On the Crystallinity of Poly(alkylbenzimidazole) Salts

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Synopsis

Poly(alkyldibenzimidazole) and poly(alkylbisbenzimidazole) having five, six, seven, and eight methylene groups in each repeat unit were synthesized. Salts of these polymers with strong acids, whose pK is 4.00 or less, were prepared. Weaker acids do not form salts with the poly(alkylbenzimidazole)s. It was found that polymers having an even number of methylene groups per repeat unit tend to form crystalline salts while those polymers having an odd number of methylene groups form only amorphous salts. From among the crystalline salts, those containing poly(bisbenzimidazole)s are more crystalline than their analogous poly(dibenzimidazole)s.

INTRODUCTION

Several years ago it was reported[1-3] that the fully amorphous poly(2,2'-octamethylene-5,5'-dibenzimidazole) (I-8) and poly(2,2'-octamethylenebisbenzimidazole) (II-8) cocrystallize with solvents such as formic or trifluoroacetic acid, to yield stoichiometrically solvated polyalkylbenzimidazole crystals.[4] Aharoni[4] and Aharoni and Signorelli[5] indicated that only rather strong acids interact with the poly(alkylbenzimidazole)s and that in the crystalline state the nature of this interaction is the formation of a salt involving the benzimidazolium ion and the conjugate base of the acid. In this brief communication we would like to report the structural features of the poly(alkylbenzimidazole)s which are apparently necessary for the formation of crystalline salts with acids.
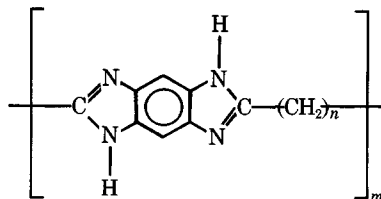
EXPERIMENTAL

For the purpose of this study four analogs each of the poly(dibenzimidazole) family were prepared, by the procedure of Iwakura et al.,[3,4,6] and evaluated,
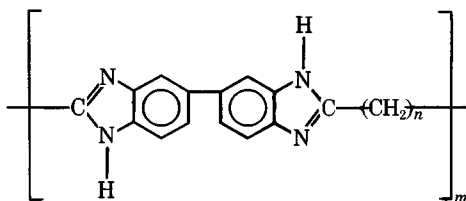
I

and the poly(bisbenzimidazole) family

II

with $n = 5, 6, 7$ and 8. For brevity they will be denoted by the Roman numeral associated with the respective family, followed by an Arabic number specifying the number of —CH$_2$— groups per repeat unit.

Salts were prepared by dissolving the polymer and the desired acid in a common solvent, usually formic acid but occasionally dimethylsulfoxide, and then evaporating the solvent to dryness, followed by drying under vacuum at temperatures of 110–130°C, to reach constant weight.

Infrared scans were obtained from KBr pellets of the pulverized samples in a Perkin-Elmer Model 283B Spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns of the polymers and their salts were obtained from pulverized samples by means of a Norelco diffractometer operating in parafocus geometry and using monochromatized copper K$_\alpha$ radiation. All patterns of the polymers and their salts were obtained at the same machine setting from samples of the same thickness held in the same sample holder. Percent crystallinity was estimated by subtracting from the recorded intensity a background, essentially the same for all polymer-containing samples; then the area above the resulting baseline was divided into an amorphous halo and a multiplicity of crystalline peaks, the relative amounts of which were estimated by cutting and weighing the respective parts of the WAXD pattern charts. This procedure is essentially that of Hermans and Weidinger as described by Alexander.[7]

Dilute solution viscosities were measured in Cannon-Ubbelohde internal dilution glass viscometers held in baths thermostated at 25°C (room temperature) and 85°C.

RESULTS AND DISCUSSION

All synthesized polymers were found to be soluble in organic and inorganic acids whose pK in aqueous solutions were smaller than 4.00. Thus, the polymers were soluble in formic acid (pK 3.75), phosphoric acid (first pK 2.12) and the rather strong, fluorinated organic acids, and insoluble in organic acids such as acetic (pK 4.75), glutaric (first pK 4.31), and acrylic (pK 4.25).

