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Final Technical Report

STEP-GROWTH PROPAGATION OF HIGH MOLECULAR WEIGHT RIGID ROD POLYMERS

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The synthesis of two isomeric poly(benzothiazoles) via the self-polycondensation of two isomeric (o-aminomercapto)benzoic acids was investigated. Poly(2,6-benzothiazole) was prepared from 4-amino-3-mercaptobenzoic acid in polyphosphoric acid at concentrations 3 to 10%. Intrinsic viscosities between 3 and 4.6 dL/g in methanesulfonic acid were obtained. The purity of the requisite monomer for poly(2,5-benzothiazole), namely 3-amino-4-mercaptobenzoic acid was not sufficient to obtain high molecular weight polymer. The polymers are candidate matrix resins for molecular composites with the rigid polymer, poly(p-phenylene benzobisthiazole)

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ABSTRACT

The synthesis of two isomeric poly(benzothiazoles) via the self-polycondensation of two isomeric (o-aminomercapto)benzoic acids was investigated. Poly(2,6-benzothiazole) was prepared from 4-amino-3-mercaptobenzoic acid in polyphosphoric acid at concentrations of 3 to 10%. Intrinsic viscosities between 3 and 4.6 dL/g in methanesulfonic acid were obtained. The purity of the requisite monomer for poly(2,5-benzothiazole), namely, 3-amino-4-mercaptobenzoic acid, was not sufficient to obtain high molecular weight polymer. The polymers are candidate matrix resins for molecular composites with the rigid rod polymer, poly(p-phenylene benzobisthiazole) (PBT).

CONTENTS

ILLUSTRATIONS

INTRODUCTION

The primary goal of the Air Force Ordered Polymer Program is the development of new structural materials that will be suitable for advanced aerospace applications because of the following characteristics:

- Structural stability and retention of mechanical properties on exposure to extreme environments of temperature, humidity, and aerospace solvents.
- Low density.
- Isotropic mechanical properties comparable to state-of-the-art graphite-reinforced composites.
- Ease of fabrication.

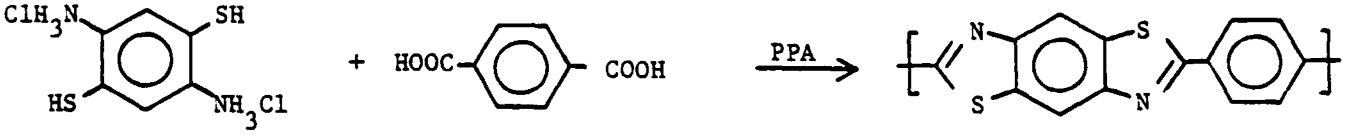
The Ordered Polymer Program has centered its study on the utilization of rigid rod polymers. By the very nature of obtaining high mechanical properties from these polymers, the properties are necessarily anisotropic. Fibers and films spun from liquid crystalline solutions of rigid rod polymers, such as poly(p-phenylenebenzobisthiazole) (PBT), have ultrahigh tensile modulus and strength in the spinning direction only. A key word in the desirable characteristics stated above is isotropic properties.

One approach to obtaining at least pseudo-isotropic properties would be to laminate cross-plies of unidirectional ribbons in a manner analogous to fiber-reinforced composite technology. This approach would suffer one of the same drawbacks of conventional composites--possible delamination. Another approach to obtaining superior isotropic properties, and the subject of this report, has been termed molecular composite technology.

A molecular composite is visualized as a microscopic analogy to a chopped fiber composite. The concept relies on the development of a technology that enables fabrication of a molecular dispersion of two intrinsically incompatible polymers--a rod and a coil. The rigid rod polymer is seen as the reinforcement and the coillike polymer as the load-transferring matrix resin. Three significant achievements of the Ordered Polymer Program led to this study of benzothiazole polymers as candidate matrix resins:

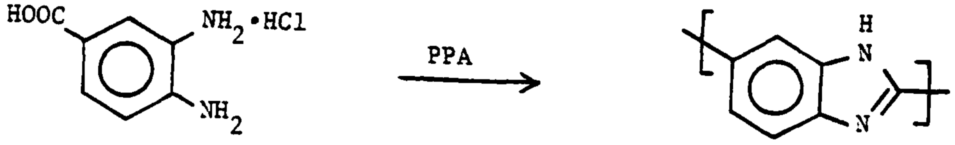
- The synthesis of PBT.
- The fabrication of a high-strength blend of PBT and ABPBI.
- The development of theory for the thermodynamic properties of mixtures of rodlike particles.

PBT was first prepared at SRI under Air Force Contract No. F33615-76-C-5109 in November 1977.[1] Since that time, work has continued at SRI under Air Force Contract No. F49620-78-C-0110 on the optimization of synthesis parameters of rigid rod polymers and under Contract No. F33615-79-C-5110 on the large-scale synthesis of PBT. At present, PBT can be consistently prepared with an intrinsic viscosity of greater than 15 dL/g (in methanesulfonic acid, MSA, at 30°C) by the polymerization of 2,5-diaminobenzene-1,4-dithiol dihydrochloride (**1**) with terephthalic acid (**2**) in PPA.[2] The high molecular weight, thermal and oxidative stability, and rodlike character of PBT have made it the prime candidate for study in the ordered polymer program.



1 **2** PBT

The second achievement was the preparation of a film from a blend of 10% PBT and 90% ABPBI by researchers ar the Air Force Materials Laboratory.[3] ABPBI is a high molecular weight benzimidazole polymer prepared by the AB-polymerization of 3,4-diaminobenzoic acid hydrochloride (3) in PPA.



