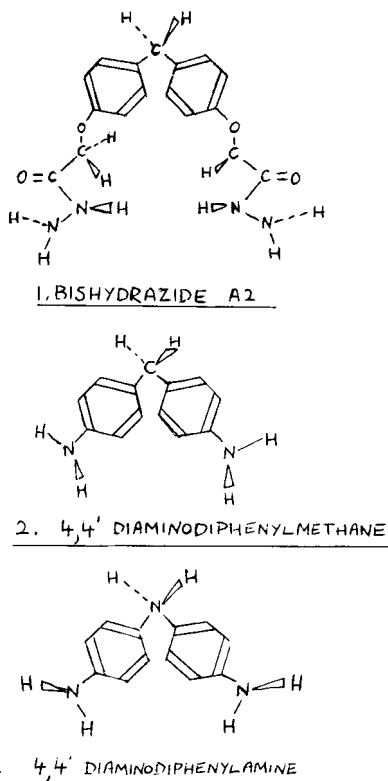


Fig. 1. Structures of bishydrazide A² and diamines.

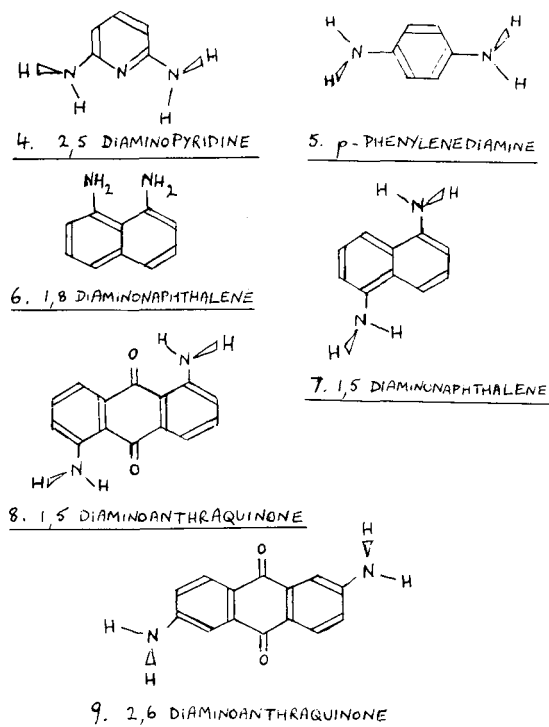


Fig. 1. (continued from previous page)

Elemental Analyses

Elemental analyses were obtained for four of the polyamides. The analyses agree fairly well with the expected values. Three features of the analyses were considered to be of particular interest:

1. Microanalysis failed to detect any trace of chlorine. This implies that if α -chloro bischloride A2 is a major impurity,⁴ then all the α -substituted chlorine has been subjected to nucleophilic substitution. As this represents only 3.8% of the total chlorine present in the bischloride A2 it would result, on average, in one branch point on approximately every 25 bisacid A2 residues in the polymer. This would yield two branch points on a polymer molecule incorporating a typical diamine and having a molecular weight of 23,000, not a very high degree of branching.

2. The presence of sulfur in amounts which are not proportional to the amount of bisacid A2 residue present implies either that the sulfur is present as a small insoluble molecule which becomes trapped in the polymer matrix, or that the sulfur is present as a reactive group which is incompletely reacted during polycondensation.

3. The generally high nitrogen counts imply either a preponderance of amine end groups or a degree of additional reaction involving the amine by a mechanism other than amidation by the acid chloride group and/or the incorporation of solvent into the polymer. Taking into account the purity of the acid chloride and the ratio of reactants used, the former would imply that there was some secondary mechanism by which chloride functionalities are removed from the reaction mixture, but no mechanism can be suggested for this at present.

¹H NMR Spectra

Proton NMR spectra of the polymers were recorded in d^6 DMSO. The spectra serve to characterize the polymers chemically and also provide a means by which any irregularities in the polymers may be sought. All polymers show similar adsorption for the bisacid A2 skeleton. It is interesting to note that in three out of six polymers the hydrazide and amide adsorptions overlap to such an extent that they are indistinguishable on a 60 MHz c.w. spectrometer. This indicates that the magnetic environments of the groups represented in Figure 2 are equivalent. All spectra showed a broad peak between 3–4 ppm. This may possibly be assignable to amine end groups.

