

# Reactions of Diaminoalkanes with Bismaleimides: Synthesis of Some Unusual Polyimides\*

JERRY E. WHITE<sup>†</sup>, *The Dow Chemical Company, Central Research-Plastics Laboratory, Midland, Michigan 48640*, MARK D. SCAIA and DEBORAH A. SNIDER, *Dow Chemical Company, Granville Research and Development Center, Granville, Ohio 43023*

## Synopsis

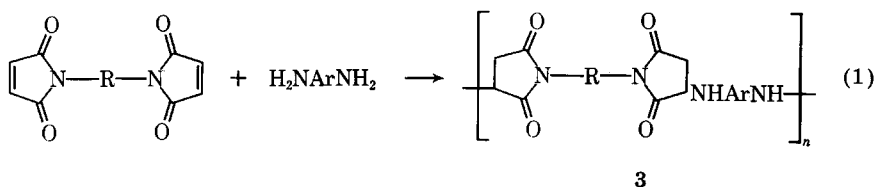
Michael additions of the secondary diamines *N,N'*-dimethyl-1,6-hexanediamine (14) or piperazine to the electrophilic carbon-carbon double bonds of *N,N'*-bismaleimido-4,4'-diphenylmethane (2) or *N,N'*-bismaleimido-1,8-octane (4) afford four unusual, high-molecular-weight ( $\eta_{inh} = 0.49\text{--}2.16$  dL/g) polyimides (10-13). The most interesting of these, polymer 12 (the product of 4 and 14), is a tough elastomeric resin with a glass transition temperature ( $T_g$ ) near 0°C; in contrast, 10, 11, and 13 exhibit  $T_g > 86^\circ\text{C}$ . Freshly prepared 12 is soluble and thermoplastic (12 is readily compression molded at 110°C), but the bulk polymer crosslinks slowly under ambient laboratory conditions and eventually (48 days) becomes insoluble, while 10, 11, and 13 remain soluble indefinitely. Along with further comparisons of the properties of 10-13, details of the synthesis and characterization of these new polyimides are described. Also discussed are reactions of bismaleimide 2 with 1,6-diaminohexane, which unlike the formation of linear 10-13, generate crosslinked, insoluble products.

## INTRODUCTION

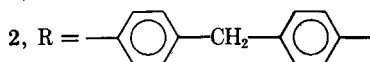
Nucleophilic or Michael addition of diaminoarenes ( $\text{H}_2\text{NArNH}_2$ ) to *N,N'*-bismaleimide (1)<sup>1</sup> or to *N,N'*-bismaleimidoarenes<sup>2</sup> (e.g., 2) can afford linear, high-molecular-weight polyimides [general structure 3, eq. (1)] that are typified by rigid backbones, high glass transition temperatures ( $T_g = 210\text{--}300^\circ\text{C}$ ) and limited solubility.<sup>2</sup> In order to extend eq. (1) to the synthesis of polymers structurally related to 3 but with more flexible backbones and consequent lower  $T_g$ , we studied the reactions of some diaminoalkanes with bisimide 2 and with *N,N'*-bismaleimido-1,8-octane<sup>3</sup> (4), a monomer which showed particular promise as a precursor to polyimides with exceptionally mobile chains. Although superficially analogous to the straightforward polymerizations of eq. (1), additions of aliphatic diamines to bismaleimides often are complicated by crosslinking side reactions that lead to insoluble products. Even so, we found that under appropriate conditions, secondary (2°) diamines react with 2 or 4 to yield soluble polyimides (cf. 10-13 described below) that generally exhibit the molecular flexibility we were seeking. One of the resins (12), which can behave as a thermoplastic elastomer, is especially interesting and is discussed in some detail:

\* Presented in part at the Michigan Molecular Institute 10th Anniversary Polymer Symposium, 14th Central Regional Meeting of the American Chemical Society, Midland, Michigan, June 1982.

<sup>†</sup> To whom correspondence should be addressed.



