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AT HIGH TEMPERATURES
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SYNTHESIS OF POLYMERS WITH HIGH RESIDUES AT HIGH TEMPERATURES

I. Crosslinked Polyimides.

The entire experimental effort under this grant is being expended solely on the synthesis of crosslinked polyimides of varying crosslink densities. The polymers selected for synthesis and evaluation are copolymers derived from m-phenylenediamine (MPDA), pyromellitic dianhydride (PMDA) and mellitic trianhydride (MTA). Polymers varying in crosslink density from $\rho = 0$ for the MPDA-PMDA system to $\rho = 0.5$ for the MPDA-MTA system are possible by varying the ratio of PMA to MTA. In all systems the ratio of the MPDA to the anhydrides was maintained at 1:1 for MPDA:PMDA and 3:2 for MPDA:MTA.

The polymerizations were performed as solutions in N,N-dimethyl acetamide. The concentration of DMAC used was established at a value which yielded clear solutions of the polymers, which were also free of crosslinked gel. After a series of preliminary experiments a general procedure was established for the syntheses. The general procedure consisted in dissolving the MPDA in a portion of the total amount of DMAC used, in a three-necked, ground-glass flask equipped with a mechanical stirrer, nitrogen inlet and thermometer and cooling bath.

The remainder of the DMAC was used to dissolve the MTA or mixture of MTA-PMDA by heating the mixture to 80°C under a nitrogen atmosphere. If allowed to cool to about 70°C, the anhydrides precipitated from the DMAC; accordingly, the solutions of anhydrides were used at 70-80°C and added rapidly and directly to the vigorously stirred solution of MPDA cooled to $\sim 0^\circ\text{C}$ by an ice-water bath. The cooling bath was removed when the temperature of the reaction mixture was reached in the 25-30°C range; then the cooling bath was removed and the solution allowed to react at room temperature for one hour. Then

one-half of the solution was used to prepare films by casting on glass plates and drying the films at 125-130°C for ~ 24 hours in an air-circulating oven. The polymer was precipitated from the remaining half of the viscous solution by pouring it into a large volume of benzene while being mechanically stirred. The precipitated polymer was washed three times with benzene, isolated by filtration and dried at 25°C at 0.5 mm Hg pressure for 16 hours.

The yields of the polymers was calculated on the basis of the hemi-amic acid form. The polymers precipitated from their DMAC solutions by benzene and dried at 25°C contained high amounts of complexed DMAC, thereby giving apparent yield in substantial excess of 100% of theory. To obtain polyhemi-amic acid yield data, the amount of retained DMAC cannot be determined by drying at high temperatures since cyclization also occurs liberating water which then gives values of lower than theoretical yields. Prolonged extraction by ether in a Soxhlet apparatus followed by drying at 25-30°C at 0.1-0.5 mm Hg is effective in removing the DMAC, in which case the yields correspond to the theoretical yield. Yields were also calculated from the films of the polymers cast and heat-treated for 24 hours at 125-130°C. In most cases, the experimentally determined yield, based on the hemi-amic structure, approached the theoretical value. However, the yield was lower than theoretical for the hemi-amic acid structure for the polymer (DA-55-133) of $\rho = 0$ from the 1:1 ratio of MPDA:PMDA and for the polymer (DA-55-112) of $\rho = 0.1$ from 1.1:0.8:0.2 ratio of MPDA:PMDA:MTA. These lower hemi-amic acid values appear to be due to imide formation by cyclization as established by determination of the acid number of these polymers. Infrared spectra of the precipitated polymers and of the films were recorded as KBr discs.

The acid equivalents of the polymers were performed with samples which had been ground in a vibrating capsule for 5 minutes; the size corresponding

to at least 50 particles per milligram. The acid equivalents of the samples were determined by adding approximately 35 mg of the finely-ground sample to a large excess ($\sim$ 35 ml.) of 0.0115 N NaOH and the mixture allowed to stir for 10 minutes; then the mixture back-titrated with 0.0129 N HCl and the value calculated by difference.