Some results of intrinsic viscosity measurements at 85°C are presented in Table I. For each polymer, the values in the different solvents were obtained from the same sample. The intrinsic viscosity values in phosphoric acid and in 0.1M NaCl in formic acid, were much smaller than those obtained in formic acid (96–97%). This, and the occasional curvature in plots of reduced viscosity,

TABLE I
Typical Intrinsic Viscosities of Poly(alkylbenzimidazole)s[a]

Polymer	Formic acid	Phosphoric acid	Formic acid/0.1M NaCl	Polymer	Formic acid	Phosphoric acid	Formic acid/0.1M NaCl.
I-5	0.66	0.29	—	II-5	1.64	—	—
I-6	3.31	1.38	0.94	II-6	1.44	—	—
I-7	1.60	0.70	0.83	II-7	5.34	1.12	—
I-8	2.18	0.60	—	II-8	3.06	0.70	1.34

[a] Viscosities in the three specified solvent systems were obtained at 85°C. Room temperature measurements in formic acid yielded slightly higher viscosities. Several additional batches of polymers I-6, I-7, I-8, II-7, and II-8 yielded viscosities in HCOOH close to the respective values in the table. All viscosities are reported in units of dL/g.

indicates that a polyelectrolyte effect is present in dilute solutions of poly(alkylbenzimidazole)s in formic acid. A similar observation was reported recently by Kojima[8] concerning aromatic polybenzimidazole.

It is of interest to note here that solutions of group I in H_3PO_4 gelled upon cooling from 85°C to room temperature. No gellation occurred with comparable solutions, of group II. The reason for the different behavior of the two groups is not known yet.

No liquid crystallinity, thermotropic or lyotropic, of any of the poly(alkylbenzimidazole)s and their salts was observed in this study.

The salt preparation was followed by infrared spectroscopy, and it was found that, when the ratio of 1:1 acid residues to imidazole rings was used in the feed, one found, with no exception, absorption bands belonging to the ionized acid together with some belonging to the free acid. Visual estimates indicate that in all these cases the amount of ionized acid in the sample far exceeded the amount of free acid present. When the ratio of acid groups to imidazole rings in the feed was reduced to 1:2, then no free acid was observed by infrared in the product. The infrared bands by which the ratio of ionized acid to free acid was gauged, were the free acid bands at about 1700 cm⁻¹ for formic acid, within the interval of 1750 cm⁻¹ to 1780 cm⁻¹ for perfluorosuccinic acid, perfluoroglutaric acid, and perfluoroadipic acid, and at about 1720 cm⁻¹ for phosphoric acid. The band estimated for the respective ionized acid was the symmetric stretch band of the —COO⁻ group at 1590 cm⁻¹ for formate, and 1650–1670 cm⁻¹ for the three perfluorodicarboxylates. The phosphate ion did not exhibit a unique infrared band, so that its presence and amount relative to the free acid, were gauged from
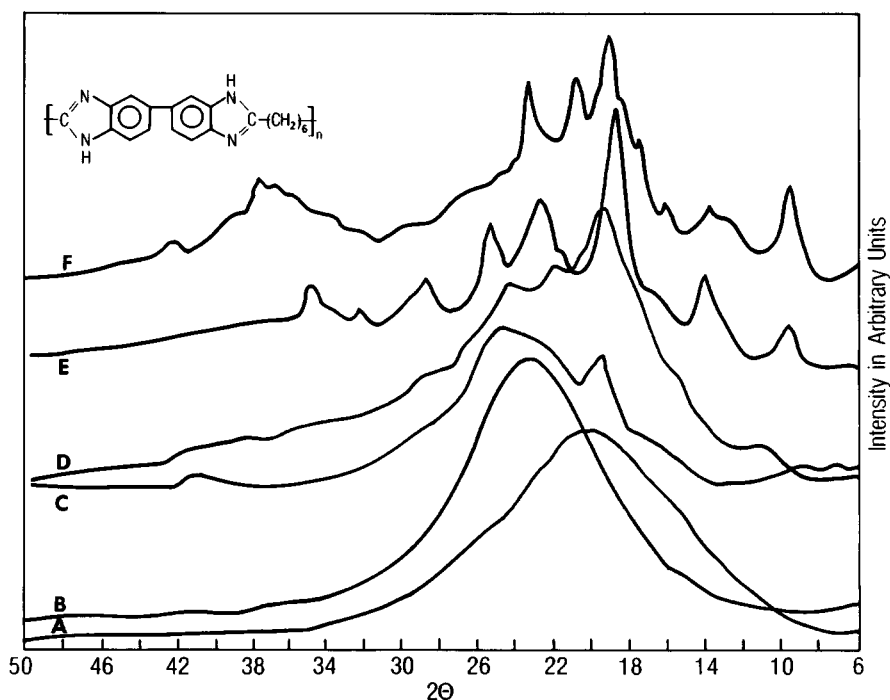