3

ABPBI

The film was cast from a solution in MSA and had a tensile strength of 89,000 psi. This tensile strength represents a value much greater than solvent-cast films of other aromatic polymers. For example, a film considered to be tough (passing the fingernail-crease test) prepared from a flexible, high molecular weight polyquinoline has an ultimate tensile strength of 6,700 psi.[4]

The third achievement was Flory's development of a theory for treating the thermodynamic properties of mixtures of rodlike particles.[5] One portion of the theory[5e] states that, in a mixture of rigid rodlike polymers and flexible random-coiled polymers, the rigid polymers will spontaneously partition themselves into highly selective anisotropic regions surrounded by isotropic regions of the flexible polymers. To quote from Flory[5e]:

> The isotropic phase offers to a rodlike solute none of the advantages of orientation. Hence, this component prefers the anisotropic phase where obstruction by neighboring species is alleviated by mutual alignment.... The anisotropic phase approaches the selectivity of a pure

> crystal in its rejection of a foreign component, in
> this case the random coil.

A high degree of selectivity is predicted to occur even at low concentrations when the axis ratios of rodlike and coiled polymers are large.

Another portion of Flory's theory[5f] treats the properties of solute molecules composed or rodlike sequences connected by flexible joints. The theory as presented is strictly valid only for rigid segments connected by universal joints; i.e., the direction of successive rigid segments cannot be constrained by the joint. The theory states that separation of an anisotropic phase in such a system depends predominantly on this axis ratio of the rigid segments.

The striking feature of Flory's theory is that so much information can be obtained by investigating the molecular geometry alone. Thus an examination of the molecular geometries of PBT and ABPBI may provide an explanation of the ordering that gives rise to the high strength composite film. PBT has been shown to be rodlike throughout its entire length by dilute solution studies conducted by Dr. Berry and coworkers[6] at Carnegie Mellon University. PBT forms nematic solutions when dissolved in MSA at concentrations of $\gtrsim$5%. The conformation of ABPBI in solution is not as well defined. The intrinsic viscosity of ABPBI has been measured at greater than 14 dL/g. This value is suprisingly high for a polymer that is not rodlike in structure (i.e., each repeat unit has an angle of catenation of 150°). However, an examination of molecular models of ABPBI shows that a self-correcting rodlike conformation is possible, as shown in Figure 1. The other extreme conformation of ABPBI is more coillike, as shown in Figure 2. We therefore envision ABPBI in solution as consisting of segments ranging from the rodlike sequences of Figure 1 to the coiled sequences of Figure 2. The segments are interconvertible by simple free rotation of the main chain bond. In the absence of a driving force for rodlike sequence generation, an equilibrium persistence length would be established.

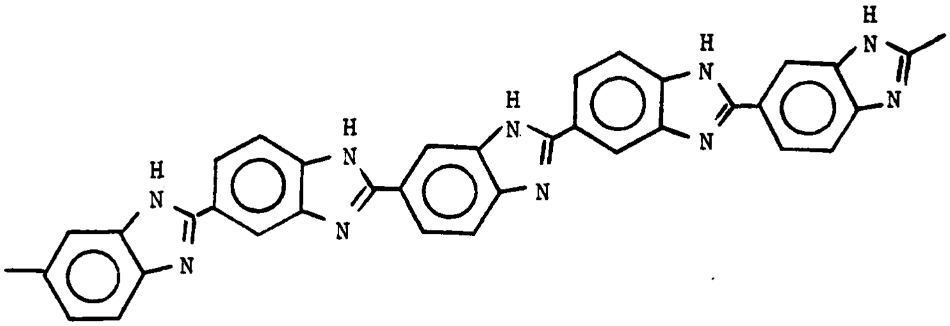


FIGURE 1 POSSIBLE RODLIKE CONFORMATION OF ABPBI

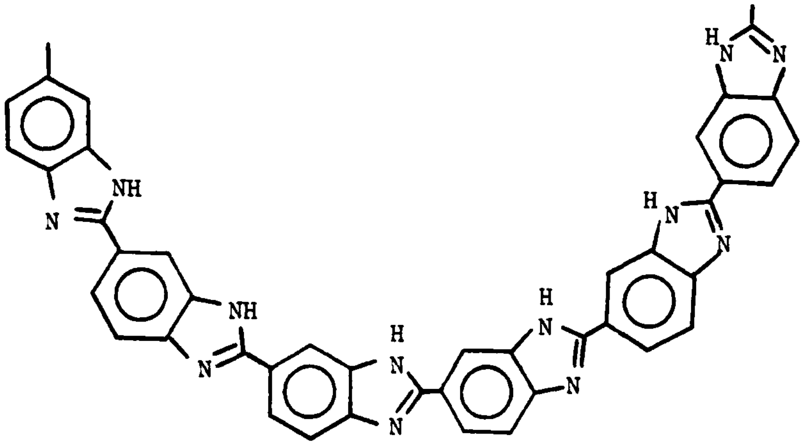


FIGURE 2 POSSIBLE COILLIKE CONFORMATION OF ABPBI

It therefore seems possible that, in a mixture of ABPBI with a rodlike polymer such as PBT (which has selectively separated into anisotropic domains), incorporation of ABPBI into the anisotropic phase would be allowable if ABPBI could conform to the spatial requirements of the region. We propose that it is possible for the ABPBI-PBT film to be viewed as represented in Figure 3.