It is known that amide solvents containing small amounts of an inorganic salt, particularly chloride, are better solvents for bisacid A2 polyamides than the amide solvents alone. This has also been observed with other systems.⁵⁻⁹ Furthermore, it has been shown^{9,10} that ¹H NMR can detect the change in magnetic environment of the amide hydrogen which arises from coordination of the amide group to the lithium ion. This effect was also observed with bisacid A2 polyamides.

5% and 10% solutions of C2/5 and C1/2 were prepared in 2.5% LiCl/DMA solvent. It was found that lithium chloride caused greater shifts in the amide resonances than in the hydrazide resonances (about 2 ppm and 0.5–0.7 ppm, respectively), presumably reflecting a difference in the ability of these two groups to donate electrons to the lithium ion.

Solubility

In order to facilitate further characterization, the solubility of several of the bisacid A2 polyamides was determined in various solvents. The polymers selected for this purpose were a readily soluble polymer, M5, a less soluble polymer, M9, and the polyamide-hydrazide C1/9. The latter was included in order to investigate the effect of incorporating the hydrazide group and to observe the effect of a larger proportion of Bisacid A2 residues in the polymer chain. The results are given in Table I.

The solvent parameters quoted are the solubility parameter δ , the hydrogen bonding group as defined by Burrell and Immergut,⁹ the dipole moment μ , the dielectric constant ϵ , and the donor number. The donor number is an empirically determined value,¹⁰ which is a measure of the ability of a solvent to donate electrons to a solute. The solubility parameter is of little signif-

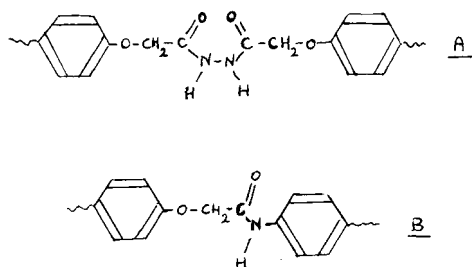


Fig. 2. Hydrazide and amide groups- the ¹H NMR spectra suggest that the magnetic environments are equivalent.

TABLE I^a
Solvent Characteristics

	HBG	DN	C1/9		M9		M5	
			C	R	C	R	C	R
Aprotic								
Acetone	20.4	17.0	-	-	-	-	-	-
Acetonitrile	24.39	14.1	-	-	-	-	-	-
Dimethylacetamide	22.13	27.8	+	+	+	+	+	+
Dimethylformamide	24.7	26.6	+	+	+	+	+	+
Dimethylsulphoxide	24.6	29.8	+	+	+	+	+	+
Dioxane	20.2	0.45	-	-	-	-	-	-
Ethyl acetate	18.6	17.1	-	-	-	-	-	-
Hexamethylphosphor- amide	21.52	38.8	+	+	+	+	+	+
<i>N</i> -methylpyrrolidone	23.16	4.09	+	+	+	+	+	+
Nitrobenzene	20.49	4.4	-	-	-	-	-	-
2Nitropropane	20.29	3.73	-	-	-	-	-	-
Pyridine	22.2	33.1	+	+	+	+	+	+
Tetrahydrofuran	18.65	20.0	-	-	-	-	-	-
Protic								
Acetic acid	25.7	1.68	-	-	-	-	-	-
Benzyl alcohol	24.8	1.66	-	-	-	-	-	-
Formic acid	27.6	1.82	-	-	-	-	-	-
Phenol	29.6	1.45	-	-	-	-	-	-
Sulfuric		110	+	+	+	+	+	+

^a δ = solubility parameter, HBG is hydrogen bonding group as defined by Burrell and Immergut,⁹ p = poor, m = medium, s = strong, ϵ = dielectric constant, μ = dipole moment, DN = donor number as defined by Gutmann,¹⁰ C indicates solubility in cold solvent (25°C), R indicates solubility in refluxing solvent, + = completely soluble, and - = insoluble.

icance for polymers, where there is strong interaction with the solvent. This is clearly the case with bisacid A2 polyamides as indeed with other polyamides.

