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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Porowska, Engelina and Tokarzewska, Maria(1979) 'Synthesis of Thermally Resistant Polyesterimides from p,p '-Phenolphthalein-bis(trimellitic) Dianhydride and Primary Aromatic Diamines', Journal of Macromolecular Science, Part A, 13: 7, 923 – 935

**To link to this Article:** DOI: 10.1080/00222337908066618

**URL:** <http://dx.doi.org/10.1080/00222337908066618>

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## Synthesis of Thermally Resistant Polyesterimides from p,p'-Phenolphthalein-bis(trimellitic) Dianhydride and Primary Aromatic Diamines

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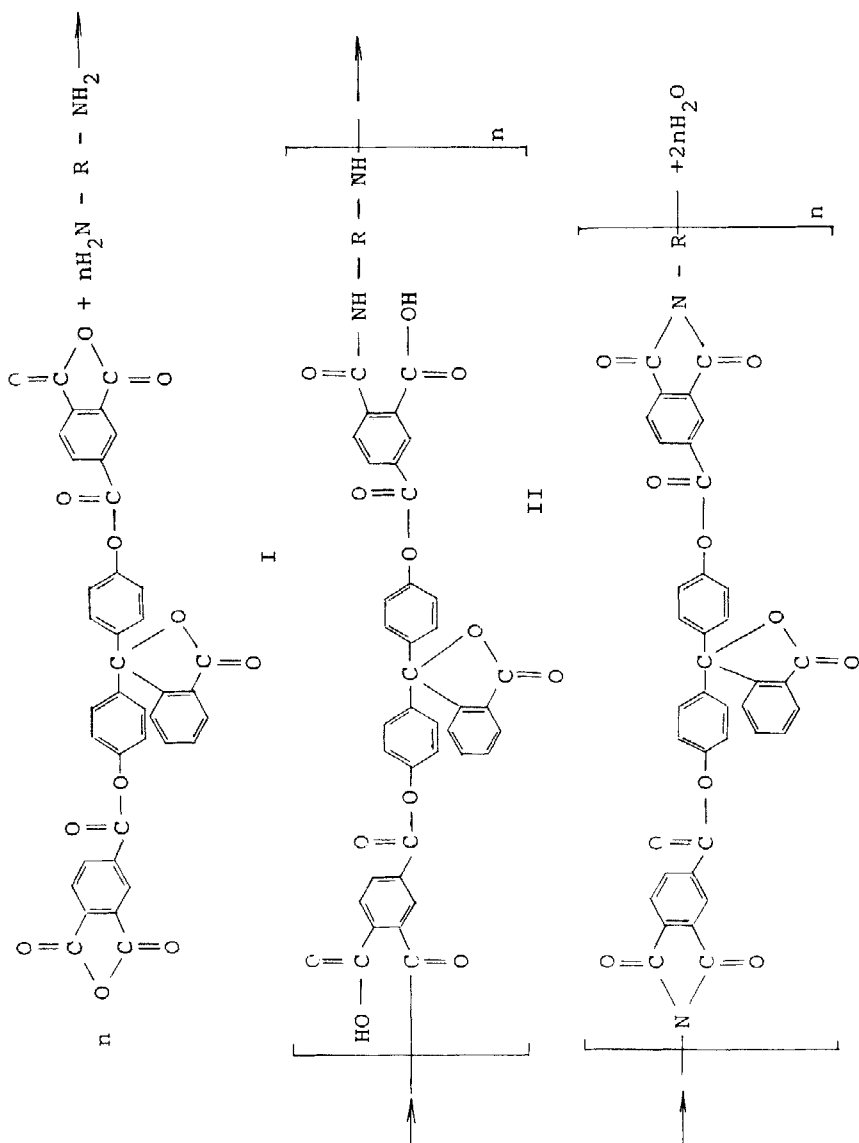
### ABSTRACT

Alternating polyesterimides soluble in m-cresol, dimethylformamide, and dimethyl sulfoxide have been obtained by the reaction of p,p'-phenolphthalein-bis(trimellitic) dianhydride with primary aromatic diamines. The course of reaction between dianhydride and diamines and the cyclization process of polyesteramidoacids have been studied. One-step synthesis of polyesterimides by polycyclization in m-cresol solution has been developed. The coatings from polyesterimides prepared possess good thermal stability and advantageous mechanical properties.