FIGURE 3 PROPOSED MECHANISM FOR STRENGTH IN ABPBI-PBT FILM

Incorporation of the rodlike sequences of ABPBI into the anisotropic phase causes depletion of the larger rodlike sequences from the distribution established in the isotropic phase. This situation then provides a driving force, i.e., the reestablishment of equilibrium, for the self-ordering of the isotropic phase.[5c]

Another possible explanation of the reinforcement observed in the ABPBT-PBT film is a nonequilibrium blend in which the rodlike polymer is randomly and molecularly dispersed in the coillike polymer. The macroscopic analogy is a chopped fiber composite. The nonequilibrium nature of this morphological structure must be emphasized, and the method of fabrication or blending adjusted accordingly, since Flory's theory indicates such a strong thermodynamic incompatibility of rod and coil. The synthesis of ABPBT would at least provide for a molecular structure that would be chemically compatible with rodlike PBT.

The benefits of applying this film-forming method to materials with the high use-temperature required by advanced aerospace application are obvious. Inducement of crystallization in amorphous high temperature polymers normally requires annealing temperatures equal to the T_g plus two thirds of the $T_m - T_g$ interval. Even if the polymer were stable at the annealing temperature required, the use temperature under this method is necessarily below the ultimate use-temperature (as determined by the polymer decomposition temperature, PDT). The molecular composite approach allows the chemist to adjust the "crystallinity" of the film by controlling the variables responsible for anisotropic phase separation. The processing temperature is also much lower than the ultimate use-temperature.

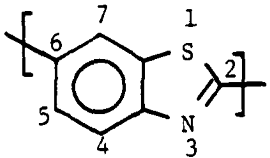
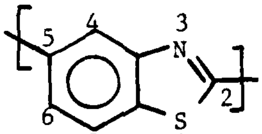
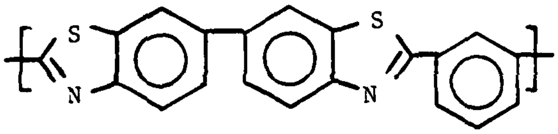
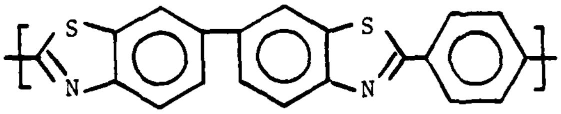
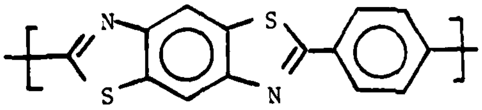
The tensile strength observed in the PBT-ABPBI film is extremely attractive; however, the result must be considered only as a demonstration of principle (as extremely important as that is in itself). As a candidate for development as a aerospace structural material, the PBI component cannot be tolerated because of its high moisture affinity. Dried PBI fibers regain as much as 13% by weight of water at 70°F, 65% relative humidity. This property makes PBIs excellent materials for high temperature textile fibers and reverse osmosis desalination membranes, but eliminates them in the structural application area.

There was clearly a need for an alternative matrix resin with a thermal stability comparable to PBT and without the moisture problem. The logical replacement for ABPBI was the geometrically analogous ABPBT.

Several laboratories investigated the synthesis of aromatic polymers containing the benzothiazole nucleus in the mid-1960s. A list of the wholly aromatic benzothiazole polymers cited in the literature is given in Table 1. None of the known flexible benzothiazole polymers even approaches ABPBI's intrinsic viscosity of 14 dL/g. Our approach was to study the chemistry of the ABPBTs and their requisite monomers in an attempt to prepare ABPBT that would be suitable for a matrix resin in molecular composites.

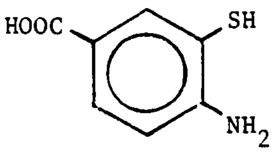
Table 1

KNOWN AROMATIC BENZOTHIAZOLE POLYMERS

Polymer	Polymerization Medium	Polymerization Temp. (°C)	η_{inh}	Ref.
 2,6-ABPBT	PPA	160	1.26	7
	PPA	200	2.03	7
	PPA	250	1.08	8
	melt	250	0.23	8
 2,5-ABPBT	PPA	250	1.29	8
	melt	250	0.29	8
	PPA	240	0.47	9
	PPA	200	1.51	9
	PPA	200	0.43	10
	PPA	200	1.02	10
 PBT	PPA	185	>15	2

RESULTS AND DISCUSSION

The majority of this year's effort was aimed at the synthesis of two monomers, namely, 4-amino-3-mercaptobenzoic acid (**4**) and 3-amino-4-mercaptobenzoic acid (**5**)



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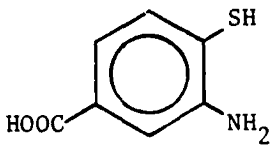
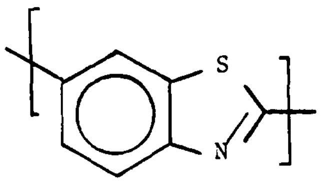
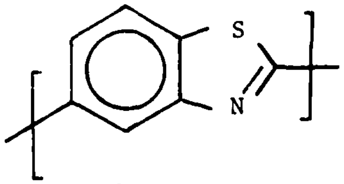


5

and the separate self-polycondensations of **4** and **5** to afford poly(2,6-benzothiazole) (2,6-ABPBT) and poly(2,5-benzothiazole)(2,5-ABPBT), respectively.