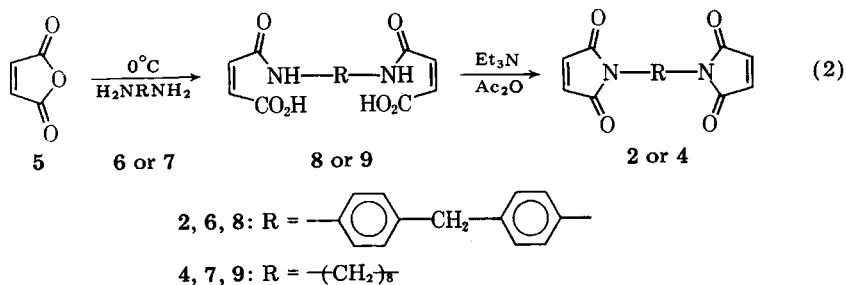
1, R = nil



## RESULTS AND DISCUSSION

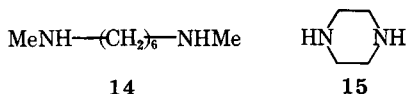
### Monomer Synthesis

Bismaleimides **2**<sup>2</sup> and **4**<sup>3</sup> were prepared using modifications (see Experimental) of Searle's method,<sup>4</sup> in which maleic anhydride (**5**) reacts quantitatively with methylenedianiline (**6**) or with 1,8-diaminooctane (**7**) in cold chloroform (CHCl<sub>3</sub>), followed by base (Et<sub>3</sub>N)-catalyzed cyclodehydration of the resulting bismaleamic acids **8** or **9** in acetone containing acetic anhydride (Ac<sub>2</sub>O) as a water scavenger [eq. (2)]. Although overall yields of **2** (51%) and **4** (18%) are poor, they do represent analytically pure samples, ideally suited for step-growth polymerizations:

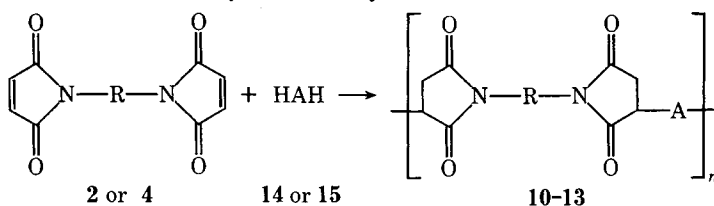


### Polymer Synthesis and Characterization

*N,N'*-dimethyl-1,6-hexanediamine (**14**) adds to bismaleimides **2** or **4** in *m*-cresol (26–27% solids) at ca. 25°C to give high-molecular-weight polyimides **10** ( $\eta_{\text{inh}} = 2.16$  dL/g) and **12** ( $\eta_{\text{inh}} = 1.26$  dL/g) in yields of about 60% within 48 h (Table I). Similarly, reactions of piperazine (**15**) with the two bisimides afford **11** [84%; prepared at 110°C owing to partial insolubility of the monomers, present in high concentration (30% solids), at room temperature] and **13** (79%), having  $\eta_{\text{inh}} = 0.86$  and 0.49 dL/g, respectively.



Unlike the acid (RCO<sub>2</sub>H)-catalyzed additions of diaminoarenes to **1** or **2**<sup>1,2</sup> [eq. (1)], polymerizations of **2** and **4** with diamines **14** and **15** (Table I) are retarded by even small amounts (5 mol %) of acetic acid (AcOH), yielding only

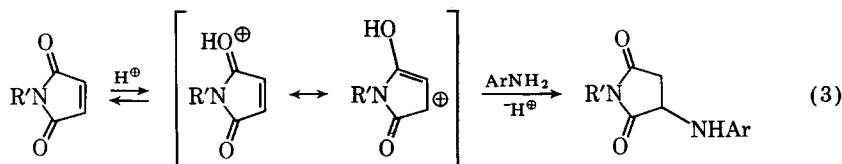
TABLE I  
 Synthesis of Polyimides 10-13


No.	—R—	—A—	% solids	Temp (°C)	Time (h)	Yield (%)	$\eta_{inh}$ (dL/g)
10			26	ca. 25	19	60	2.16 <sup>a</sup>
11			30	110	0.75	84	0.86 <sup>b</sup>
12	—(CH <sub>2</sub> ) <sub>8</sub> —		27	ca. 25	48	58	1.26 <sup>a</sup>
13	—(—CH <sub>2</sub> —) <sub>8</sub> —		20	ca. 25	72	79	0.49 <sup>a</sup>

<sup>a</sup> Chloroform (CHCl<sub>3</sub>), 0.5 g/dL, 25°C.

