introduced to the volumetric flask to form exactly 5 ml. After 4 hr, the solution was clear and 1 ml was put into a polarimetric cell. The solution was kept in a dark, cool (15–20°) place and optical rotations were determined at intervals thereafter for 96 hr. Periodate oxidation of stereoregular mannan was carried out under the same conditions as that of the galactan. The final observed optical rotation (constant from 24 to 96 hr) was α_D (obsd) +0.410 and the specific rotation (based on original galactan corrected to 44.44% C) was $[\alpha]^{20}{}_D$ +133°.

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Synthesis and Properties of Azoaromatic Polymers

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ABSTRACT: Aromatic polyimides containing an azo link show reversible photo and thermal contractile behavior. The effect appears to be associated with *trans* $\rightleftarrows$ *cis* isomerization in the noncrystalline regions but the rate of the contraction or expansion is controlled by a process other than the isomerization.

Polymers containing the azoaromatic linkage were studied earlier.[1] The main objective at that time was the preparation of polymeric azo dyes that might have advantages over natural pigments and ordinary dyes. Azoaromatic polyesters were prepared[2] by condensation of 4,4′-dicarboxyazobenzene with phenols. The preparation of aromatic azopolymers by oxidation of diamines has been reported.[3] This work was improved and expanded by Bach.[4] The preparation of polyimides from azophthalic dianhydride and aromatic and aliphatic diamines was recently disclosed.[5]

Our interest in azoaromatic polymers came from the belief that such polymers could show good thermal stability, uv absorption, and *cis–trans* isomerism.

Experimental Section

Monomers. The azo monomers were prepared by standard paths.[6] Purification of monomers was by multiple recrystallization and vacuum sublimation to constant properties. Polymerization to give polymers of good inherent viscosity was the primary test of purity.

Solvent. Dimethylacetamide was purified by distillation from calcium hydride onto Linde Molecular Sieve 5A (fired at 500°) under dry nitrogen. It was stored over the desiccant at least 24 hr prior to use.

Polymerizations. Typical examples of the polymerization methods used are as follows.

Solution Polymerization of 4,4′-Diaminoazobenzene and Pyromellitic Dianhydride. 4,4′-Diaminoazobenzene (2.245 g) was dissolved in 50 ml of anhydrous dimethylacetamide and pyromellitic dianhydride (2.30 g) was added in portions. When the polymerization was complete the polyamic acid solution was cast on a glass plate with a 25-mil doctor knife and converted to polyimide by immersion for 1 hr in a benzene–acetic anhydride–pyridine bath. The red film was stripped from the plate, clamped on a frame, and dried in air 30 min at 180°, then 30 min at 300°.

Results and Discussion

With monomers of adequate purity, the polymerizations proceeded well. The properties of two polymers are shown in Table I.

The ultraviolet spectra of thin films (~500 Å) on quartz plates show absorption characteristic of model azoaromatics. Figure 1 gives such a spectrum of 4,4′-diphenylazopyromellitimide polymer (PN_2P-PI) with the spectrum of the parent diamine in ethanol for comparison. The coalesced doublet of the polymer was resolved on the Du Pont curve analyzer to give maxima at 3440 and 3040 Å ($\Delta\nu$ = 2300 cm^{-1}). In the parent diamine, the short wavelength absorption dominates while in the polymer the longer wavelength absorption is dominant. We observe that the areas under the two curves in the polymer change from a ratio of 10:1 at room temperature to 8:1 at 200°.

The polymer is semicrystalline (Figure 2) and has a repeat unit of 18.3 Å which is that calculated for the imide unit in the *trans* configuration. This restricts the *cis* configuration to the disordered or amorphous regions.

In the process of preparing films for measurement, an unusual phenomenon was seen. Normally when one dries or heat treats a film it will expand in the heating stage (some shrinkage can occur) and contract on cooling to give taut films. With many of these polymers it was observed that the films became taut when heated and slackened on cooling.

Two kinds of experiments were performed—at constant length and constant stress. In the constant-length experiments, a strain gauge measured the stress imposed on a film sample when exposed to heat or light. Figure 3 shows the curve obtained on exposure of a PN_2 P-PI film to an infrared lamp. Temperatures measured at the film surface were ~200°. A curve for

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Table I
Physical Properties of Polymers

Monomers	η_{inh}[c]	Mod, Kpsi	Tens. str, Kpsi	Elong, %	Diel. const, 100 Hz	Vol res, ohm cm	Diss factor, 100 Hz	Remarks
				25°				
PN_2P–PI[a]	3.05	1478.0	24.4	3.2	3.67	1.3×10^{17}	0.0023	Red-tough
PN_2P–DAPI[b]	1.49	936.0	14.0	1.8	3.49	4.3×10^{14}	0.0060	Red-tough
				200°				
PN_2P–PI	3.05	591.0	11.3	4.9	3.18	1.3×10^{14}	0.0016	Red-tough
PN_2P–DAPI	1.49	501.0	10.1	2.9	>7.0	6.7×10^{10}	>0.65	Red-tough

[a] PN_2P = 4,4′-diaminoazobenzene, PI = polypyromellitimide. [b] DAPI = azodiphthalimide. [c] Polyamic acid in DMAc.