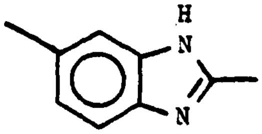


2,6-ABPBT



2,5-ABPBT

Both of these polymers seem quite similar structurally and are closely analogous to ABPBI. However, two subtle differences may give rise to important differences in the overall conformations of the two polymers. In ABPBI, the position of the double bond in the imidazole ring (with respect to the main chain bond across the fused benzene ring) has the two possibilities shown in **6** and **7**. ESCA measurements have shown that two distinct nitrogens exist in PBIs in the solid state.[11]



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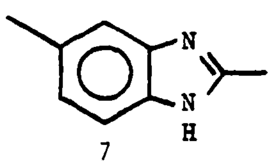

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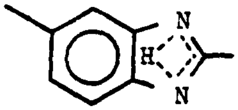
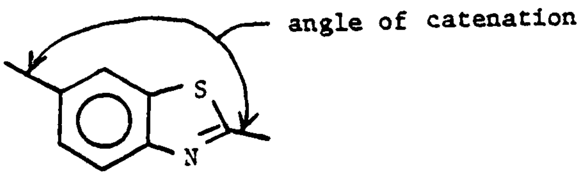
In strong acid solutions, the structure can probably be viewed as the hydrogen-bridged structure:



In 2,6-APBPT, however, the double bond is localized in a structure analogous to 6.



If we assume that the angle of catenation in ABPBI is 150°, this effect of localization, combined with the larger size of the sulfur atom compared with the nitrogen atom, should make the angle of catenation in 2,6-ABPBT greater than 150° or more rodlike in character than ABPBI. The 2,5-ABPBT structure has the shorter C=N-C bond localized within the angle of catenation; thus we expect this polymer to be less rodlike than either 2,6-ABPBT or ABPBI.

Synthesis of 4-Amino-3-Mercaptobenzoic Acid (4)

To obtain any ortho-aminothiol monomer with sufficient purity to obtain high molecular weight polymer, the final step of the synthesis must be efficient and must not rely on a complex work-up procedure. The sensitivity of the thiol moiety toward oxidation requires that handling (both time and possible exposure to air) be minimized. We now also believe that protonation of the thiol group by hydrochloric acid, previously believed to be localized at the amino group, can effect elimination of hydrogen sulfide with subsequent coupling of the resultant phenyl carbonium ion with another thiol group to give a sulfide impurity (S_N1 mechanism). There is some precedent in the literature for this mechanism with mercaptomethylamine[12] and alkyl α-dimethylaminobenzyl sulfides[13] in aqueous hydrochloric acid. The choice of procedure must take into account the possibility of these side reactions and attempt to **minimize** their occurrence.

Imai et al.[7] and Hergenrother[8] used the method of Schubert[14] for the preparation of 4, involving the hydrolysis of the acetate of 2-amino-6-carboxybenzothiazole as the final synthesis step. We used a similar procedure to prepare 4 using concentrated aqueous potassium hydroxide to hydrolyze 2-amino-6-carboxybenzothiazole (8). However, we prepared 8 by a new procedure that is similar to the method used by Brewster and Dains[15] and to the preparation of the diaminobenzobisthiazole intermediate synthesis of monomer 1.

Monomer 4 was prepared as outlined in Figure 4. The full experimental details for the synthesis of 4, both as the free amine and the hydrochloride salt, are presented in the Experimental Section.

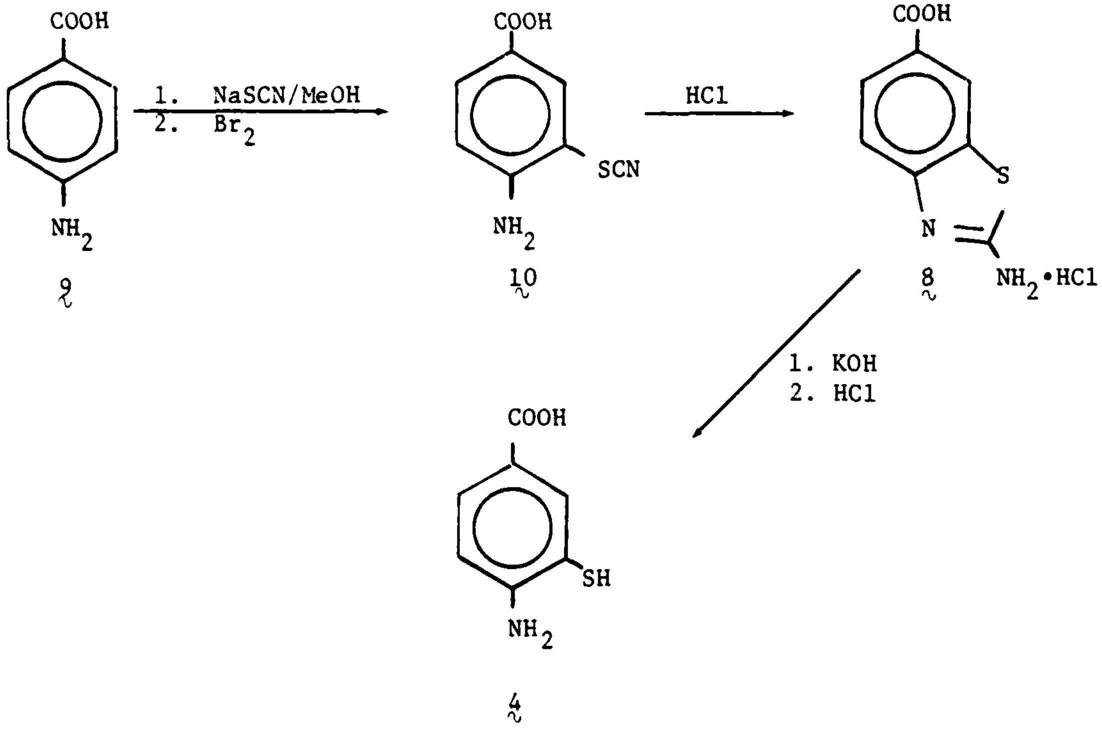
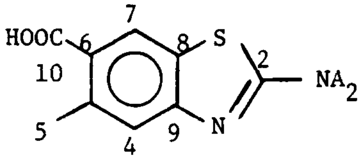