The acid equivalents for the polymers precipitated from solutions of DMAC by benzene were determined and recorded on the as-prepared product following drying at 25°C, and then corrected for the amount of retained DMAC. The corrected values were in fair agreement with the calculated values. The acid values of the films prepared from the polyamic acid solutions by heating at 125-130°C for 22 hours were in most cases lower than the theoretical values for the polyhemiamic acid which indicated that some ring closure had occurred during the heating. This conclusion was also confirmed by comparing bands for imide at 5.63 and 13.85 μ of the infrared spectra of the heated film with the spectra of the unheated precipitated polymer.

During the course of this study, an attempt was made to prepare the polyhemiamic acids at a 25% concentration in DMAC. This was found possible for polymers in the range of $\rho = 0.0$ to $\rho = 0.3$. For the polyhemiamic acids of $\rho > 0.3$ it was found necessary to use more dilute solution. For example, at $\rho = 0.4$, homogeneous, clear, non-gelled solutions were prepared at 15 and 18% concentration of polymer. The polymer of $\rho = 0.5$ from a 3:2 mole ratio of MPDA and MTA, required that a 10% solution be prepared. For this polymer of $\rho = 0.5$, the concentration differs with the data given in the 1 February 1969 to 30 April 1969 report under this grant, in which a 25% solution was reported. In the earlier experiments, the TMA was added as a solid to the solution at 40°C of PPDA dissolved in DMAC to yield an opaque, translucent reaction mixture of low viscosity which was used as such.

In the current experiments, the MTA was dissolved in DMAC at 80°C and added while warm and in solution to the MPDA dissolved in DMAC previously cooled to $\sim 0^\circ\text{C}$ to yield a clear viscous reaction solution. It was also experimentally determined that clear, viscous, homogeneous solutions could be obtained when approximately 20% of the total DMAC used in the experiment was used as the solvent for the MPDA and the remaining 80% of the DMAC was used to predissolve the MTA or mixtures of MTA and PMDA. It was also interesting to note that the viscosity of the solution of polymer of $\rho = 0$, obtained by the reaction of MPDA and PMDA was low when the PMDA was predissolved in DMAC and added to the DMAC solution of MPDA, using the same procedures and technique which was effective for the compositions containing only MTA or mixtures of MTA with PMDA. For the $\rho = 0$ composition, the preferred procedure was to add solid PMDA to the DMAC solution of MPDA at 50°C to obtain a solution of higher viscosity which could be cast into films that could be handled more readily. If the reaction was not performed at 50°C, a cloudy heterogeneous dispersion was obtained instead of a clear solution.

II. Experimental.

A. Materials.

DMAC was purchased from du Pont and distilled at 15 mm Hg pressure; a center cut of 80% was used and stored over anhydrous Na_2SO_4 . The MPDA was Eastman grade which was distilled at 15 mm Hg pressure and preserved under nitrogen in a brown glass bottle and maintained cold in a refrigerator. Reagent grade MTA was purchased from Aldrich Chemical in 10-gram lots and used as received. Polymer grade PMDA was obtained from an inventory of reagents from another project active in this laboratory.

B. Polymerizations.

1. The Following is a Typical Procedure for the Synthesis of Polymers Containing MTA.

Ex. No. DA-55-119. MPDA (0.810 g., 0.75×10^{-2} mole) was dissolved in 5 ml. of DMAC under nitrogen in a three-necked, ground glass 50-ml. flask equipped with a thermometer, a mechanical stirrer, inlet for nitrogen, cooling and heating means, etc. The solution in the flask was cooled in a water-ice bath at $\sim 0^{\circ}\text{C}$. Then MTA (1.444 g., 0.5×10^{-2} mole) was dissolved in 17.6 ml. of DMAC heated to 80°C and not allowed to cool to below 70°C . The DMAC solution of MTA was poured rapidly to the vigorously agitated solution of MPDA and cooling maintained until the temperature decreased to 28°C , at which point the ice-bath was removed and the reaction allowed to proceed at room temperature for one hour. Then one-half of the total volume of the solution (23.5 ml.) was cast onto glass plates and dried in an air circulating oven at $125\text{--}130^{\circ}\text{C}$ for 24 hours. The remaining half of the solution was poured with vigorous stirring into 150 ml. of anhydrous benzene, precipitating the polymer. Stirring was continued for approximately one hour, after which the polymer was isolated by filtration, washed three times with 10 ml. portions of benzene and dried in a vacuum oven at 25°C for 15 hours. Samples of the film and precipitated polymers were ground to very fine powder in a vibrating capsule and the infrared spectrum and acid numbers of the polymers determined on the powders. The acid numbers are reported as theoretical values of 3.0 for the polyhemiamic of this polymer of $\rho = 0.5$ and of 2.0 for the polymer of $\rho = 0.00$ and values ranging from 2.0 to 3.0 in proportion to the amount of MTA ($f = 3$) used in combination with PMDA ($f = 2$).