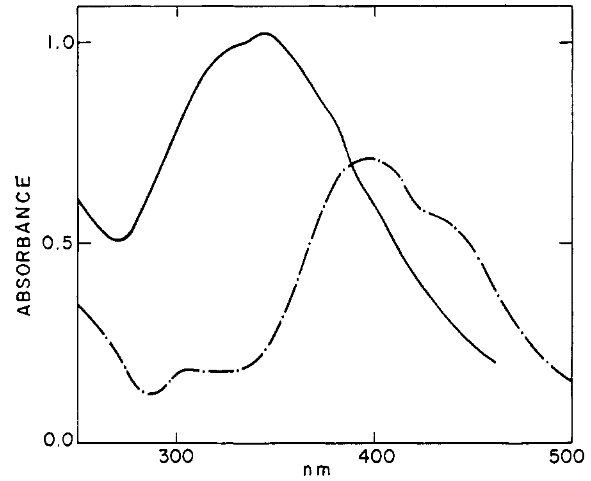

Figure 1. Comparison of absorbance of 4,4′-diaminobenzene (2.5×10^{-5} *M* in ethanol) (— · —) and the corresponding polypyromellitimide (~500 Å on quartz) (———).

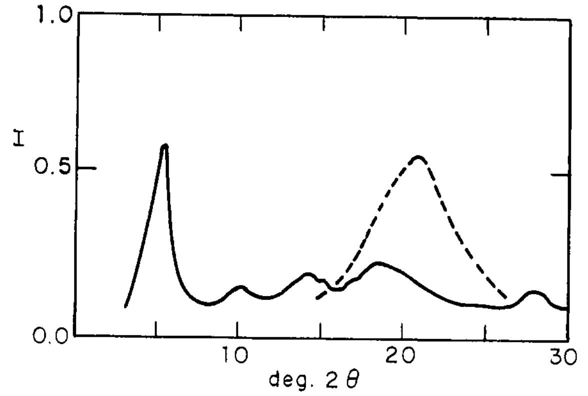

Figure 2. X-Ray goniometer trace (Cu Kα) of poly(4,4′-diaminoazobenzenepyromellitimide) film: ———, scan perpendicular to plane of film, 2000 cps scale; - - - -, scan parallel to plane of film, 5000 cps scale.

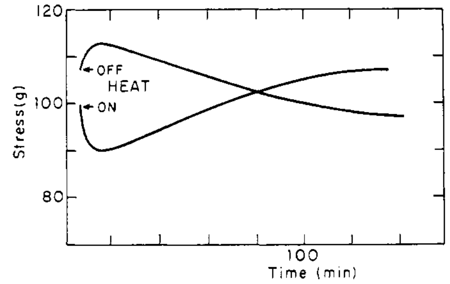

Figure 3. Stress response at constant length on heating and cooling of film of poly(4,4′-diaminoazobenzenepyromellitimide).

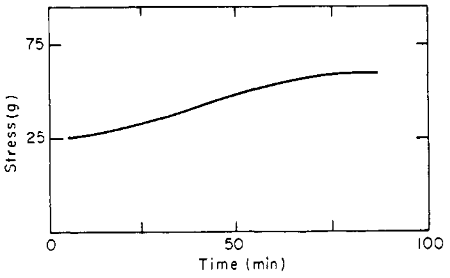

Figure 4. Stress response at constant length on exposure to light of poly(4,4′-diaminoazobenzenepyromellitimide) film.

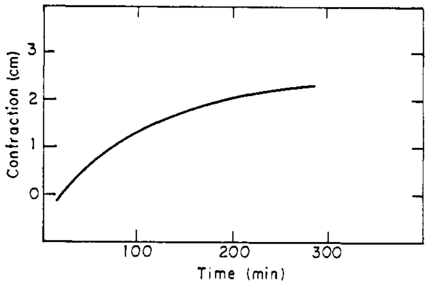

Figure 5. Length change at constant stress at 200° for poly(4,4′-diaminoazobenzenepyromellitimide) film; 1 cm = 0.23% deformation.

Kapton polyimide film is also shown as an example of normal thermal expansion response. When the azopolymer is heated, it begins to show normal expansion effects before the slower contractile process takes over. Reverse effects are seen on turning the heat source off.

Figure 4 shows a curve for irradiation of the PN_2-P–PI film with an aqueous copper sulfate filtered low power mercury lamp. The effect is small but real.