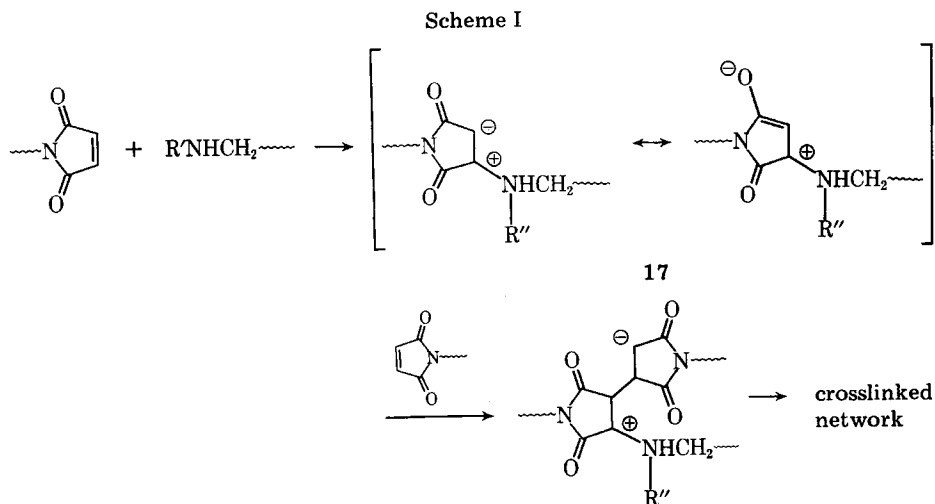
<sup>b</sup> *m*-Cresol, 0.5 g/dL, 25°C.

oligomeric oils after several days at ambient temperature when AcOH is present. In the polymerization of eq. (1), AcOH probably protonates the imide carbonyl oxygens, enhancing the electrophilicity of the maleimido function [cf. 16, eq. (3)] and thus its lability to nucleophilic attack by amine. For the polymerizations in Table I, however, such an association (i.e., 16) is likely precluded by a stronger one between the acid and the relatively basic 2° diamines (14 or 15), eliminating any catalytic effect of AcOH and apparently disrupting the stoichiometric balance between free amino and maleimido functionalities:

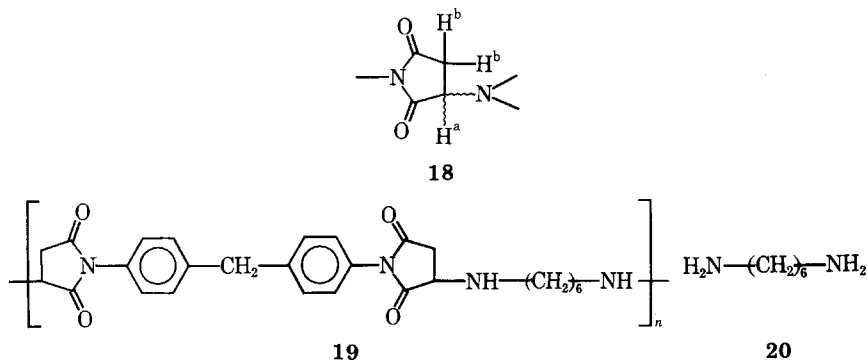


16

*m*-Cresol was chosen as a solvent for synthesis of 10-13, since it acts as a proton source and effectively neutralizes the resonance-stabilized, charged intermediates (17) expected<sup>1,2</sup> for nucleophilic additions of amines to maleimides. In aprotic media, 17 are sufficiently long lived to promote crosslinking and gelation *via* Scheme I. For example, polymerization of bismaleimide 2 with an equivalent amount of 2° diamine 14 in dimethylformamide (DMF) at ambient temperature exothermically produces insoluble, crosslinked products within minutes, while (as noted above) the same reactants cleanly yield soluble polyimide 10 in *m*-cresol. Cresol has been used analogously in the synthesis of polyimidosulfides (structurally very similar to 10-13) by Michael addition of alkanedithiolates to 2 and to other *N,N'*-bismaleimidoarenes<sup>5</sup>:



