N,N'-Biisomaleimide. I. Ring-Opening Polymerization with Diamine

Y. L. Fan

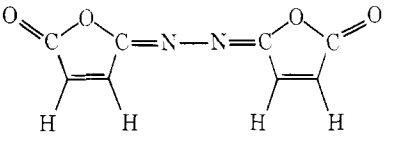
Union Carbide Corporation, Chemicals and Plastics Research and Development Department, Bound Brook, New Jersey 08805. *Received May 6, 1975*

ABSTRACT: The polymerization of N,N'-biisomaleimide with various diamines was investigated. Ring-opening polymers having a nylon-like structure were obtained. These polymers have been characterized by their spectroscopic data and physical properties. The latter are strongly influenced by the state of the labile maleic double bond and hydrazide linkage in the backbone.

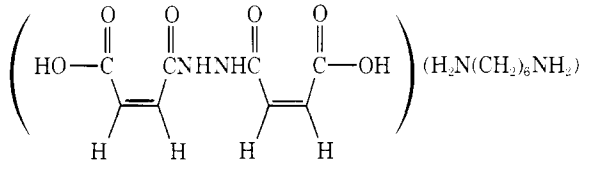
In 1958, Feuer and Rubinstein reported the synthesis of a new heterocyclic compound from the reaction of hydrazine and maleic anhydride.[1] That compound was later identified to be the N,N'-biisomaleimide (I)[2] instead of the N,N'-bimaleimide assigned by the original authors. Reactions of I and its derivatives with a variety of organic reagents were also described by the latter group.[2,3]

The polymerization of alkylene bis(isomaleimide) with an α pyrone was studied by Cotter and his coworker.[4,5] The reaction was reported to proceed sluggishly and produce a low molecular weight polymer. Nevertheless, the product was characterized as an amide-like linear polymer.

In contrast to its alkylene derivatives, I was found to undergo very rapid reaction with the dinucleophiles, particularly the diamines, leading to a polymeric product.



I



II

In the present work, a systematic study on the ring-opening polymerization of I with various diamines was carried out. The polymerization of salt of a precursor of I with 1,6-hexamethylenediamine (II) was also conducted. The polymeric products were identified and their properties described.

Experimental Section

N,N'-Biisomaleimide (I) was prepared from hydrazine and maleic anhydride and purified according to the procedures given in the literature.[2] The product used for polymerization had an mp of 260° (lit. 260°[2]). Anal. Calcd for $C_8H_4N_2O_4$: C, 50.00; H, 2.04; N, 14.58. Found: C, 50.15; H, 2.19; N, 14.68.

Solution Polymerization. Method A. Into a 50-ml three-necked flask, fitted with a mechanical stirrer, thermometer, nitrogen inlet, and a drying tube, there was placed 0.01 mol of a diamine and 20 ml of purified dimethyl sulfoxide (DMSO). Upon dissolution (or forming a uniform slurry), 0.01 mol of I was added rapidly into the reaction vessel. An exothermic reaction occurred immediately and an external cooling bath was used to maintain the desired reaction temperature. The polymer was recovered by coagulation in an acetone–ether mixture. After repeated washings, the polymer was collected by filtration and dried at 75° under vacuum.

Method B. In this instance, the diamine was added from a DMSO solution to a slurry of I in DMSO. Polymer was recovered by a similar procedure described above except an ice–water mixture was used as the coagulant.

Melt Polymerization. The salt (II) of 1,2-bis(3-carboxyacryl-yl)hydrazine,[2] which is the precursor of I, and 1,6-hexamethylene diamine was prepared by dissolving equal molar amounts of the two materials in DMSO. An exothermic reaction was observed upon mixing. After over-night stirring, the salt was collected by precipitation in acetone, washed thoroughly with acetone, and dried at 70° under vacuum. The conversion was usually quantitative, and the product had an mp of 165°. Anal. Calcd for $C_{14}H_{24}O_6N_4$: C, 48.83; H, 6.97; N, 16.27. Found: C, 48.42; H, 6.71; N, 15.99.