All the good solvents had a high solubility parameter, but not all solvents with a high solubility parameter were good solvents for the polyamides. A high solubility parameter is simply an indication of significant interaction between solvent molecules. Most of the good solvents had high dielectric constants (> 30) and high dipole moments (> 3.7), and they were members of a group showing medium or strong hydrogen bonding.

The combination of high dielectric constant and high dipole moment was neither necessary nor by itself sufficient to define a good solvent. This was demonstrated by the nonsolvent acetonitrile and by pyridine (the latter being a relatively good solvent). Nitrobenzene was an exception, and its solvent power at reflux is presumably due to its highly polar nature.

Donor numbers seemed to give a reasonable guide to the efficacy of aprotic solvents. The information available at present is unfortunately incomplete. All the good solvents had donor numbers above 23. Those with lower donor numbers were usually nonsolvents. Pyridine, which seemed anomalous in terms of ϵ and μ , fitted well into this trend. Nitrobenzene was again an exception with an extremely low donor number of 4.4.

The proposed mechanism of solution of polyamides has been discussed in Maguire's Ph.D. thesis.¹¹ The experimental evidence obtained with bisacid A2 polyamides seems to confirm the views expressed there. Those solvents which proved to be good solvents for bisacid A2 polyamides were either capable of hydrogen bonding (in which case they presumably interacted with the amide group) or they were solvents with good electron donor capabilities (these solvents presumably interacted both with the aromatic systems and to a lesser extent with the amide groups by hydrogen bonding). This is diagrammatically illustrated in Figure 3. [At least three weak interactions (the aromatic ring could presumably accept electrons from both sides making a total of six weak interactions) and two medium interactions, spread along the length of the chain unit.]

Molecular Weight

The limiting viscosity number of the polyamides was useful as a guide to molecular weights. Gel permeation chromatography and low angle laser light scattering photometry were used to determine absolute molecular weights and molecular weight distributions. A limited number of polyamides was investigated, but because of the similarity in the structure of the polyamides the results could be extrapolated from polymer to polymer.

Limiting Viscosity Numbers (LVN)

An initial estimate of molecular weight was obtained by measuring the LVN of the polyamides. The results for all the polymers are given in Table II. It was found that polymers with an LVN of up to 0.3 were powdery and that polymers with an LVN of above 0.4 formed viscous solutions and yielded tough plastic beads on precipitation.

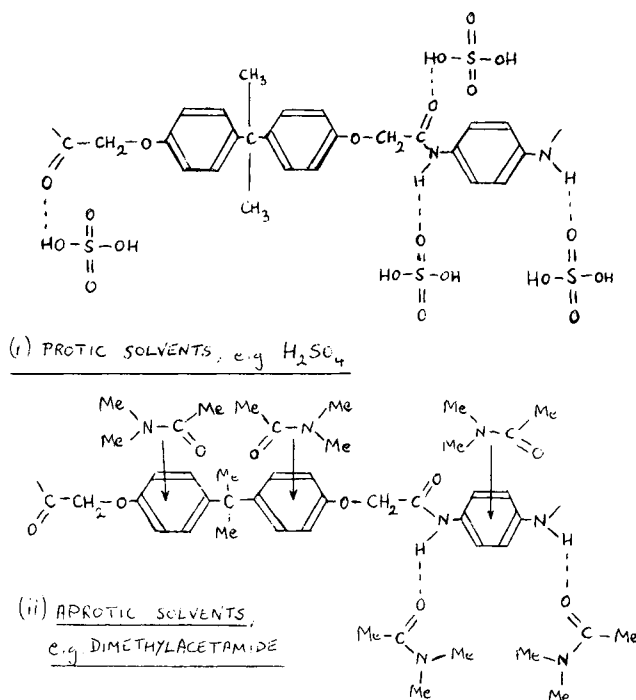


Fig. 3. (i) Protic solvents, e.g., H_2SO_4 (four strong interactions per chain unit, occurring only at the amide groups). (ii) Aprotic solvents.