The carbonyl ( $\text{C}=\text{O}$ ) regions of the IR spectra of polymers 10–13 exhibit only bands [ $1790(\text{w})$ , ca.  $1710(\text{s}) \text{ cm}^{-1}$ ] characteristic<sup>1,2</sup> of imide  $\text{C}=\text{O}$  stretching absorptions, indicating that the imide rings of 10–13 remain intact during the polymerizations shown in Table I despite earlier suggestions<sup>1,6–8</sup> that ring opening (attack by amine at  $\text{C}=\text{O}$ ) and the resultant amide formation might predominate. Also consistent with the polyimide structures shown,  $^1\text{H}$  NMR spectra of 10, 12, and 13 ( $100^\circ\text{C}$ ; tetrachloroethane- $d_2$ ) contain triplets centered at ca. 3.6 ppm, owing to absorption of the ring methine proton ( $\text{H}^a$ , 18), along with poorly resolved multiplets at 2.2–2.7 ppm, corresponding to the nonequivalent ring methylene protons,  $\text{H}^b$ . A spectrum of polymer 11 was not recorded because of the insolubility of this highly rigid polymer (*vide infra*) in suitable deuterated solvents. Elemental analyses (Table II) of the polyimides are in reasonably good agreement with the compositions calculated based on structures listed in Table I.

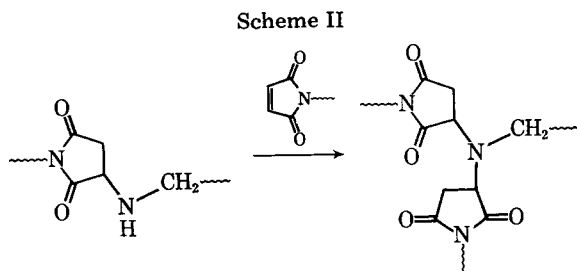


Attempts to prepare a linear, soluble polyimide (19) by addition of 1,6-diaminohexane (20) to  $N,N'$ -bismaleimido-4,4'-diphenylmethane (2) were unsuccessful; reactions of 20 with 2 in *m*-cresol (ca. 25% solids) yield only gelatinous, insoluble products within 15 min at  $110^\circ\text{C}$  or after several hours at room temperature. Cresol obviates any crosslinking through the pathway of Scheme I (see above), circumstantially suggesting that the  $2^\circ$  amino functions generated

TABLE II  
Elemental Analyses of Polyimides 10–13

No.	Found (Calcd) (%)		
	C	H	N
10	68.40 (69.29)	6.91 (6.83)	10.76 (11.15)
11	65.54 (67.54)	5.41 (5.45)	12.07 (12.61)
12	63.95 (64.24)	8.99 (9.00)	12.43 (12.49)
13	59.8 (61.50)	7.52 (7.76)	14.02 (14.35)

along the growing chains of **19** are sufficiently nucleophilic to add to unreacted maleimide moieties so that branches and ultimately crosslinks form as postulated in Scheme II. Alternatively, occasional attack of the succinimido rings of **19** by primary amino end groups might yield ring-opened amides<sup>1,7</sup> as branch points for eventual network formation, although aminolysis of this sort seems unlikely since the relatively unhindered, strongly nucleophilic 2° diamines **14** and **15** afford soluble polymers **10–13** with no evidence (IR, NMR) for amide formation:



### Polymer Properties

Because of the structural diversity among polyimides **10–13**,  $T_g$  [differential scanning calorimetry (DSC)] of the materials vary considerably from ca. 0°C for highly flexible **12** to 86°C and 95°C for moderately mobile **10** and **13**, respectively (Table III). In contrast, polymer **11**, the adduct of bisimide **2** and piperazine (**15**), is infusible, showing no  $T_g$  by DSC. This observation indicates a highly rigid backbone in **11**, further reflected by the insolubility of the polymer in  $\text{CHCl}_3$ , tetrahydrofuran (THF), DMF, and dimethylsulfoxide, solvents in which products **10**, **12**, and **13** are quite soluble (at least 10 wt % polymer at room temperature). All four polyimides are amorphous and show no indication (DSC) of undergoing first-order, endothermic melting transitions.

When heated under nitrogen [thermogravimetric analysis (TGA)], **10–13** exhibit initial weight loss ( $T_d$ ) at 249–307°C (Table III); amine elimination (reversal of the Michael addition process) is the probable decomposition pathway.<sup>2</sup>

At room temperature, cast or molded films of reasonably flexible **10** and **13** are tough and easily creased without cracking, but polyimide **12**, the product of bisimidoctane **4** and *N,N'*-dimethyl-1,6-hexanediamine (**14**), is elastomeric. Compression-molded (110°C at 138 MPa) films of freshly prepared **12** ( $\eta_{\text{inh}} = 1.70 \text{ dL/g}$  after molding) show a yield stress of 1.5 MPa and an ultimate tensile