II was charged into a polymerization tube and heated to 165°. A nitrogen inlet capillary to the bottom of the tube provided agitation of the melt. The polymerization was continued for a period of 2 hr while the temperature was raised gradually to 175°. After cooling to room temperature, the product was removed from the tube, washed repeatedly with acetone, and dried at 70° under vacuum. A dark brown solid was obtained, and the conversion was usually 95% or greater. This apparent polymeric product was insoluble in DMSO, formic acid, or m-cresol, and was infusible up to 310°.

Isomerization Measurement. Isomerization of the growing polymer chains was measured by following the NMR signals of the maleic (6.4 ppm) and fumaric (7.1 ppm) protons of samples taken from the polymerization medium during the course of a polymerization. Formation of the fumaric double bonds usually precedes the polymer precipitation.

Instrumentation. NMR spectra were measured with a Varian A-60 spectrometer in either DMSO or formic acid solution. Chemical shifts were expressed in ppm using tetramethylsilane as an internal standard. Ir spectra were obtained from either solution-cast films, or potassium bromide pellets, or Nujol emulsions using a Beckman IR-5 instruments. Solution-cast films were used for the x-ray measurements.

Mass Spectrometer Analysis. Polymer (1.58 g) was placed in a Pyrex combustion tube and evacuated at 10^{-6} mm at 70° for 15 hr. Thereafter, the pump values were closed and the tube was held at 185° for 10 hr. The gaseous products were analyzed by a Varian Model 66 cycloidal double-focusing instrument.

Polymer Characterization. Unless otherwise specified all reduced viscosities were measured in DMSO at 25°. Melting points were taken with a Thomas-Hoover capillary apparatus. Glass transition temperatures were determined from the temperature-modulus data measured with an Instron at a heating rate of 2°/min. Mechanical properties were determined in accordance with the ASTM procedures using solution-cast films.

Results and Discussion

Solution Polymerization. I reacts energetically with a diamine in DMSO solution producing a thermoplastic polymer. Results of the solution polymerization of I with various aliphatic diamines, and with aromatic and heterocyclic diamines, are summarized in Tables I and II, respectively.

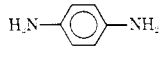
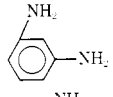
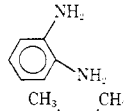
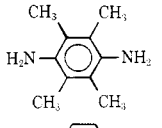
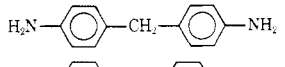
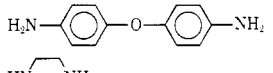
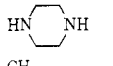
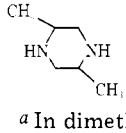
With the exception of some lower diamines, which resulted in insoluble, low molecular weight products, high molecular weight polymers were produced with the aliphatic diamines. NMR measurements have shown that the growing polymer chains underwent a rapid cis–trans isomerization at the maleic double bond in the presence of hy-

Table I
Solution Polymerization[a] of *N,N'*-Biisomaleimide with Aliphatic Diamines

Diamine	Method	Time, hr	Recovery, %	R.V.,[b] dl/g	Characteristics of polymer
H_2NNH_2	A	18.5	99	*c*	Yellow solid
$H_2N(CH_2)_2NH_2$	B	20	80	*c*	Yellow solid
$HNCH_3(CH_2)_2NCH_3H$	A	21	89	0.46	Pinkish, brown solid
$H_2N(CH_2)_4NH_2$	A	4	95	0.97	Yellow, fibrous polymer
	B	18	90	0.40	Yellow, fibrous polymer
$H_2N(CH_2)_6NH_2$	A	72	87	0.35	Yellow, fibrous polymer[d]
	B	15	67	0.29	Yellow, fibrous polymer[e]
$H_2N(CH_2)_8NH_2$	A	21	84	0.32	Yellow, fibrous polymer
$H_2N(CH_2)_{10}NH_2$	A	21	83	0.36	Yellow, fibrous polymer
	A	2.5	99	0.47	Yellow, fibrous polymer

[a] In dimethyl sulfoxide solution at room temperature. [b] Measured in dimethyl sulfoxide at 25°. [c] Insoluble. [d] Calcd for ($C_{14}H_{20}O_4N_4$): C, 54.55; H, 6.49; N, 18.18. Found: C, 54.24; H, 6.12; N, 17.81. [e] Found for ($C_{14}H_{20}O_4N_4$): C, 54.29; H, 6.13; N, 17.98.