Gel Permeation Chromatography (GPC)

This technique has found extensive application in the polymer field since macromolecules may be separated according to their hydrodynamic volume.¹² If the K and a values of the Mark-Houwink equation for the polymer under investigation are not known, the use of the Einstein equation on the

TABLE II
Yields, LVN's and Appearance of Polymers

Polymer	Yield (%)	LVN (dL g ⁻¹)	Appearance
M2	93	0.85	Good white beads
M3	72	0.45	Powdery green beads
M4	35	0.19	Brittle brown foam
M5	96	0.70	Good white beads
M6	40	0.11	Pale yellow powder
M7	82	0.50	Good pink beads
M8	89	Insoluble	Red powder
M9	92	0.55	Good green beads
C1/2	90	0.43	Good white beads
C1/3	95	1.01	Good green beads
C1/4	62	0.30	Brittle brown solid
C1/5	70	0.55	Good white beads
C1/7	86	0.53	Good pink beads
C1/8	83	Insoluble	Red powder
C1/9	91	0.48	Good green beads
T1/3/7	88	0.44	Good pink beads

theoretical treatment of Flory and Huggins applied to a column calibrated with polystyrene can produce "polystyrene-equivalent" molecular weight data for polymers in solution.

A number of typical polymers (M2, M5, C1/6, C2/5, and T1/3/6) were selected for examination by GPC, using DMA as the solvent. C1/6 and T1/3/6 formed microgels and were totally excluded from the columns (see below). All the other polymers showed some tendency to block the columns. The results for M2, M5 and C2/5 (as well as results from L.A.L.L.S.P.) are given in Tables III and IV. The ratios of M_0 , M_w , and " M_w apparent" (M_a) were obtained by the usual methods.

The differences between " M_w apparent" and " M_w light scattering," and the discrepancy between the ratio of M_0 values and the ratio of light scattering molecular weights implies that, for a given molecular length, the polyamide molecule occupies a larger hydrodynamic volume in DMA than does polystyrene. This reflects the stiffer nature of the polyamide molecules.

The total exclusion of two polymers and the tendency to block the columns exhibited by the other three is almost certainly due to the formation of microgel, highly branched or lightly crosslinked polymer, which dissolves in good solvents to form a homogeneous (and not a colloidal) solution, but which is nonetheless filtered by microporous filters with a pore size of the order of half a micron.

It has already been shown⁴ that the bischloride A2 used to prepare the polymers contained trifunctional monomers to the extent of about 4% and that these consisted almost entirely of α -chloro-bischloride A2. Under the conditions of the polycondensation reaction such trifunctional monomers are liable to produce, at most, one branching point per 25 chain units (and probably considerably fewer due to the much greater reactivity of acid chloride compared with that of the alkyl halide groups). Furthermore, the preponderance of amine end groups indicated by ¹H NMR investigations suggests that some mechanism is removing acid chloride functionalities from the polycondensation reaction.

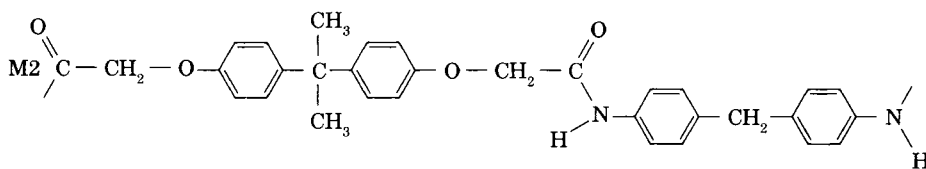
These observations strongly suggest that bischloride A2 is reacting with the polyamide chain to form branching points. This would explain the observed formation of microgel in the present investigation as well as the complete gelling of reaction mixtures previously observed by Lenk.¹³ It is also at least partially responsible for the high "effective molecular weight" of bischloride A2.