FIGURE 4 SYNTHESIS OF 4-AMINO-3-MERCAPTOBENZOIC ACID (4)

The thiocyanogenation of p-aminobenzoic acid (9) was conducted by the addition of bromine to a cold methanol solution of sodium thiocyanate and 9. Direct isolation of the resultant precipitate gave 4-amino-3-thiocyanobenzoic acid 10, as shown by mass spectral and infrared analysis. Isolation in the presence of either acetic of hydrochloric acid gave the salt of the 2-amino-6-carboxybenzothiazole (8) directly in a 48% to 65% yield. A comparison of the reported C-13 nmr spectrum[16] and the spectrum obtained from our sample is presented in Table 2. There is a fair one-to-one correspondence with the reported spectrum, but the large difference in the chemical shift for C-9 is not understood.

Table 2

C-13 nmr SPECTRUM OF 8 IN DMSO-d_6 IN PPM REFERENCED TO Me_4Si



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Assignment	Reported[16]	Found
2	169.1	170.3
4	116.8	114.1
5	127.0	126.7
6	122.8	124.8
7	122.3	
8	130.7	128.9
9	156.1	142.4
10	166.8	166.4

Isolation of **4** as the hydrochloride salt was effected by transferring the entire hydrolysis solution anaerobically through Teflon tubing into cold, 12-N hydrochloric acid. After washing the resultant precipitate with a minimum of cold water to remove the potassium chloride, the HCl salt of **4** could be recrystallized from a solution of stannous chloride (5% by wt) in dilute hydrochloric acid by adding concentrated hydrochloric acid. The fine, colorless needles gave an elemental analysis that agreed well with a one-to-one HCl salt. The free amine could be isolated by neutralizing a solution of the HCl salt of **4** with either potassium hydroxide or sodium bicarbonate, then extracting the yellow solution with ethyl acetate. The slightly yellow powder obtained by removing the ethyl acetate under reduced pressure could be recrystallized from various solvents, including dichloroethane, toluene, dichloromethane, chloroform, and water. Since the free amine appeared to be sensitive to heat, methylene chloride was found to afford the best balance of solute loading and minimal decomposition when the solvent was boiled. The free amine of **4** obtained in this way had a sharp melting point of 200°C.

Synthesis of 2,6-ABPBT: Polymerization of 4-Amino-3-Mercaptobenzoic Acid (**4**)

Polycondensations of **4** were conducted by heating solutions of varying concentrations of **4** in polyphosphoric acid (PPA) under argon. The various conditions used and the intrinsic viscosities obtained are presented in Table 3. The variations in synthesis parameters that were employed, for the polymerization of the HCl salt of **4**, such as heating schedule, monomer concentration, and the use of either commercial or freshly prepared PPA, appeared to have little influence on the resultant intrinsic viscosity. All these polymerizations resulted in polymers that gave intrinsic viscosities in the range of 3.0 to 3.8 dL/g.

One polymerization was conducted with the free amine of **4**. The monomer was obtained by recrystallizing from methylene chloride immediately before use. The intrinsic viscosity obtained in methanesulfonic acid for this polymer was 4.57 dL/g. Without knowing the relationship between intrinsic viscosity and molecular weight, i.e., the Mark-Houwink parameters, it is not known whether this increase of 20% to

Table 3

SYNTHESIS OF 2,6-ABPBT

Polymer No.	ABPBT yield, g (% of theor.)	ABPBT Conc. (wt%)	Dehydrohalogenation Time (h)	Dehydrohalogenation Temp. (°C)	Heating Schedule Time (h)	Heating Schedule Temp (°C)	[η], dL/g	Comments
3584-3	3.6 (92.5%)	8.9	24	40[a]	0.5	90	3.0	Solvent was 15.8 g 85% H_3PO_4 and 24.2 g P_2O_5 heated to 150°C for 24 h. HCl salt of monomer was used.
					0.5	110		
					0.5	130		
					24	150		
3584-7	1.8 (92%)	4.5	24	40[a]	48	150	3.5	Solvent was 50 g commercial grade 115% PPA. HCl salt of monomer was used.
			3	70	48	190		
3584-11	10.9 (99%)	4.6	14	40[a]	48	150[a]	3.6	Solvent was 230 g commercial PPA. HCl salt of monomer was used.
			4	70[a]	24	190[a]		
			20	70				
3584-15	43 (93%)	6.8	24	25[a]	1	85[a]	3.0	Solvent was 990 g commercial PPA. HCl salt of monomer was used.
			4	40[a]	1	100[a]		
			44	40[a]	1	115[a]		
			48	70	1	130[a]		
					72	150[a]		
3580-68	1.1 (97%)	2.94	-	-	0.25	25-100[a]	4.57	Free amine used.
					0.25	100-140[a]		
					0.5	140-160		
					18	110		
					10	180		
3380-63	0.78 (96%)	3.77	-	-	1	100[a]	3.50	HCl salt.
					2	140[a]		
					2	170[a]		
					8	200[a]		
3380-73	4.81 (92%)	10.0	18	50[a]	0.5	130	3.80	HCl salt.
			1	60	0.5	140		
			0.5	70	8	180		
			0.5	80	5	150		
			0.5	90	16	190		
			0.5	100	30	160		
			0.5	110	12	200		
					7	170		

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[a] Heating was conducted under argon flow at atmospheric pressure; all others were conducted under reduced pressure.