TABLE III  
 Thermal Properties of Polyimides 10-13

No.	$T_g$ (°C)	$T_d$ (°C) <sup>a</sup>
10	86	249
11	—	280
12	ca. 0	285
13	95	307

<sup>a</sup> Initial weight loss in a nitrogen atmosphere (see Experimental).

strength of 9.3 MPa with ca. 1700% elongation; such films, when elongated 1000%, vigorously "snap" to their original shape when allowed to do so. The reason for the elastomeric nature of thermoplastic, soluble 12 is not clear, but could involve pseudo-crosslinks that are generated through secondary valence interactions<sup>9</sup> among the polar carbonyl groups abundantly available in 12. In any event, complicating the assessment of these interactions is the slow, irreversible formation of actual covalent crosslinks in 12 during storage of the resin under ambient laboratory conditions. Evidence for such crosslinking includes the observation that the  $\eta_{inh}$  of one sample, kept in the dark at ca. 25°C, increased from 1.26 dL/g (determined immediately after isolation) to 1.60 dL/g after 34 days, and, within 48 days, this 12, which remained amorphous (DSC) and elastomeric, gave only a gel in solvents (CHCl<sub>3</sub>, THF, DMF) that readily dissolve the virgin polymer. Intermolecular bond formation is more rapid at elevated temperatures (for example, another sample of 12 became insoluble after only 30 min at 160°C) and may be due to the onset of reactions of Scheme I in bulk 12; of course, *m*-cresol, the proton source that prohibits Scheme I during synthesis of 12, is not present in the purified material. The other more rigid polyimides (10, 11, and 13), having relatively immobile end groups at room temperature, remain soluble indefinitely.

## EXPERIMENTAL

**General.** Diamines 14, 15, and 20 and *m*-cresol were obtained from the Aldrich Chemical Co. and were distilled (under nitrogen or at reduced pressure) shortly before use. All other reagents and solvents, purchased from various commercial sources, were used as received. Glassware was oven dried (150°C) prior to each experiment, and all reactions were allowed to run under a blanket of nitrogen.

Inherent viscosities ( $\eta_{inh}$ , Table I) of 10-13 (0.5 g/dL) were determined using Cannon-Ubbelohde viscometers, sizes 50 (CHCl<sub>3</sub>) and 100 (*m*-cresol), maintained at 25°C with a constant temperature water bath.

Infrared (IR) spectra of 10-13 were recorded for samples as films cast from CHCl<sub>3</sub> onto NaCl plates (10, 12, 13) or as KBr pellets (11) with a Perkin-Elmer Model 727B Spectrophotometer; <sup>1</sup>H NMR spectra of polymers 10, 12, and 13 were obtained of samples in tetrachloroethane-d<sub>2</sub> at 100°C (hexamethyldisiloxane as the internal standard) using a Varian Model EM 390 Spectrometer (90 MHz), fitted with a Model EM 3940 Variable Temperature Probe. Elemental analyses were performed by Dow Chemical Co., Michigan Division Analytical Laboratories.

The  $T_g$  of 10–13 were determined for bulk samples in closed pans heated at 10°C/min using a DuPont Model 990 Thermal Analyzer with Cell Base Module II (DSC); values shown in Table II were measured at the intersection of tangents to the change in slope in the trace of relative (to air) heat capacity vs. temperature. Decomposition temperatures (Table II;  $T_d$  defined here as initial weight loss) of the polymers were obtained for bulk samples heated at 10°C/min under a nitrogen flow of 40 mL/min using a DuPont Model 951 Thermogravimetric Analyzer (TGA).

***N,N'*-Bismaleimido-4,4'-Diphenylmethane (2).**<sup>2</sup> A solution of methylenedianiline (6, 113.8 g, 0.57 mol) in  $\text{CHCl}_3$  (500 mL) was added dropwise to a stirred, chilled (ice bath) solution of maleic anhydride (5, 113.8 g, 1.16 mol) also in  $\text{CHCl}_3$  (600 mL). After the addition was complete, the resulting mixture was allowed to stir at room temperature for 2 h; the precipitated bisamic acid 8 (223.0 g, 98%) was collected and allowed to air dry. A mixture of the 8 (160.0 g, 0.41 mol),  $\text{Ac}_2\text{O}$  (82.8 g, 0.81 mol), nickel (II) acetate tetrahydrate (37 g), and triethylamine ( $\text{Et}_3\text{N}$ , 27.0 g, 0.27 mol) in acetone (370 mL) was allowed to stir at ca. 25°C. After 2.5 h, the 8 was completely dissolved and the resulting solution was allowed to stir for an additional 48 h, during which bismaleimide 2 (90.0 g, 62%) precipitated. Recrystallization of this crude 2 from 1:1  $\text{CHCl}_3$ /methanol (MeOH) gave 2 as light yellow needles [76.5 g, 52% based on starting 5 and 6]: mp 162°C (DSC), lit<sup>2</sup> 158°C.