The branching points most probably arise by reaction of the acid chloride with previously formed amide linkages to yield an imide, as shown in Figure 4. This reaction is a standard route for the preparation of certain imides, but the rate of the reaction greatly depends on the acid and on the reaction

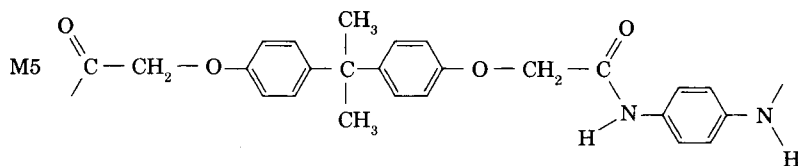
TABLE III
Polystyrene Equivalent Molecular Weight Data

	M_w	M_n	M_a	$M_w:M_n:M_a$
M2	99,770	34,370	322,000	2.90:1:9.37
M5	87,440	30,770	205,400	2.84:1:6.70
C2/5	49,140	25,460	78,540	1.93:1:3.09

TABLE IV
Molecular Weight Data for M2, M5, and C2/5



Molecular weight of repeat unit = 506
 PE M_w = 99,770, light scattering M_w = 26,300
 Polystyrene equivalent: 22 units
 Ratio of M_0 M2:PS = 506/1144 = 0.442
 Ratio of M_w M2:PS = 26,300/99,770 = 0.264
 M_w apparent = 49,870



Molecular weight of repeat unit = 416
 PE M_w = 87,440, light scattering M_w = 27,600
 Polystyrene equivalent: 18 units
 Ratio of M_0 PS:M5 = 416/936 = 0.444
 Ratio of M_w PS:M5 = 27,600/87,400 = 0.316
 M_w apparent = 38,750

C2/5

Molecular weight of repeat unit = 922
 PE M_w = 49,140, light scattering M_w = 13,060
 Polystyrene equivalent: 14 units
 Ratio of M_0 C2/5:PS = 922/2132 = 0.432
 Ratio of M_w C2/5:PS = 13,060/49,140 = 0.266
 M_w apparent = 23,440

conditions (and in particular on the nature of the solvent). The factor which governs the reactivity of the acid chloride is the electrophilicity of the carbonyl carbon.¹⁴ Acetyl chloride is the most reactive of the homologous series of simple aliphatic acid chlorides and bischloride A2 is an acetyl chloride with an electronegative substituent, the oxygen atom. It would therefore be expected that bischloride A2 should be even more electrophilic than acetyl chloride.

Furthermore, Weinstock et al.¹⁵ have shown that the reaction between acyl halides and secondary amides is inhibited by the HC formed which protonates the amide nitrogen and leads to cleavage reactions. If the HCl is effectively removed, e.g., by carrying out the reaction using an amide

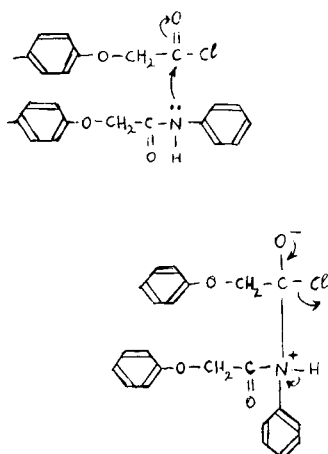


Fig. 4. Suggested mechanism for the generation of branching points.

solvent as an acceptor, the reaction will proceed smoothly to completion under mild conditions; imide formation is then entirely feasible. This is not a problem in the preparation of *fully* aromatic polyamides because the aromatic acyl chlorides have a much lower electrophilicity.

In the case of bischloride A2 this mechanism leads to the removal of acyl halide functionalities from the polycondensation reaction and, as a consequence, to a preponderance of amino end groups. This explains why optimum molecular weight polymers are obtained at reactant proportions other than theoretical isostoichiometry, and why the formation of highly branched polymers (microgel) is evidently commonly occurring.

Further evidence in favor of this explanation derives from an inspection of the ratios of $M_w:M_n$ for M2 and M5. It was seen that these ratios are considerably higher than 2, the latter being the value expected for the most probable distribution obtained in a polycondensation reaction. This implies a broadening of the molecular weight distribution, a typical feature of branched polymer systems.

Low Angle Laser Light Scattering Photometry (LALLSP)

LALLSP utilizes a laser to enable measurements of the light scattered from a polymer solution to be made at very low angles ($<7^\circ$). The results obtained from polymers M2, M5, and C2/5 indicated that all polymers showed some tendency to block the 0.4 fluoropore filter used on the LALLSP. This further confirms the presence of microgel. The values for the molecular weight were comparable to those of lower molecular weight aliphatic polyamides. They represent a weight average degree of polymerisation of approximately 50 chain units. This would be a very desirable level for a linear polymer, but in a highly branched polymer this is both more readily achieved and less indicative of the formation of chains of truly great length.