52% in viscosity over the polymers obtained from hydrochloride salt represents a significant increase in molecular weight. If 2,6-ABPBT is appreciably coillike ($a < 1$), this increase would represent a large increase in molecular weight and the method of choice would probably be the use of the free amine. However, we expect 2,6-ABPBT to be appreciably rodlike ($1<a<1.8$); thus the percentage of molecular weight increase would be less than the percentage of increase in viscosity. Nevertheless, we recommend that methods for the isolation and polymerization of the free amine be studied further.

Synthesis of 3-Amino-4-Mercaptobenzoic Acid (5)

The synthesis of monomer 5 was attempted by two different routes; see Figures 5 and 6. The method in Figure 5, because of its analogy with the successful syntheses of both monomers 1 and 4, was thought to be a reasonable route to monomer 5. However, direct thiocyanogenation of commercially available 3-aminobenzoic acid (11) was not attempted due to the possibility of substitution para to the amino group. Treatment with ammonium thiocyanate in dilute hydrochloric acid did afford the thiourea of benzoic acid 12. However, the cyclization to the carboxy benzothiazole did not proceed under a variety of conditions that usually afford the heterocyclic ring. The mechanism for this cyclization involves a polarization of the sulfur electrons by bromine, and then an electrophilic attack by sulfur on the ring. Owing to the position of the carboxyl group in the position meta to the thiourea group, the ring is deactivated toward electrophilic substitution. Unchanged thiourea was recovered in all attempts.

The route to 5, shown in Figure 6, did afford the desired monomer, but the product could not be sufficiently purified to give monomer suitable for preparation of high molecular weight polymer. Commercially available 3-nitro-4-chlorobenzoic acid (13), when treated with sodium sulfide, gives a mixture of 14 and 15, produced by chloro-group substitution and nitro-group reduction, respectively. Further reaction of this mixture with additional sodium sulfide reduces the nitro group of 14, but will not substitute the chloro-group of 15 because it is now deactivated

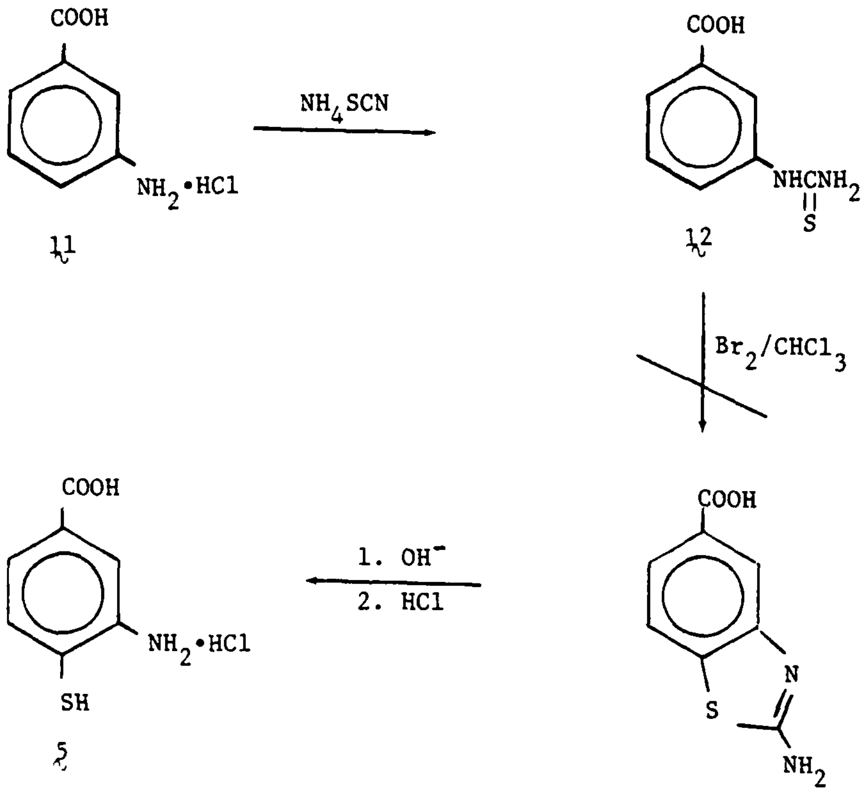

FIGURE 5 ATTEMPTED SYNTHESIS OF 3-AMINO-4-MERCAPTOBENZOIC ACID (5)