Alternating polyesterimides containing ester groups in alternation with imide rings in a macromolecule were obtained by Loncrini [1] in the reaction of dianhydrides containing ester groups with primary diamines. The polyesterimides obtained by Loncrini were insoluble

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in organic solvents, and the last step of cyclization was performed in coatings.

This paper deals with the synthesis of alternating polyesterimides using *p,p'*-phenolphthalein-bis(trimellitic) acid dianhydride as a parent substrate [2]. Introduction of large volume substituents in form of a lactone ring into the polymer chain made it possible to prepare soluble polymers by polycyclization in solution at a high temperature. The polymers were prepared by the reaction of dianhydride (I) with primary diamines according to a two-step scheme.

In the first step, the reaction results in the formation of polyester-amine acids (II). In the second step, run at high temperature, polyesteramide acids undergo a cyclization through functional groups with water evolution yielding a polyesterimide having a chain-ring structure (III).

## EXPERIMENTAL

### Apparatus and Methods of Characterization

Infrared spectral analysis was carried out with a Zeiss UR-10 spectrophotometer (C. Zeiss, Jena, GDR).

Differential scanning calorimetry (DSC) was conducted under nitrogen by using a Perkin-Elmer DSC-1B differential microcalorimeter.

Thermal analysis was run in air by use of a OD-102 derivatograph (MOM, Budapest, HDR) based on the Paulik, Paulik, and Erdey system.

Molecular weights were determined from vapor pressures over polymer solutions by use of the 302B Hewlett-Packard apparatus.

Relative viscosities of 0.5% polymer solutions were determined from the flow time of both the solution and solvent measured with a Ubbelohde viscometer (Labortherm, GDR) having a capillary constant of 0.004985.

### Materials

*p,p'*-Phenolphthalein-bis(trimellitic) acid dianhydride had a melting point of 135-138°C, and a content of free carboxy groups of 0.73% [2].

4,4'-Diaminediphenylmethane, pure with melting point 91.5-92°C was obtained from BASF, Germany.

4,4'-Diaminediphenyl ether was prepared from diaminediphenyl ether hydrochloride, melting point 190°C (Hoechst, Germany).

Solvents used were *N,N'*-dimethylformamide, pure, boiling point 153°C (VEB - Laborchemie, Apolda, GDR), dimethyl sulfoxide, pure,

boiling point 189°C (Reakhim, USSR), *m*-cresol, pure, boiling point 202°C (Reakhim, USSR), methanol, analytically pure, boiling point 64.7°C (Oświęcim Chemical Works, Poland), and acetone, analytically pure, boiling point 56.5°C (POCh, Gliwice, Poland).

Owing to the hydrolysis of *p,p'*-phenolphthalein-bis(trimellitic) dianhydride under the influence of moisture resulting in acid formation, all materials mentioned were completely dried before use.

### Course of Reaction between *p,p'*-Phenolphthalein-bis(trimellitic) Dianhydride and Primary Diamines

The reaction of *p,p'*-phenolphthalein-bis(trimellitic) dianhydride with primary diamines was carried out in *N,N'*-dimethylformamide (DMF) or *m*-cresol using 16% and 25% solutions of equimolar quantities of the substrates. The process was carried out under nitrogen to avoid the oxidation of amine groups.

The course of the polymerization reaction was examined by determining the inherent viscosity of polyesterimide acids being formed. Before synthesis, the diamine was dissolved in a predetermined quantity of dimethylformamide and cooled to a temperature of 10–12°C. Then, dianhydride was introduced into the prepared solution and mixed with it; subsequently under continuous nitrogen flow, the reagents were rapidly heated to 25 ± 1°C. The reactions were run at this temperature and their progress was determined by taking aliquots of the reaction at specific periods of time. The obtained polyesteramide acid was precipitated with methanol from the sample taken, then washed with a mixture of methanol and acetone and finally dried at 25–30°C under reduced pressure. From these samples, 0.5% solutions in dimethyl sulfoxide were prepared and their inherent viscosity were determined.

Similarly, the course of reaction in *m*-cresol was studied but with temperature increasing up to 30°C due to the poorer solubility of the substrates in *m*-cresol. For the same reason, the course of reaction in *m*-cresol was observed only in 16% solutions.