Thermogravimetric Analyses

Thermogravimetric analyses (TGAs) were obtained for all the polymers. All the polymers exhibited a weight loss of a few percent up to about 150°C ,

which was ascribed to the loss of residual moisture or alcohol from the washing process. Two of the polymers exhibited a second weight loss of less than 3% at 150–200°C, which could not be accounted for. All the polymers then showed a very similar pattern. No weight loss occurred until a temperature was reached at which the onset of degradation was very fast. Degradation continued at a rapid rate until complete oxidation had occurred. In order to compare the different polymers, a "limit of thermal stability" (LTS) was defined, which was arbitrarily chosen to be the temperature at which the rate of weight loss was 0.5 mg/min at a heating rate of 125°C/h with a sample mass of 100 mg.

In the polyamide series (M2–M9) the highest thermal stabilities were found for those diamines which are themselves inherently stable. Aromatic diamines are often easily oxidized but 1,5-diaminoanthraquinone, 4,4'-di(aminophenyl) methane, 1,5-diaminonaphthalene, and *p*-phenylene diamine have unusual thermal and oxidative stability. The polymers which were found to have lower thermal stabilities contained 2,6-diaminopyridine, 4,4'-diaminodiphenylamine, and 1,8-diaminonaphthalene.

Differential Scanning Calorimetry

The phase behavior of the polymers was investigated by differential scanning calorimetry (DSC). The series of *p*-phenylene diamine polymers described by Maguire¹¹ were used to determine whether the molecular weights of the polymers were sufficiently high for T_g to be independent of molecular weight.

The T_g 's were between 152 and 155°C and did not vary with molecular weight until the acid chloride was in an "effective excess," (i.e., after the molecular weight maximum had been reached), whereafter it fell rapidly. At this stage all of the amino functionalities would have been satisfied, and it is suggested that the acid chloride subsequently reacts with amide groups on the chain, thus forming a macromolecule having many short side chains. These side chains cause an increase in the free volume of the molecule and may also have a plasticising effect (which therefore accounts for the fall in T_g).

It is evident that polymers with an LVN of above 0.5 (and possibly lower) have a sufficiently high molecular weight for T_g to be independent of molecular weight. The T_g 's were found to fall within the range 130–180°C, which has been shown¹¹ to be typical for semiaromatic polyamides.

The highest T_g was exhibited by the polyamide based on 2,6-diaminoanthraquinone which contributes a great deal of rigidity to the polymer chain. The lowest (107°C) was found in 4,4'-di(aminophenyl)methane and 2,6-diaminopyridine, but this may have been partly due to low MW. All T_g 's observed had a range of 5–10°C. The polyamides contained only half as many bisacid A3 residues as the polyamide-hydrazides and consequently had stiffer chains and higher T_g 's. The polyamide-hydrazides showed a fairly clear relationship between the stiffness imparted by the monomer and the T_g of the polymer; 2,6-diaminoanthraquinone ($T_g = 195^\circ\text{C}$) produced the highest T_g of the polyamide-hydrazides.

Overall, the trend predicted from theoretical considerations¹¹ was fairly closely followed. No melting endotherm was evident in any of the polymers

below temperatures at which chemical changes could be detected. This implies that the polymers were either totally amorphous or that the melting point was higher than the limit of thermal stability. This type of phase behavior is very similar to that of commercial amorphous semiaromatic and stiff-chain aliphatic polyamides, that is to say, of materials which have been discussed thoroughly from this point of view elsewhere.¹⁴

Morphology by Wide Angle X-Ray Scattering

X-ray diffraction patterns were obtained for the precipitated polymer and for cast and pressed films. All samples showed the broad diffuse halo typical of amorphous materials. A few samples showed some indications of crystallinity, but these were too faint to be quantified by microdensitometry and suggest a degree of crystallinity of a few percent at the most.