Measurements at constant stress are shown in Figure 5. The geometry of the system was such that a deflection of 1 cm corresponds to a deformation of 0.23% in the sample. The deformation is of the order of 0.6% on cycling from room temperature to ~200°. The difference in the length of a *cis* and *trans* repeat unit is ~6 Å out of 18.3 Å. The film sample used had strong planar orientation with little preferred orientation in the plane. Total conversion of *trans* to *cis* should result in contraction of such a sheet by $(\sim 1/3)(1/\sqrt{2})$(% *trans*). If related to isomerism, the ultraviolet absorption change would correspond to ~0.5%. The agreement with experiment may be adventitious but is of the right order of magnitude.

The assumption that contraction on heating is associated with *trans* ⟶ *cis* conversion seems reasonable and the occurrence of a photoeffect as well as a thermal effect is supportive. There are, however, problems. Half-lives for the contractile process may be obtained from the constant-strain or constant-stress curves. For pyromellitimide the value of $t_{1/2} \sim 38$ min at temperatures near 200°. On returning to room temperature a relaxation $t_{1/2} \sim 40$ min is observed. The values are the same at room temperature and 200° indicating little or no activation energy.

Studies of solution isomerization of simple azo compounds[7,8] show the process to be activated ($\Delta H^{\ddagger} \sim 22$ kcal) with $t_{1/2} \sim 50$ min for comparable compounds slightly above room temperature. π acid and base catalysis was reported.

On comparison with our results, it seems that the rates of isomerization are not controlling the rates of dilation or contraction. Catalysis by adjacent π acids or bases is an attractive possibility but cannot be asserted on present data. It seems probable that the process is controlled by viscoelastic characteristics of the polymer which have small activation energies but these processes cannot be specified as of now.

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Kinetics and Mechanism of the Polymerization of Styrene by Triphenylmethyl Chloride and Mercuric Chloride in 1,2-Dichloroethane, and the Initiation Rate Constant

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ABSTRACT: The polymerization of styrene initiated by triphenylmethyl chloride and mercuric chloride in 1,2-dichloroethane was investigated. The equilibrium involved between triphenylmethyl chloride and mercuric chloride in 1,2-dichloroethane is $Ph_3CCl + HgCl_2 \rightleftharpoons Ph_3C^+HgCl_3^-$. The ion pair $Ph_3C^+HgCl_3^-$ does not dissociate into free ions and mercuric chloride does not help to solvate the ion pair. The visible spectrum of the polymerizing system shows the presence of trityl cations. The rate of polymerization is first order in triphenylmethyl chloride and mercuric chloride, and second order in styrene. The rate of consumption of triphenylmethyl chloride is first order in triphenylmethyl chloride, mercuric chloride, and styrene. A mechanism consistent with the kinetic data has been suggested and the rate of consumption of triphenylmethyl chloride is directly related to the rate of initiation.

The cationic polymerization of styrene has been extensively studied. However, due to the use of complex and highly reactive catalyst–cocatalyst systems only a few generalizations can be made. The use of triphenylmethyl chloride and mercuric chloride to form the well-characterized stable trityl cation *in situ* seemed advantageous. Trityl salts have been used for the polymerization of styrene.[1,2]

The evaluation by kinetics of individual rate constants in cationic polymerization of styrene has only been achieved in a few cases. The propagation, termination, and transfer rate constants have been determined for the nonstationary polymerization of styrene by sulfuric acid.[3,4] In our preliminary communication[5] we reported a spectrophotometric method of measuring the initiation rate constant and this method has been subsequently used by other investigators.[6]

Experimental Section

Purification of Styrene. Styrene (M) was shaken with 10% potassium hydroxide solution to remove *t*-butylcatechol and then washed with distilled water. The styrene was partially dried over anhydrous calcium chloride, allowed to stand over baked barium oxide, and then fractionally distilled under reduced pressure. It was degassed by freezing and pumping several times on a high vacuum line and the middle fractions were used immediately.

Triphenylmethyl chloride (Ph_3CCl) was prepared by refluxing triphenylcarbinol and acetyl chloride in petroleum ether mixture for 1 hr.[7] On cooling, Ph_3CCl crystals were deposited and these were recrystallized from solvent composed of 10% acetyl chloride in petroleum ether. Care was taken to remove all traces of acetyl chloride. The crystals were dried in a vacuum desiccator. Fresh samples of Ph_3CCl were prepared as required.

AR mercuric chloride ($HgCl_2$) was used without further purification. **1,2-Dichloroethane** was partially dried over calcium chloride, refluxed over phosphorus pentoxide, and fractionally distilled through a 35-cm Vigreux column. **Acetyl chloride** was fractionally distilled using a 35-cm Vigreux column.

Procedure. Drybox technique was used for all experiments. The drybox was flushed with dry nitrogen for about 2 hr before use and a brisk flow of nitrogen was maintained during actual manipulations. We feel that this procedure is satisfactory for this system, and it has been shown that water concentration in the range of $1–3 \times 10^{-3}$ M has no effect on the rate of reaction of styrene with Ph_3CSnCl_5.[6]

The progress of polymerization was followed by measuring [styrene] with time. This was achieved by measuring the

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