The inherent viscosity of solutions of the polyesteramide acids obtained from 4,4'-diaminodiphenylmethane (DKFMM) and 4,4'-diaminodiphenyl ether (DKFME) are presented in Fig. 1 as a function of processing time in dimethylformamide and *m*-cresol solutions. DKFMM and DKFME polyesteramide acids, prepared in 16% solutions, form coherent and clear coatings after evaporation of solvent. On the other hand, the film formation from 25% polymer solutions was accompanied, as observed, by crater formation in the coating before complete solidification.

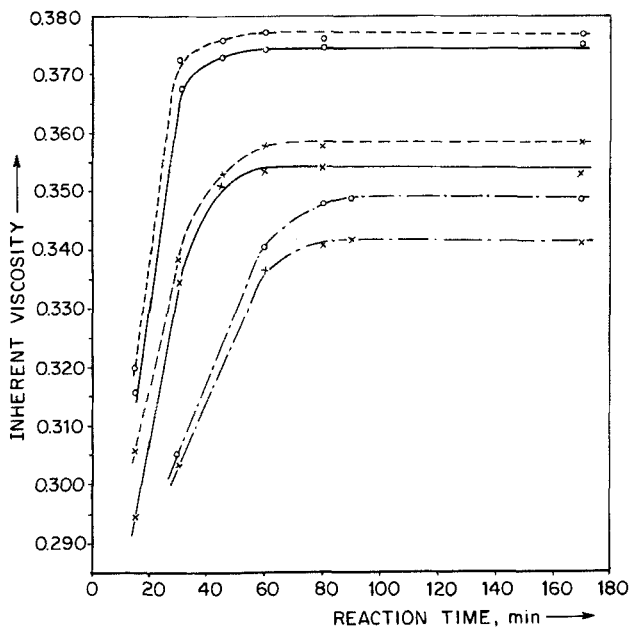


FIG. 1. Inherent viscosity of (○) DKFME and (x) DKFMM poly-esteramide acid solutions: (—) 16% solution in DMF; (---) 25% solution in DMF; (- · -) 16% solution in m-cresol.

### Cyclization of Polyesteramido Acids

The cyclization of polyesteramide acids was examined by infrared spectrophotometric analysis and differential scanning calorimetry. To run the measurements, the solutions of polyesteramido acids were applied by means of an applicator onto aluminum plates for infrared spectrophotometric analysis and onto glass plates for differential scanning calorimetry. Then, the solvent was evaporated under reduced pressure at an ambient temperature. The thickness of films formed was about 10  $\mu\text{m}$ . Thermal cyclization of polyesteramide acids was conducted at successively increasing temperatures: 100°C, 200°C, 240°C, and 300°C with 1 hr at each temperature. After every heating step, the spectra of the films were recorded by using a reflection attachment with an incident beam angle of 20°. For the same cyclization steps, differential scanning calorimetry was carried out at a temperature increment

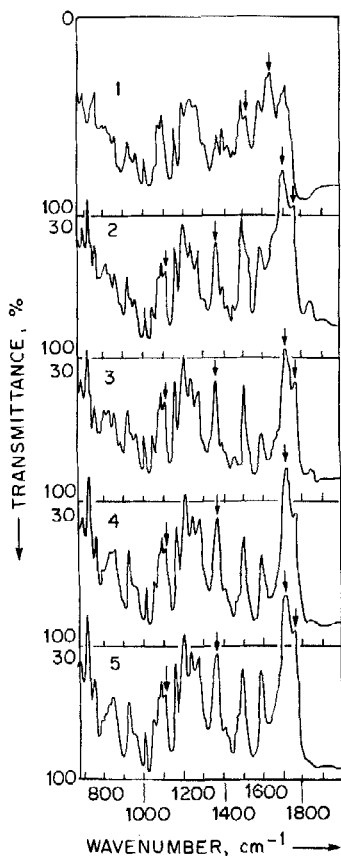


FIG. 2. IR spectra of DKFMM polyesteramide acid products obtained (1) without heat cyclization; (2) with cyclization 1 hr at 100°C; (3) with cyclization 1 hr at 100°C followed by 1 hr at 200°C; (4) with cyclization for 1 hr each at 100°C, 200°C, and 240°C; (5) with cyclization for 1 hr at 100°C, 200°C, 240°C, and 300°C.

rate of 8°C/min and sensitivity of 4 mcal/sec. Owing to the similar results obtained for both polyesteramido acids, the IR spectra and DSC curves illustrating the cyclization process are given only for DKFMM polyesteramide acid.