***N,N'*-Bismaleimido-1,8-Octane (4).**<sup>3</sup> A solution of diaminoctane (7, 100.9 g, 0.70 mol) in  $\text{CHCl}_3$  (400 mL) was added dropwise to a stirred, chilled (ice bath) solution of 5 (137.2 g, 1.40 mol) also in  $\text{CHCl}_3$  (600 mL). The resulting mixture was allowed to stir at ca. 25°C overnight, after which precipitated bisacid 9 (234.7 g, 98%) was collected and allowed to dry. A slurry of 9 (100.0 g, 0.29 mol), nickel (II) acetate tetrahydrate (2.6 g),  $\text{Et}_3\text{N}$  (19.2 g, 0.19 mol), and  $\text{Ac}_2\text{O}$  (118.6 g, 1.16 mol) in acetone (265 mL) was allowed to stir at reflux for 6 h; the resulting solution was allowed to stand overnight at room temperature, and bismaleimide 4 (38.0 g) precipitated. This 4 was collected by filtration, and water was added to the filtrate to precipitate additional crude 4 (27.0 g). The combined portions of 4 were washed with water, allowed to air dry, and recrystallized three times from 5:3  $\text{CHCl}_3$ /MeOH to give 4 as pale yellow needles [16.2 g, 18% (based on starting 5 and 7)]: mp 123°C (DSC), lit<sup>3</sup> 120–2°C.

Although 4, prepared as above, is sufficiently pure to yield high-molecular-weight 12 and 13, further purification of the bisimide was effected by chromatographic separation of the compound on silica gel columns (Waters Prep Pak 500) with a solution of 15% ethyl acetate in methylene chloride (v/v) as the eluent using a Waters Model Prep LC 500 Liquid Chromatograph. This procedure afforded 4 as sparkling white needles [mp 123°C (DSC)] with 67–70% recovery.

**Poly[(2,5-Dioxo-3,1-Pyrrolidinediyl)-4,1-Phenylene(methylene)-4,1-Phenylene (2,5-Dioxo-1,3-Pyrrolidinediyl)(Methylimino)-1,6-Hexanediy] (Methylimino)]—Polymer 10.** A solution of 2 (10.000 g, 0.028 mol) and *N,N'*-dimethyl-1,6-hexanediamine (14, 4.027 g, 0.028 mol) in *m*-cresol (40 mL) was allowed to stir (magnetic stirrer) at ca. 25°C. After 1 h, the solution had become so viscous that stirring was no longer effective; the solution was allowed to stand for 18 h and then was mixed with MeOH, using a Brinkman Polytron homogenizer to give off-white granular solid (17.6 g, 125%) which was precipitated

from  $\text{CHCl}_3$  (50 mL) with excess MeOH (600–700 mL) three times. The polymer then was powdered with fresh MeOH with the homogenizer. Drying *in vacuo* (25°C) for 48 h gave 10 as tan, fibrous powder (8.350 g, 60%): IR 2920, 1790 ( $\text{C}=\text{O}$ ), 1700 ( $\text{C}=\text{O}$ ), 1505, 1378, 1165, and 745  $\text{cm}^{-1}$ .

**Poly[1,4-Piperazinediyl (2,5-Dioxo-3,1-Pyrrolidinediyl)-1,4-Phenylene-1,4-Phenylene (2,5-Dioxo-1,3-Pyrrolidinediyl)]—Polymer 11.** A mixture of 2 (14.000 g, 0.039 mol), piperazine (15, 3.365 g, 0.039 mol) and *m*-cresol (40 mL) was magnetically stirred at 110°C for 45 min, after which the resulting solution had become so viscous that stirring was no longer possible. The hot solution carefully was mixed with a large (1 L) excess of MeOH in a Waring blender to give granular 11, which was powdered in fresh MeOH using the homogenizer. Drying *in vacuo* (80°C) for 24 h gave 11 as tan powder (14.512 g, 84%): IR 2925, 2810, 1790 ( $\text{C}=\text{O}$ ), 1700 ( $\text{C}=\text{O}$ ), 1500, 1380, 1160, 1000, and 780  $\text{cm}^{-1}$ .