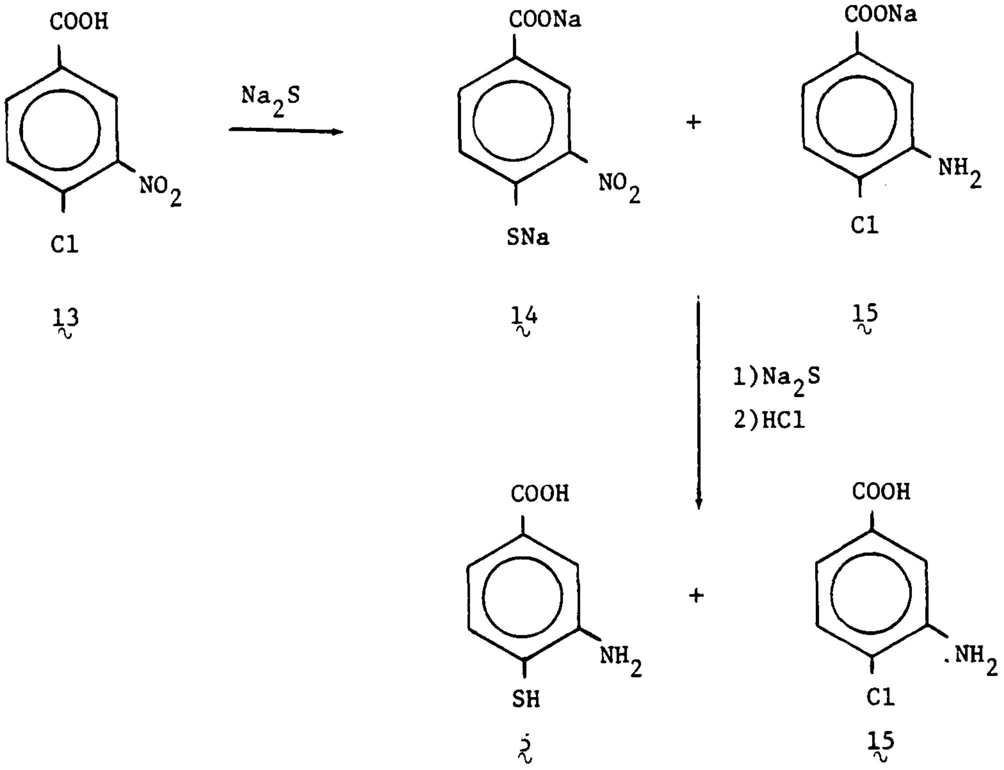

FIGURE 6 SYNTHESIS OF 3-AMINO-4-MERCAPTOBENZOIC ACID (5)

toward nucleophilic substitution by the ortho-amino group. Attempts to separate the mixture of 5 and 15 included various solid-liquid extractions, column chromatography (silica gel), and recrystallizations in aqueous and nonaqueous solvents. The solubility characteristics of both 5 and 15 are dominated by the carboxyl- and amino-groups and are therefore too similar to allow separation. The presence of 10% to 20% of 15 in the product by all methods employed was clearly evident in the mass spectrum of the mixture. Attempts to remove the impurity were monitored by observing the P+2 and P+4 peaks in the mass spectrum.

CONCLUSIONS AND RECOMMENDATIONS

The synthesis and polymerization 4-amino-3-mercaptobenzoic acid gave poly(2,6-benzothiazole) (2,6-ABPBT) with intrinsic viscosities in the range of 3.0 to 4.6 dL/g. We believe that additional material should now be prepared and blended as PPA solutions with PPA solutions of PBT. A study of the dilute solution properties of ABPBT to determine the degree of rodlike character of ABPBT would supply important missing information in the understanding of ABPBT-PBT blends.

The synthesis routes to 3-amino-4-mercaptobenzoic acid that were investigated did not provide monomer of sufficient purity to give high molecular weight polymer. Alternative routes to the monomer will have to be investigated.

EXPERIMENTAL PROCEDURES

4-Amino-3-Mercaptobenzoic Acid (4)

To a 12-L, 3-necked flask was attached a mechanical stirrer, thermometer, addition funnel, and argon source. 4-aminobenzoic acid (828 g, 6 mol), sodium thiocyanate (1030 g, 12.7 mol), and 6 L of anhydrous methanol were added. The system was flushed with argon and stirred until the solution was clear. The system was then cooled in a ice/HCl bath to -5°C with rapid stirring. Under an argon atmosphere and with the temperature maintained between -5° to -10°C, bromine (1016 g, 6.35 mol) was added over a 3.5-h period. The mixture was then stirred an additional 2 h, during which the temperature was not allowed to rise above 5°C.

The light yellow precipitate that formed was collected by filtration, stirred with an equal volume of water, and filtered again. The material was placed in 6 L of 1-N HCl, heated to boiling, filtered, and to the filtered solution was added 3 L of concentrated HCl. Upon cooling, colorless crystals precipitated from solution. The crystals were collected and recrystallized using the same procedure. The crystals were collected and dried to give 657 g (50% yield) of 2-amino-6-carboxybenzothiazole hydrochloride (8): mp 288°-299°C (dec.); IR, 3320 cm^{-1} (N-H), 3050 cm^{-1} (O-H), 1720 cm^{-1} (C=O), 1605 cm^{-1} (C=C), 1640 cm^{-1} (thiazole); mass spectrum M^{+} = 194; see text for C-13 nmr spectrum.

To a 1-L, 3-necked flask with mechanical stirrer and argon source was added 364 g of water. The water was boiled for 20 min with argon bubbled through it. The water was then cooled, and 436 g of 85% potassium hydroxide (6.6 mol) was added. Upon cooling and maintaining under an argon atmosphere, 100 g (0.43 mol) of 8 was added and the mixture was heated at the reflux temperature for 4 h. The precipitate that formed was removed by filtration in an argon atmosphere, and the clear yellow filtrate was slowly added to 575 mL of cold concentrated hydrochloric acid.

The precipitate that formed was collected and recrystallized twice from 1.5 L of water by adding concentrated hydrochloric acid until the product dissolved, adding 5 g of stannous chloride, and heating to 70°C. An additional liter of concentrated HCl was added and the solution allowed to cool. The yield was 29 g (33%, 17% overall) of 4: mp 192°-194°C; IR, 3380 (N-H), 3000 (O-H), 2520 (S-H), 1700 (C=O), 1605 cm^{-1} (C=C); mass spectrum, M^+ 169.

Anal. Calcd for $C_7H_8ClNO_2S$: C, 40.88; N, 6.81; H, 3.93 Found: C, 40.75; N, 6.75; H, 3.89.