The IR spectra are presented in Fig. 2, and the DSC curves are shown in Fig. 3.

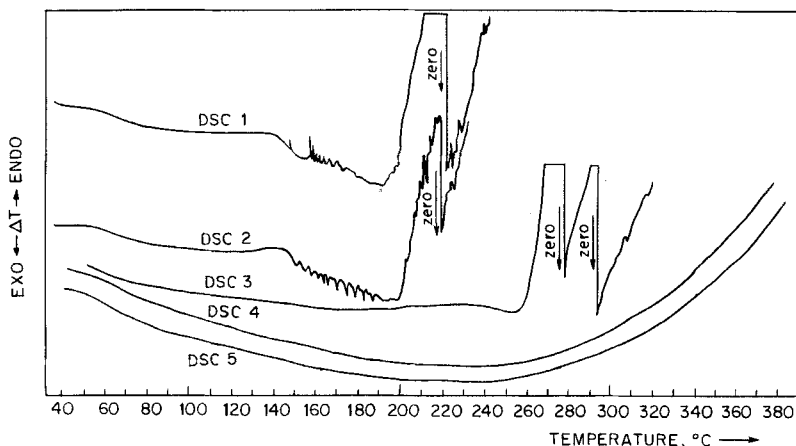


FIG. 3. DSC curves of products obtained with and without thermal cyclization: (1)-(5) as in Fig. 2.

Additionally the solubility of polyesterimides formed in that process has been tested. The results are collected in Table 1.

#### Synthesis of Polyesterimides by Polycyclization in Solution at High Temperatures

DKFMM (33.3 g, 0.05 mole) and 270 g of *m*-cresol were placed in a reactor equipped with a stirrer, thermometer, reflux condenser with Dean-Stark receiver and inert gas inlet tube. Then, 9.9 g (0.05 mole) of diaminediphenylmethane or 10.0 g (0.05 mole) of diamino-diphenyl ether and 25 ml of xylene were introduced to the vigorously agitated mixture. The mixture of all reagents was gradually heated under continuous nitrogen flow. At about 140°C, xylene and water was distilled off. The mixture was subjected to further heating from 140°C to 170°C for 1 hr under xylene reflux. After that time, xylene was rapidly distilled off, while the reaction temperature increased to 200°C. The process was continued at this temperature for 6 hr.

The polycyclization reaction at 200°C was examined by determining the inherent viscosity of polymer aliquots obtained from the batch during the course of reaction. The relationship of inherent viscosity with processing time is shown in Fig. 4.

The IR spectra of the polycyclization products at 200°C were also obtained after 4 and 6 hr of processing. These spectra of DKFMM polyesterimide are shown in Fig. 5.



TABLE 1. Solubility of DKFMM and DKFME Polyesterimides Dependent on Cyclization Temperature and Time<sup>a</sup>

Additional heat treatment at	Solubility					
	Dimethylformamide		Dimethyl sulfoxide		m-Cresol	
	DKFMM	DKFME	DKFMM	DKFME	DKFMM	DKFME
200°C/1 hr	+	+	+	+	+	+
200°C/1 hr + 240°C/1 hr	+	+	+	+	0	0
200°C/1 hr + 240°C/1 hr + 280°C/1 hr	0	+	0	+	0	0
200°C/1 hr + 240°C/1 hr + 300°C/0.5 hr	0	0	0	0	0	0

<sup>a</sup> After initial heating 1 hr at 100°C.

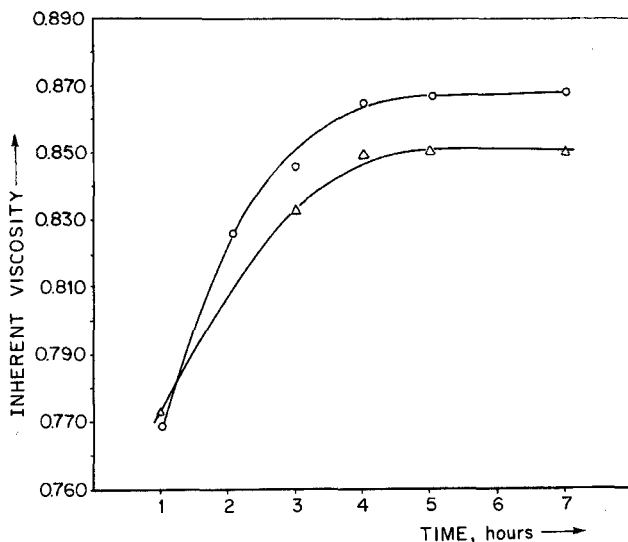


FIG. 4. Inherent viscosity of (○) DKFME and (△) DKFMM as a function of processing time.