**Poly[(2,5-Dioxo-1,3-Pyrrolidinediyl)(Methylimino)-1,6-Hexanediyl-(Methylimino)(2,5-Dioxo-3,1-Pyrrolidinediyl)-1,8-Octanediyl]—Polymer 12.** A solution of 4 (10.000 g, 0.033 mol) and 14 (4.747 g, 0.033 mol) in *m*-cresol (40 mL) was allowed to stand at ca. 25°C for 48 h and then poured into MeOH (600 mL) to precipitate tacky, resinous 12. The polymer was worked under MeOH in a Teflon beaker with a Teflon spatula until the material became tough and rubbery. This 12 was reprecipitated from  $\text{CHCl}_3$  (50 mL) with MeOH (600–800 mL) three times, taken up a final time in  $\text{CHCl}_3$  (50 mL), and cast on Teflon plates, which were allowed to stand under a stream of nitrogen for 72 h. Drying *in vacuo* at 25°C for 24 h and then at 80°C for 24 h gave 12 as a light green, transparent film (8.520 g, 58%): IR 2940, 2855, 1790 ( $\text{C}=\text{O}$ ), 1700 ( $\text{C}=\text{O}$ ), 1435, 1400, 1355, and 1145  $\text{cm}^{-1}$ .

**Poly[(2,5-Dioxo-1,3-Pyrrolidinediyl)-1,4-Piperazinediyl (2,5-Dioxo-3,1-Pyrrolidinediyl)-1,8-Octanediyl]—Polymer 13.** A solution of 4 (10.000 g, 0.033 mol) and 15 (2.834 g, 0.033 mol) in *m*-cresol (50 mL) was allowed to stir for 72 h at room temperature. The solution then was poured into MeOH (1 L) to precipitate fibrous 13, which was powdered in fresh MeOH using the homogenizer. Drying *in vacuo* (25°C) for 24 h gave 13 as yellow powder (10.099 g, 79%): IR 2950, 2860, 1790 ( $\text{C}=\text{O}$ ), 1705 ( $\text{C}=\text{O}$ ), 1410, 1150, and 1020  $\text{cm}^{-1}$ .

**Mechanical Properties of Polymer 12.** A sample of 12, having  $\eta_{\text{inh}} = 1.39$  dL/g, was compression-molded between Teflon sheets in a Dake laboratory press at 110°C and 138 MPa to give films with thicknesses of about 500  $\mu\text{m}$ ;  $\eta_{\text{inh}}$  of the resin which remained soluble after molding was 1.70 dL/g. Yield stress (1.1–3.1 MPa; 1.5 MPa average), ultimate tensile strength (7.6–11.7 MPa; 9.3 MPa average) and elongation (1570–1970%; 1700% average) were determined at 25°C for 12 specimens, 2.54 cm in width, using an Instron Model 1125 Tensile Tester with a crosshead speed of 50 cm/min.

The authors are grateful to Mr. Stephen Konopnicki for various analytical services performed throughout the project.

## References

1. M. G. Gherasim and I. Zugravescu, *Eur. Polym. J.*, **14**, 985 (1978).
2. J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1185 (1973).



3. H. D. Stenzenberger, K. U. Heinen, and D. O. Hummel, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2911 (1976).
4. N. E. Searle, U.S. Pat. 2,444,536 (1948).
5. J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 159 (1976).
6. D. G. Smyth, A. Nagamatsu, and J. S. Fauton, *J. Am. Chem. Soc.*, **82**, 4600 (1960).
7. T. V. Sheremeteva, G. N. Larina, M. G. Zhenevskaya, and V. A. Gusinskaya, *J. Polym. Sci., Part C*, **16**, 1631 (1967).
8. M. G. Hargreaves, J. G. Pritchard, and H. R. Dave, *Chem. Rev.*, **70**, 439 (1970).
9. R. Bonart, *Polymer*, **20**, 1389 (1979).

Received May 24, 1983

Accepted October 14, 1983