Fig. 1. WAXD patterns of polymer I-6 and its salts: (A) pure polymer; (B) formate salt; (C) perfluorosuccinate salt; (D) perfluoroglutarate salt; (E) perfluoroadipate salt; (F) phosphate salt.
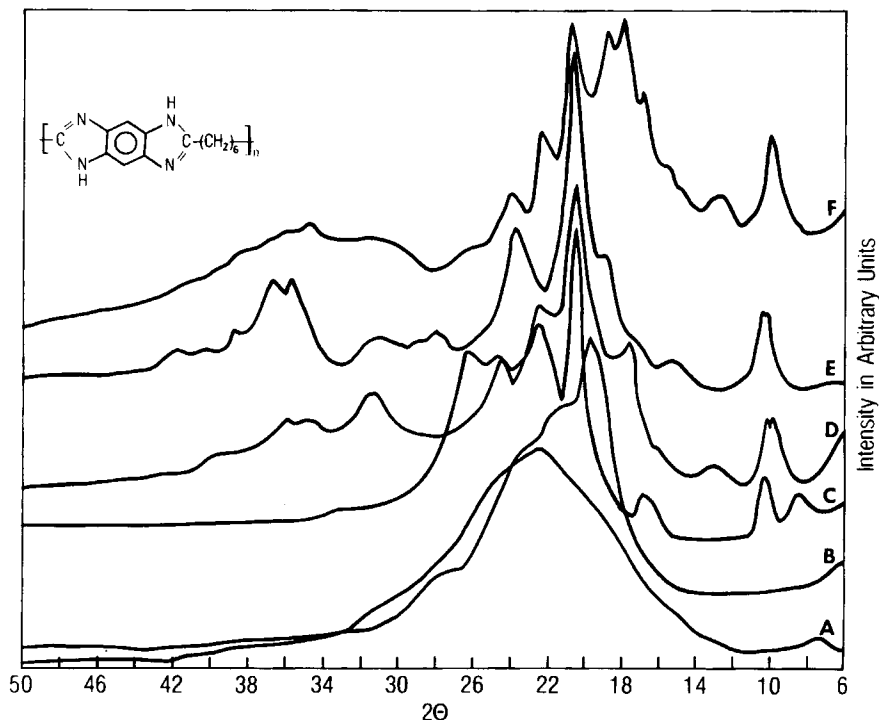
Fig. 2. WAXD patterns of polymer II-6 and its salts: (A) pure polymer; (B) formate salt; (C) perfluorosuccinate salt; (D) perfluoroglutarate salt; (E) perfluoroadipate salt; (F) phosphate salt.

the decrease in intensity of the band at about 1720 cm^{-1}. These observations were found to hold for salts originating from polymer families I and II and polymers having both even and odd number of methylenes per repeat unit.

WAXD patterns of the solid perfluorodiacids were obtained and proved to be very rich, especially in the high angle region. These patterns usually contained over 30 reflections, of which a substantial number was very intense and sharp. In no instance could we find even traces of the crystalline perfluorodiacids in the polymer/acid samples that were tested. All polymer containing samples were scanned twice, once as prepared and dried, and the other after a 4-h additional anneal at 110°C. There were hardly any changes in the WAXD patterns of each sample, and even those amounted only to a minute sharpening of existing reflections.

The WAXD results indicate that all the pure poly(alkylbenzimidazole)s, with or without annealing, were fully amorphous. Their salts were divided into two clearly distinguishable groups: The salts of polymers with even number of —CH$_2$— units per repeat were crystalline, while the salts of polymers having odd number of —CH$_2$— groups were amorphous. Figure 1, the WAXD patterns of the pure and salts of polymer I-6, and Figure 2, the corresponding patterns of polymer II-6, exemplify the results obtained from the even numbered, I-6, I-8, II-6, and II-8 polymers. The amorphous patterns, curves A in Figures 1 and 2, are typical of all the WAXD patterns obtained from salts of I-5, I-7, II-5, and II-7, with at least the following three acids: formic, perfluoroglutaric, and phosphoric.

TABLE II
Wide-Angle X-Ray Diffraction Data For Polymers I-6 and II-6 and Their Corresponding Salts[a]

Polymer I-6

Pure			Formic acid			Perfluoro-succinic acid			Perfluoro-glutaric acid			Perfluoro-adipic acid			Phosphoric acid		
2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)
20.0	BVVS (amorph)	0.444	23.2	BVVS (amorph)	0.383	11.0	VW	0.804	9.75	S	0.905	9.75	VS	0.905	9.5	VW	0.930
						19.5	S	0.455	14.0	S	0.633	12.8	W	0.692	19.6	S	0.453
						22.0	W	0.404	18.8	VS	0.472	13.9	M	0.637	24.6	BVS (amorph)	0.362
						24.4	M	0.365	22.8	S	0.390	16.2	W	0.547			
						29.0	VW	0.308	25.4	S	0.351	17.6	W	0.504			
									28.7	S	0.311	19.3	VS	0.460			
									32.0	W	0.280	21.0	S	0.423			
									34.6	M	0.259	23.2	S	0.383			
									38.2	W	0.236	36.3	W	0.247			
												37.2	W	0.242			
												38.4	W	0.234			
												41.6	W	0.217			