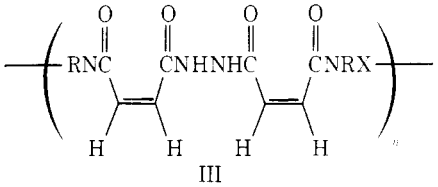
Table II
Solution Polymerization[a] of *N,N'*-Biisomaleimide with Aromatic and Heterocyclic Diamines

Diamine	Method	Time, hr	Recovery, %	R.V.,[b] dl/g	Characteristics of polymer
	A	15	99	0.23	Dark yellow solid
	A	19	94	0.19	Pale green solid
	A	19	34	0.07	Brown solid
	B	17	54	0.11	Pale yellow solid
	A	19	99	0.36	Yellow fibrous solid[c]
	A	17	95	0.19	Yellow solid
	B	7	76	0.11	White solid
	B	20	61	0.18	Yellow solid

[a] In dimethyl sulfoxide at room temperature. [b] Measured in dimethyl sulfoxide at 25°. [c] Calcd for $C_{21}H_{18}O_4N_4$: C, 64.61; H, 4.61; N, 14.35. Found: C, 64.17; H, 4.52; N, 14.61.

drazine or ethylenediamine. Because of a much limited solubility of the fumaric form the growing chains are terminated through precipitation. This finding is consistent with the results of an earlier report on the amine-catalyzed cis–trans isomerization.[6]

On the basis of model reaction studies reported earlier,[6] a linear polymer is believed to have formed through the ring opening of I. Polymers derived from the aliphatic or aromatic diamines may be represented by the general formula III. Where R is a hydrogen atom or an alkyl radical,



III

and X is a divalent organic radical. These polymers may be considered, therefore, as a class of (amide–hydrazide) copolymers.

Polymers derived from the aromatic or heterocyclic diamines are usually of low molecular weight. The relatively low percentages of polymer recovery in many instances are suspected to result from side reactions which led to the formation of low molecular weight by-products. Potential side reactions include a nucleophilic addition of diamine to the double bond, and transamidative cleavage at the hydrazide linkage.[6]

Melt polymerization of II should lead to the formation of a linear polymer identical with III. However, the molten polymer apparently underwent a postcyclization due to the hydrazide linkage to the corresponding poly(1,3,4-oxadiazole).[7] Consequently, only an insoluble, dark brown product was obtained. Elemental and infrared analysis indicated that the recovered product corresponded to a partially transformed polymer containing both the hydrazide and the oxadiazole units.[8]

Polymer Structure. The ring-opening structure III, as suggested by the earlier model reaction studies, is supported by spectroscopic data obtained in the present work.

Table III lists the characteristic frequencies in the infrared region of these polymers. The presence of amide and

Table III
Infrared Frequencies of Polymers Derived from N,N'-Biisomaleimide and Aliphatic Diamines

$H_2N(R)_nNH_2$ n =	NH stretching, cm^{-1}	Amide I, cm^{-1}	Amide II, cm^{-1}	Amide III, cm^{-1}	Sample form
2	3240	1590	1500	1270	DMSO solution
	3250	1590	1490	1260	KBr pellet
6	3240	1620	1540	1270	DMSO solution
	3310	1620	1550	1270	Film cast from formic acid solution
8	3230	1630	1540	1270	DMSO solution
	3300	1610	1540	1270	KBr pellet
10	3240	1620	1550	1270	DMSO solution
	3300	1620	1550	1270	Film cast from formic acid solution
Model compd[6]	3240–3340	1580–1600	1550	1285–1316	KBr pellet

hydrazide linkages in these polymers are consistent to the observed spectra. However, due to an overlapping of the frequencies, a distinction could not be made between those arising from the amide and from the hydrazide linkages.