Preparation of soluble polyesterimides made it possible to determine their molecular weights. Molecular weights of polyesterimides prepared in a two-step sequence, i. e., by reaction of dianhydride with diamine in methylformamide solution at 25°C followed by cyclization of polyesteramide acids in films at 100°C (1 hr) + 200°C (1 hr) + 240°C (1 hr), were also determined. The results are presented in Table 2.

#### Properties of DKFMM and DKFME Polyester Imides

The properties of the polyester imides were examined to evaluate their practical applications. They are summarized in Table 3.

### DISCUSSION AND CONCLUSIONS

From the relationship of inherent viscosity of the prepared polyesteramide acid solutions versus reaction time (Fig. 1) it may be concluded that the reaction between dianhydride and diamine is characterized by a high growth of macromolecules at the initial reaction step. After 1-1.5 hr of reaction, the growth of polymer macromolecules was slowed down. The course of reaction seems therefore to be almost independent on the concentrations of parent substrates.

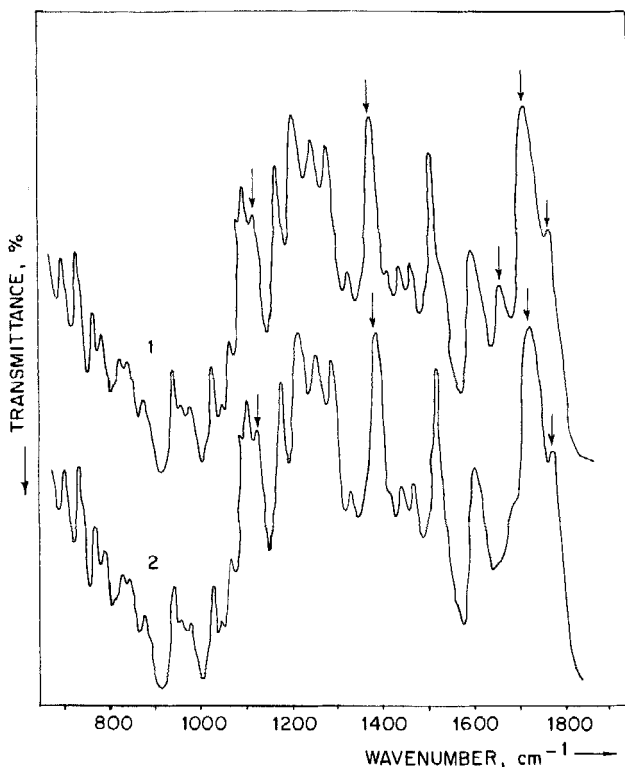


FIG. 5. Infrared spectra of product of polycyclization in *m*-cresol at 200°C: (1) after 4 hr processing; (2) after 6 hr processing.

The limiting values of the inherent viscosity numbers determined for polyesteramide acids which were synthesized in *m*-cresol and dimethylformamide are closely similar. The polyesteramide acids obtained are soluble in dimethylformamide, dimethyl sulfoxide, and *m*-cresol and insoluble in aromatics, ketones, and chlorine derivatives. They form clear, coherent films that undergo cyclization when heated. Analysis of IR spectra of polyesteramide acids treated by gradually increasing temperatures shows considerable changes in absorption bands (Fig. 2).

In the spectrum of DKFMM polyesteramide acid, there are two bands characteristic of the amide group: the strong amide band related to carbonyl group stretching vibrations at  $1652\text{ cm}^{-1}$  and the a medium intensity amide band related to deformation vibrations of  $-\text{NH}-$  accompanied by stretching vibrations of  $-\text{C}-\text{N}-$  at about  $1530\text{ cm}^{-1}$  [3].