Polymer II-6

Pure			Formic acid			Perfluoro-succinic acid			Perfluoro-glutaric acid			Perfluoro-adipic acid			Phosphoric acid		
2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)	2θ	I	d (nm)
7.3	VVW	1.21	19.7	VS	0.450	9.8	S	0.903	10.1	S	0.876	9.7	S	0.911	8.0	W	1.105
22.0	BVVS (amorph)	0.404	21.5	W	0.413	12.8	W	0.692	14.7	VW	0.602	12.4	W	0.714	10.0	M	0.884
			23.8	W	0.374	17.5	M	0.507	18.6	W	0.477	16.5	VW	0.537	16.5	W	0.537
			28.2	VVW	0.316	20.3	VVS	0.437	20.3	VVS	0.437	17.5	S	0.507	20.3	VVS	0.437
						22.0	M	0.404	23.1	S	0.385	18.4	M	0.482	22.4	S	0.397
						24.1	M	0.369	27.4	VW	0.325	20.3	VS	0.437	26.0	S	0.343
						31.0	S	0.288	30.7	W	0.291	22.0	M	0.404	33.4	VVW	0.268
						34.2	W	0.262	35.2	M	0.254	23.5	M	0.379			
						35.6	M	0.252	36.0	M	0.249	25.5	VVW	0.349			
						38.6	VW	0.233	41.2	W	0.219	35.3	BW	0.254			

[a] I = estimated peak intensity; VVW = very very weak; VW = very weak; W = weak; M = medium; S = strong; VS = very strong; VVS = very very strong; B = broad, associated with an amorphous (amorph) halo. All d-spacings are given in nm.

In Table II are given the numerical values of the angle 2θ and the corresponding d-spacings of the X-ray reflections obtained from polymers I-6, II-6, and their salts. The intensities of the reflections were estimated visually and are given merely for completeness.

A one-to-one comparison of crystallinity level was performed between each pair of polymer salts sharing the same acid and having the same number of —CH_2— groups per repeat unit. Thus, for example, the perfluoroglutarate salts of I-6 and II-6 were compared, or the phosphates of I-8 and II-8, etc. In general, the percent crystallinity increased within each family of polymer salts in the same order in which they appear in Figures 1 and 2, that is from curve B to curve F in each. Numerically, the % crystallinity increased from 10 or less at the lowest up to about 60–65% for the phosphate salts. Furthermore, when salts containing the same acid and having the same number of —CH_2— groups, of polymers belonging to families I and II, were compared, the ones of family II were more crystalline than those of family I. The change of crystallinity was usually on the order of 10–20% and not larger, but consistently appeared for all polyamides having an even number of —CH_2— groups in each repeat unit.

It is our belief that the formation of crystalline salts from the amorphous parent poly(alkylbenzimidazole)s having an even number of —CH_2— groups in their repeat units is due to the combination of the following: (1) the ability of each acid residue to be associated, through ionic and hydrogen bonds,[4] with two imidazolium rings; (2) the electrostatic repulsion of the charged imidazolium rings, extending the —CH_2— sequence to its fullest[4,9]; and (3) the ability of consecutive benzimidazole residues in polymers with even number of —CH_2— groups to remain linear or colinear with the benzimidazole residues adjacently placed on the chain. This ability does not exist in the case of poly(alkylbenzimidazole)s having an odd number of —CH_2— groups in their repeat units. The inability to maintain linearity is, apparently, the cause for the odd polymers retaining amorphicity in their salt form.

The formation of unique crystalline salts or adducts, one component of which is a polymer, is not new in itself. In addition to the poly(alkylbenzimidazole)s reported here and in Refs. 1–5, there appeared, for instance, in the recent literature the case of novel stoichiometric crystalline adducts of polyamides and perfluorodiacids.[10] In all of the above, the number of strong (H— or ionic) bonds between adjacent polymer chains is maintained or increased in the salt or adduct. This is opposite to the well-known nylon/LiCl adducts, where the bonds between the polyamide chains are disrupted, with the resulting destruction of polymer crystallinity.[11,12]

CONCLUSIONS

The results indicate that crystalline salts are formed by poly(alkylbenimidazole)s in which the flexible chain contains an even number of methylene groups. Polymers containing odd number of —CH_2— groups per repeat unit, form amorphous salts only. From among the crystalline salts, those originating from poly(bisbenzimidazole)s possess higher percent crystallinity than the analogs originating from poly(dibenzimidazole)s. The salts are formed only by strong acids whose pK is 4.00 or less.

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