NMR spectra measured at different temperatures showed distinctively the structural features of this type of polymer. Table IV lists the characteristic signals of a polymer derived from the 1,6-hexamethylenediamine. At temperatures below 70°, the polymer existed exclusively in the maleic form, and the amide and hydrazide protons were clearly distinguishable. Upon heating to 120°, the polymer became increasingly less soluble as a result of isomerization to the fumaric double bond. Such a structural transformation has been mentioned earlier as a major limitation in achieving high molecular weight polymers.

Physical Properties. As described in Tables I and II, most of the polymers derived from I and diamines are yellow, fibrous solids. They are soluble in DMSO and acidic solvents, such as the formic acid, although some hydrolytic cleavage is suspected to take place in the latter solutions. Film or fiber may be fabricated from these solutions.

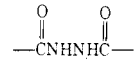
X-ray diffraction patterns indicated these polymers to be largely amorphous. Some physical and mechanical properties of two representing members are shown in Table V.

Because of their high polarities, the measured physical properties were substantially influenced by the amount of moisture absorbed. Their room temperature mechanical properties are comparable to those of the nylons, which is reasonable in view of their structural similarities.

Analysis by mass spectrometer of the gaseous products evolved when heating a III derived from 1,6-hexamethylenediamine revealed that in addition to water, which is the anticipated postcyclization by-product, carbon dioxide, oxygenated hydrocarbon, and hydrocarbon compounds were also observed. The latter corresponds to the decomposition products of a poly(hexamethylenadipamide),[9] and strongly suggests that degradation at the amide units also occurred during the postcyclization.

These polymers have a T_g beyond 100°. When they were heated to a temperature between 150 and 200°, depending on the polymer compositions, an apparent chemical transformation took place and a dark brown solid was obtained. Temperature-modulus measurements also showed a retention of substantial properties above T_g. This behavior, which was also observed during the melt polymerization mentioned earlier, is attributed to the postcyclization of the hydrazide units to the corresponding, thermally stable 1,3,4-oxadiazole structure.

Table IV
Characteristic NMR Signals of Polymer Derived from N,N'-Biisomaleimide and 1,6-Hexamethylenediamine[a]

Assigned proton type	Chemical shifts, ppm (multiplicity, area ratio) 70°C	120°C
	6.41 (s, 4)	6.41 (s)[c]
		7.11 (s)[c]
	8.86 (t,[b] 2)	*d*
	11.5 (s, 2)	*d*

[a] Measured in DMSO. [b] Usually appeared as an unresolved broad singlet. [c] Area ratio changed continuously toward higher Fumaric content. [d] Due to a decreasing polymer solubility in the medium, these signals became too weak to detect.

Table V
Some Physical and Mechanical Properties of Polymers Derived from N,N'-Biisomaleimide and Aliphatic Diamines

	$H_2N(CH_2)_nNH_2$ n = 4	n = 10
R.V., dl/g[a]	0.97	0.47
T_g, °C	125	130
Tensile strength,[b] psi	9600	8000
Tensile modulus,[b] psi	400000	440000
Elongation,[b] %	4	3.5
Tensile impact strength,[c] (ft lb)/in.[3]	45	10
Oxygen permeability,[d] (ml (STP) mil)/(100 in.[2] 24 hr atm)	1.4	10
Water permeability,[d] (ml (STP) mil)/(100 in.[2] 24 hr atm)	4450	1200

[a] Measured in DMSO at 25°. [b] ASTM D638. [c] ASTM D1822. [d] ASTM D1434-66 Method M.

The barrier properties of these polymers are worth mentioning. While they possess a relatively low oxygen permeability, they are highly permeable to water vapor. By increasing the length of the methylene bridge in the backbone, their permeability behavior may be altered from a nylon-like material toward the direction of that of the polyethylene which is characterized by a high oxygen permeability but very low water vapor transmission.

References and Notes

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