TABLE 2. Molecular Weights of Polyesterimides Prepared by Polycyclization in Solution and in Two-Step Synthesis

Synthesis	Polyesterimide	Inherent viscosity	Number-average molecular weight
Polycyclization	DKFMM	0.87	18100
in solution	DKFME	0.85	17600
Two-step synthesis	DKFMM	0.30	7100

As the cyclization reaction proceeds with heating, the complete decay of these bands occurs and the bands related to imide ring absorption appear: a doublet characteristic of the carbonyl group stretching vibrations at 1721 and 1771  $\text{cm}^{-1}$  in the final cyclization step and bands related to asymmetrical and symmetrical stretching vibrations of imide rings at 1376  $\text{cm}^{-1}$  and 1115  $\text{cm}^{-1}$  [4-7].

The absorption bands do not change when the polyesterimides are subjected subsequently to heating at 300°C. It means that thermal cyclization is almost completed in the temperature range of 200-240°C.

A diminution of cyclization reaction in this range of temperature is also proved by differential scanning calorimetry (Fig. 3). The character of DSC-4 and DSC-5 curves does not show any heat effects that are specific for chemical reactions or physical phenomena. Polyesterimides formed during thermal cyclization at 200°C remain soluble in *m*-cresol, dimethylformamide, and dimethyl sulfoxide (Table 1).

An increase of cyclization temperature results in a gradual decrease of the solubility of the products. This decrease of solubility can be explained by the fact that in polyimides heated to temperatures higher than the cyclization temperature, cleavage of the  $-\text{CO}-\text{N}$  bond in the imide rings occurs, followed by its recombination which results in turn in the formation of crosslinked structure between polymer chains. These reactions were described earlier by Rudakow and his associates [8]. Polycyclization in *m*-cresol solution was possible owing to the solubility of polyesterimides containing large polar groups in macromolecules. Polymers obtained by the method described above have molecular weights almost three times those of polymers synthesized by the conventional two-step sequence (Table 2).

TABLE 3. Properties of Polyesterimides Obtained

	Polyesterimide	
	DKFMM	DKFME
<b>Thermal resistance</b>		
Initial decomposition temperature, (°C)	ca. 330	ca. 340
Weight loss on heating to 400°C (%)	10	8
<b>Dielectric strength at various temperatures of (kV/mm)<sup>a</sup></b>		
20°C	55-48.5	55-48.5
40°C	50-48.5	50-48.5
80°C	50-47	50-47
100°C	50-48.5	50-48.5
120°C	48.5-47	48.5-47
<b>Mechanical properties of coatings<sup>b</sup></b>		
Flexibility ( $\phi$ mm)	2	2
(Polish Standard PN-69/C-81528-B)		
Drawability (mm)	8	8
(Polish Standard PN-59/C-81529)		
Impact strength (kg-cm)	50	50
(Polish Standard PN-54/C-81526)		
Relative hardness		
(Polish Standard PN-73/C-81530)	0.96	0.96

<sup>a</sup>Coating thickness 16-18  $\mu$ m.

<sup>b</sup>About 20  $\mu$ m.

During the cyclization reaction in solution, not only does a closure of imide rings occur, but there is also a further increase of polymer macromolecules. This phenomenon can be explained on the basis of the studies of degradation processes of polyamide acids and pyromellitic polyimides [5, 9, 10] which proved that the water formed during cyclization causes hydrolytic degradation of polyamide acids, resulting in lower molecular weight product which contains terminating amine

and carboxy groups. During cyclization in solution, accompanied by continuous water stripping in the form of an azeotropic mixture with xylene and permanent dry nitrogen flow, the carboxy end groups form anhydride rings under the influence of high processing temperature. Also, the reaction of molecules terminated with amine groups occurs that again yields an increase of molecular weight.

Use of *m*-cresol instead of dimethylamides of organic acids or dimethyl sulfoxide, generally applied in a synthesis of polyimides is also suitable. It enables one to eliminate their destructive influence on imide rings [11]. The growth of macromolecules during polycyclization in solution is slowed down at the initial reaction period (Fig. 4). However, for the chemical change from polyesteramide acids to polyesterimides to occur needs the reaction to proceed for a longer period of time.

The infrared spectra (Fig. 5) show that the extension of heating time up to 6 hr results in a high degree of cyclization, i. e., there are no bands related to absorption of amide groups visible in the polymer spectrum.

The coatings from polyesterimides prepared by polycyclization in solution characterize have very desirable properties (Table 3). It may be expected that these new polyesterimides will be competitive with other known thermally resistant film-forming polymers.

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Accepted by editor December 7, 1978

Received for publication December 11, 1978