2. The Following is a Typical Experiment Using Solid, Undissolved PMDA Added to a Solution of MPDA in DMAC.

Ex. No. DA-55-133. MPDA (0.756 g., 0.7×10^{-2} mole) was dissolved under nitrogen in 9.1 ml. of DMAC in a 50 ml. reaction flask identical to and equipped similarly to the apparatus used in DA-55-119 above. The temperature of the solution was $\sim 26^{\circ}\text{C}$. Then, finely ground PMDA ($1.526 \text{ g. } 0.7 \times 10^{-2}$

mole) was added to the vigorously stirred solution while nitrogen was flushing through the apparatus, causing the temperature to rise to 35°C. On the completion of the addition of PMDA, a turbid, non-clear dispersion was obtained. The reaction mixture was then heated to 50°C, at which temperature a clear, homogeneous solution was obtained. Then the reaction mixture was cooled by means of an ice-water bath to 35°C and the reaction allowed to proceed at 35°C for an additional hour. Then, the procedure of DA-55-119 was used to cast films and to precipitate polymers, both of which were evaluated similarly to the products of DA-55-119.

3. Experimental Data on Polymers.

The experimental data for the benzene precipitated polymers dried at 25°C is summarized in Table 1 and for the films cast at 125-130°C for DMAC solutions is summarized in Table 2.

4. Gelled Polymers.

Gelled polymer solutions were obtained in a number of cases when attempts were made to prepare the polymers at a 25% concentration in DMAC. For example, large amounts of gel were found when the polymer of $\rho = 0.5$ (DA-55-119) was prepared as 25 or 20%, but clear solutions, free of gel, were obtained at a 10% concentration. Similarly, gel was present when the polymer of $\rho = 0.4$ (DA-55-127) was prepared at 25 and 20% concentration in DMAC but the solutions were free of gel when prepared at an 18% concentration or less. The following is a typical experiment in which gellation occurred:

DA-55-115. MPDA (1.080 g., 1×10^{-2} mole) was dissolved in 2 ml. of DMAC under nitrogen in the reaction flask and cooled to $\sim 0^\circ\text{C}$ by means of an ice-water bath. Then, MTA (1.926 g., 0.66×10^{-2} mole) was dissolved in 10 ml. of DMAC preheated to 80°C and cooled to $\sim 70^\circ\text{C}$, and added to the MPDA solution with vigorous stirring; the temperature of the reaction mixture was 28°C. The mixture gelled immediately. The cooling bath was removed and an

Table 1

Data on Benzene Precipitated Polymers Dried at 25°C

Polymer No.	ρ	Monomers* (mole ratios)	% Conc. in DMAC	Yield at 25°C. % of theory	COOH Groups Per Unit		
					experimental	corrected	theoretical
DA-55-133 -P	0.0	MPDA (1.0) PMDA (1.0)	25	170.5	1.13	1.92	2.00
DA-55-112 -P	0.1	MPDA (1.1) PMDA (0.8) MTA (0.2)	25	177.5	1.39	2.47	2.20
DA-55-121 -P	0.2	MPDA (1.2) PMDA (0.6) MTA (0.4)	25	158.5	1.67	2.64	2.40
DA-55-123 -P	0.3	MPDA (1.3) PMDA (0.4) MTA (0.6)	25	127.7	1.92	2.45	2.60
DA-55-127 -P	0.4	MPDA (1.4) PMDA (0.2) MTA (0.8)	13	125.5	2.21	2.78	2.80
DA-55-129 -P	0.4	MPDA (1.4) PMDA (0.2) MTA (0.8)	15	122.9	2.44	2.98	2.80
DA-55-119 -P	0.5	MPDA (1.5) MTA (1.0)	10	148	2.24	3.31	3.00