Samples of M2 subjected to tensile testing on an Instron machine exhibited necking and cold drawing, and developed "Lüder lines." X-ray diffraction patterns of the stretched region showed orientation patterns similar to those found for oriented nylon 66 film. None of the other polymers behaved in this way. Differential scanning calorimetry and WAXS therefore indicated that the polymers were amorphous in the precipitated, pressed, and cast form. This is almost certainly a consequence of the polymers being highly branched.

Tensile Testing of Cast Films

Tensile tests were carried out on strips cut from cast films. Many of the films were fragile and presented problems of sample preparation and handling. As a consequence, they gave widely scattered results.

The better polymers based on bisacid A2 were comparable in performance with commercial amorphous polyamides. The low values obtained for the modulus and tensile strengths of some polymers were ascribed to the low molecular weights of the polymers to which the figures relate.

Polymers Incorporating Trifunctional Monomers

Frazer & Wallenberger¹⁶⁻¹⁹ and Preston and Hofferbert²⁰ have shown that the use of trifunctional monomers can greatly improve the mechanical properties of semiaromatic polyamides. One polymer of this type (T1/3/7) was prepared and characterized. The results have been included along with the other polymers under the section relevant to the determination of the various polymer parameters. They will nevertheless be summarized here.

The formulation of T1/3/7 was

Bischloride A2	50
Bishydrazide A2	25
1,5-Diaminonaphthalene	22.5
4,4'-Diaminodiphenylamine	2.5

This formulation is only slightly different from polymer C1/7, which was also included for the purpose of comparing properties.

Kogarko *et al*²¹ and Karyakin *et al*²² have shown that the secondary amine function is less reactive than the primary amine function towards acid chlorides. The presence of the secondary amine group should therefore result in a greater degree of branching in T1/5/7 than in C1/7. Table V compares the two polymers.

GPC indicated that both polymers were branched and formed microgel. Viscosity measurements indicated that T1/5/7 was probably of lower molecular weight than C1/7, although an element of uncertainty is introduced when the degree of branching is unknown. The glass transition temperature and the tensile data indicated that T1/5/7 had a higher degree of branching, since the T_g was higher and the tensile strength greatly exceeded that of the less branched polymer.

CONCLUSIONS

1. The polymers produced from bischloride A2 by the low temperature solution polycondensation method have molecular weights which may exceed 25,000.

2. The polymers so formed are highly branched and form microgel.

3. It is suggested that the branching points are produced by imide formation.

4. The polymers are amorphous. This is almost certainly due to the high degree of branching which occurs during the polycondensation reaction.

5. The properties of the polyamides are comparable to those of commercially produced amorphous polyamides.

6. The inclusion of small amounts of trifunctional monomer improves the tensile properties and raises the T_g of the polymers.

Since bischloride A2 appears to be even more reactive with amines than acetyl chloride (normally regarded as the most reactive acid chloride in the unsubstituted homologous series), it would be of considerable interest to ascertain whether gel formation can be prevented by the use of *secondary* amines. The use of these would preclude any possibility of imide formation and might enable one to produce the desired long-chain polyamides even though *some* branching due to the small amount of identifiable α -chloro bischloride A2 present might still cause such a polyamide to be branched if the α -chlorine atom showed appreciable reactivity with primary or secondary amines.

TABLE V
Comparison of an Amide/Hydrazide Copolymer and a Copolymer Incorporating a Trifunctional Monomer

Property	C1/7	T1/5/7
LVN (dl g ⁻¹)	0.53	0.44
GPC	Totally excluded	Totally excluded
ITS (°C)	255	250
T_g (°C)	140	147
Ext. at break (%)	1.5	3.0
Modulus (Pa $\times 10^{-8}$)	17.1	21.8
Tensile strength (Pa $\times 10^{-7}$)	2.94	6.85

SUMMARY

Several new polyamides based upon bisacid A2 have been prepared, and their properties are reported. The polyamides were formulated such as to enable one to investigate structure/property relationships. Using a variety of suitable methods with a view to elucidating these relationships, we arrived at a number of conclusions of which the following were the most significant:

Polymers prepared by low temperature solution polyamidation of the type described have molecular weights which may be around or well in excess of 25,000. They are branched and form microgel. Branching is almost certainly due to imide formation.

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