3-Amino-4-Mercaptobenzoic Acid (5)

Method 1

In a 2-L, 3-necked flask was added 100 g (0.53 mol) of 4-chloro-3-nitrobenzoic acid and 400 mL deaerated water. A mechanical stirrer, addition funnel, and reflux condenser were attached. The system was flushed with argon. Under an argon atmosphere 300 g (1.25 mol) sodium sulfide nonanhydrate in 300 mL deaerated water was added. The mixture was heated at the reflux temperature for 7 h.

The solution was cooled, and glacial acetic acid was added dropwise until the pH was between 6.5 and 7.0. The solution was filtered to remove the insoluble material that had formed. Acetic acid was added to the clear orange filtrate until the pH reached 4.5. Upon standing, a yellow powder formed. The precipitate was collected, washed with 1 L of water, and collected again.

The yellow powder was placed in 1 L of 1-N HCl and heated to 70°C. Stannous chloride (5 g) was added to reduce any disulfide that might have formed, and the solution was filtered. Concentrated HCl was added to the pale yellow filtrate to adjust the solution to 6N HCl. Upon cooling, pale yellow crystals precipitated. The crystals were collected and placed in a solution of 1 L of water, 200 mL of concentrated HCl, and 5 g of stannous chloride. The solution was heated to 80°C and 20 g activated charcoal was added. The solution was stirred several minutes and filtered. To the clear filtrate was added 700 mL of concentrated HCl.

Colorless crystals precipitated. Yield: 59 g: mp 250°-259°C; IR, 3100 (N-H), 2800 (O-H), 2500 (S-H), 1705 (C=O), 1610 cm^{-1} (C=C); mass spectrum: m/e (intensity), 169 M^+ for 5 (100), 171 M^+ for 3-amino-4 chlorobenzoic acid (15) with Cl^{35} (15), 173 M^+ for 15 with Cl^{37} (5);

Anal. Calcd for $C_7H_8ClNO_2S$: C, 40.88; N, 6.81; H, 3.93.
Found: C, 40.51; N, 6.76; H, 3.79.

Method 2

To a 1-L, 3-necked flask was attached a mechanical stirrer and argon source. Ammonium thiocyanate (48 g, 0.63 mol) and 100 mL of water were added and stirred until clear.

In a 500-mL Erlenmeyer flask was added 41 g (0.30 mol) of 3-aminobenzoic acid, 250 mL of concentrated HCl (0.30 mol), and 2 g of activated charcoal. The solution was heated to 80°C, filtered, and poured immediately into the flask containing the ammonium thiocyanate. The flask was flushed with argon and the golden, clear solution heated at the reflux temperature for 24 h. The light tan powder that formed was collected and washed twice with 500 mL hot water and dried in a vacuum dessicator for 2 d to give 29 g of 1-(3-carboxyphenyl) thiourea: mp 255°-261°C; IR, 3160 (N-H), 3000 (O-H), 1690 (C=O), 1590 (C=C), 1550 (metasubstituted benzene), 1300 cm^{-1} (C=S); mass spectrum: M^+-OH, M^+ = 179.

Anal. Calcd for $C_8H_8N_2O_2S$: C, 48.96; N, 14.28; H, 4.12.
Found: C, 45.19; N, 9.97; H, 3.14.

To a 500-mL, 3-necked flask fitted with mechanical stirrer, reflux condenser, and argon source was added 24.5 grams (0.125 moles) of 1-(3-carboxyphenyl)-thiourea and 200 mL of reagent chloroform. Bromine (22 g, 0.137 mol) in 50 mL of chloroform was admitted through an addition funnel over a period of 6 h. The mixture was stirred at room temperature for 12 h, then heated at the reflux temperature for 24 h.

The reaction mixture was filtered and the solid dried under reduced pressure for 4 h. The solid was then washed with 200 mL of 10% sodium bisulfite solution. The solid was collected by filtration and dissolved in 100 mL of 5% sodium bicarbonate. Acidification with concentrated HCl produced 19.3 g of material. Infrared spectrum of the material proved it to be the starting material, 1-(3-carboxyphenyl) thiourea.

Polymerization of 4-Amino-3-mercaptobenzoic Acid

Unless otherwise specified, all polymerizations were conducted in commercially obtained (FMC) 115% polyphosphoric acid (PPA). Before each polymerization the PPA was deaerated by heating to 150°C, applying reduced pressure for 1 h, then flowing argon over the acid for 30 min. The process was repeated three times; then reduced pressure was applied for an additional 20 h. Intrinsic viscosity measurements were obtained using methansulfonic/acid as a solvent and extrapolating inherent and reduced viscosities to zero concentration.

To a 100 mL, 3-necked flask fitted with a mechanical stirrer and argon source was added 15.8 g of 85% phosphoric acid. Under an argon atmosphere, 24.2 g of phosphorus pentoxide was slowly added while the system was stirred rapidly in an ice bath. After heating under argon to 150°C for 6 h and then cooling to 25°C, 6.0 g 4-amino-3-mercaptobenzoic acid hydrochloride was added. The reaction mixture was heated to 50°C for 24 h to effect dehydrochlorination. Reduced pressure was then applied and the mixture heated to 70°C to complete the dehydrochlorination.

The reaction mixture was heated to 150°C over a 2-h period during which time the color changed from a light gold to a dark red. The mixture was maintained at 150°C for 24 h. It was then cooled to $\sim$90°C and poured into 3 L of cold water to remove the polyphosphoric acid.

The polymer was extracted for 2 d with methanol in a Soxhlet extractor. The substance was then boiled for 15 minutes in water, frozen, freeze-dried, and then dried under reduced pressure at room temperature for 2 d to give 3.6 g (92.5%) of ABPBT. $[\eta] = 3.0$ dL/g. See Table 2 for other polymerization conditions.

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