* MPDA = m-phenylenediamine; PMDA = pyromellitic dianhydride;
MTA = mellitic trianhydride.

Table 2
Data on Films Dried at 125-130°C for 24 Hours

Polymer No.	ρ	Monomers (mole ratio)	% Conc. in DMAC	Yield at 130°C	COOH Groups per Unit		
					experimental	corrected	theoretical
DA-55-133 -F	0.0	MPDA (1.0) PNDA (1.0)	25	86.9	1.48	1.48	2.00
DA-55-112 -F	0.1	MPDA (1.1) PNDA (0.8) NTA (0.2)	25	94.0	1.22	1.22	2.20
DA-55-121 -F	0.2	MPDA (1.2) PNDA (0.6) NTA (0.4)	25	101.2	1.62	1.64	2.40
DA-55-123 -F	0.3	MPDA (1.3) PNDA (0.4) NTA (0.6)	25	102.8	1.99	2.04	2.60
DA-55-127 -F	0.4	MPDA (1.4) PNDA (0.2) NTA (0.8)	18	110.0	2.25	2.47	2.80
DA-55-129 -F	0.4	MPDA (1.4) PNDA (0.2) NTA (0.8)	15	89.8	2.23	2.28	2.80
DA-55-119 -F	0.5	MPDA (1.5) NTA (1.0)	10	105.8	2.00	2.80	3.00

additional 12 ml. of DMAC added to aid the stirring which was continued for another hour at ambient temperature. The gel failed to dissolve, so the temperature was raised to 40°C for 30 minutes; solution did not occur and the reaction was terminated.

Stirring had broken up the gel into small pieces which were highly swollen and elastic and distributed throughout a small amount of ungelled solution. The product was centrifuged for 15 minutes to separate 8.5 ml. of DMAC solution of soluble polymer (DA-55-115-S) as a supernatant liquor. A sample, 4 ml. of DA-55-115-S-F was cast as a film at 115-130°C, yield 0.385 g. The remainder of DA-55-115-S-P (4.5 ml.) was precipitated in benzene and dried at 25°C at 0.5 mm Hg pressure, yield 0.526 g.

The centrifuged gel was added to benzene and subjected to vigorous agitation to yield a fine powder which was washed three times with benzene and dried at 25°C in vacuo; yield of DA-55-115-G, 2.8127 g. The isolated, dried gel was insoluble in hot DMAC.

Apparent total yield of isolated polymer, 3.7237 (123.8% of theory), of which 93.5% was gel and 30.3% was sol. The theoretical -COOH number of gel and sol is 3.0; found for the sol, apparent -COOH, 2.75; corrected 2.40; for the gel, apparent -COOH 2.31; corrected, 3.32.

III. Schedule of Program.

A. Thermogravimetric analysis, both TGA and DTA will be performed on the benzene-precipitated polymers, dried at 25°C and at 250°C. The -COOH number of the 250°C polymers will also be determined.

B. Samples of the polymers will be heated at 350°C to determine the extent of ring closure. DTA and TGA will be performed on the 350°C polymers.

C. New samples of precipitated polymers of $\rho = 0.0$ and $\rho = 0.5$ will be prepared and isolated, and solubility in DMAC evaluated as a function of

time to determine stability. Copolymers will be prepared from the redissolved polymers at various ratios of $\rho = 0.0$ to $\rho = 0.5$.

IV. Dr. S. Riccitiello, Ames Laboratory, visited the Chemistry Department University of Notre Dame on July 23, 1969 to review this project. The Principal Investigator believes that the rapport established during this visit was most beneficial.