Conformational Properties of Structurally Rigid Polyamides. Hydrodynamic and Dielectric Properties of Polyamides from *trans*-1,2-Cyclohexanedicarboxylic Acid and *trans*-2,5-Dimethylpiperazine

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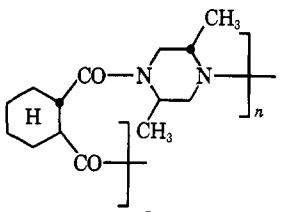
ABSTRACT: The results of some hydrodynamic and dielectric measurements, together with some optical data, for the polyamide derived from *trans*-1,2-cyclohexanedicarboxylic acid and *trans*-2,5-dimethylpiperazine are reported. The overall evidence suggests that the polymer chains assume a preferred conformation in solution and behave as rigid rods in which the structural units possess approximately the same conformational preference exhibited by the model amide II (see text).

The optical properties of a stereoregular sample of polyamide I have been reported[1] to show a marked enhancement of rotatory strength as compared to the model compound II, and this has been interpreted as indicating that the polymer assumes a preferred conformation in solution.[1]



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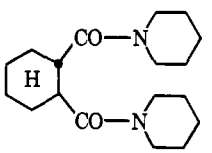

II

Optical data, however, cast no light on the problem of the identity of the specific conformations present in this polymer, and other conformation-dependent properties remained to be investigated.

We report here the results of some hydrodynamic and dielectric measurements which confirm that the polymer assumes a preferred conformation in solution. The overall evidence suggests that the polymer chains behave as rigid rods in which the structural units possess approximately the same conformational preference exhibited by the model amide II.

Results

The synthesis of optically active and racemic polyamide I has been already achieved by two independent methods, the Schotten–Bauman reaction[2] (interfacial method) and the active-ester method.[3] In the present case, the interfacial polycondensation was selected, and experimental conditions were explored (by varying the reactant ratio) which allow one to obtain racemic polyamides of different molecular weights.[4] The results obtained are collected in Table I. In Figure 1 is reported the variation of the inherent viscosity with the reactant ratio for three series of polycondensations. A series of *d,l* copolymers, with increasing content of *d*(+) isomer, prepared by the interfacial method,[2] was also included in the present study. Pertinent data are shown in Table II. In order to obtain a narrow fraction suitable for the calibration of a Mark–Houwink relationship, two samples of racemic polymer were fractionated by an extraction method. Fractionation data are reported in Table III.

The molecular weight distribution was remarkably narrow, both samples showing a low molecular weight tail superimposed with a sharp peak at the higher molecular weights (Figure 2). The narrow distribution suggests that a continuous fractional precipitation occurs during the reaction.[4]

The molecular weights of some of the fractions obtained were measured by membrane osmometry and by end group analysis (infrared), intrinsic viscosities were measured in dichloroethane (Table IV), and a $[\eta]$–M relationship was calibrated ($K = 1.35 \times 10^{-7}$, $a = 1.39$; Figure 3). Since the fractionation experiments had shown that the polymers possess a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \simeq 1.1$), the molecular weights of a number of unfractionated samples, racemic and optically active, were also measured by end group analysis (infrared) and plotted against their intrinsic viscosities. The results, shown in Figure 4, indicate that racemic and optically active polymers fit approximately the same $[\eta]$–M relationship with a slope of about 1.3.

The dipole moments of some racemic and optically active sample of different molecular weight were measured in benzene (Table V). The mean dipole moment for residue, $(\mu^2/n)^{0.5}$, was found constant irrespective of the molecular weight and steric purity of the polymers. The dipole moment values of our samples were found to be constant over the range of frequencies between 10^3 and 10^6 Hz (Table VI), indicating the absence of a critical frequency within this range. This result is in agreement with predictions based on theory.[5] From the Debye equation for the dielectric relaxation time of a sphere[6] combined with the Einstein equation for the limiting viscosity number of a sphere,[7] we can write

$$\tau = 1.2M\eta_0[\eta]/RT \quad (1)$$

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(1) C. G. Overberger, G. Montaudo, Y. Nishimura, J. Sebenda, and R. A. Veneski, *J. Polym. Sci., Part B*, 7, 219 (1969); see also C. G. Overberger, G. Montaudo, M. Mizutori, J. Sebenda, and R. A. Veneski, *ibid., Part B*, 7, 225 (1969); C. G. Overberger, R. A. Veneski, and G. Montaudo, *ibid., Part B*, 7, 877 (1969); C. G. Overberger, G. Montaudo, Y. Nishimura, J. Sebenda, and R. A. Veneski, presented at the IUPAC Symposium, Budapest, 1969; C. G. Overberger and Y. Shimokawa, *J. Polym. Sci., Part B*, 9, 165 (1971).

(2) Y. Nishimura, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1966.

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(4) T. W. Morgan, "Condensation Polymers: by Interfacial and Solution Methods," Interscience, New York, N. Y., 1965.

(5) T. W. Bates, K. J. Ivin, and G. Williams, *Trans. Faraday Soc.*, **63**, 1964 (1967).

(6) P. Debye, "Polar Molecules," Chemical Catalog, New York, 1929.

(7) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 606.

where $\tau = 1/2\pi f_c$ and η_0 is the solvent viscosity. For our polymer in DCE at 25°, $[\eta] = 1.35 \times 10^{-5} M^{1.89}$ cm³ g⁻¹ and $\eta_0 = 5.5 \times 10^{-3}$ g cm⁻¹ sec⁻¹. Inserting these values in the above equation, we obtain the relation

$$\log f_c = 16.64 - 2.39 \log M \quad (2)$$

from which it is possible to calculate the critical frequency

TABLE I
INTERFACIAL POLYMERIZATION OF (±)-*trans*-1,2-CYCLOHEXANEDICARBONYL CHLORIDE WITH *trans*-2,5-DIMETHYLPIPERAZINE

Sample[a] (mol)	mol of amine/l. of H_2O	mol of acid chloride/l. of CH_2Cl_2	Soap,[b] g	Yield, %	Mp, °C dec	η_{inh}[c] (DCE, 25°)
100 (0.0056)	0.40	0.05		58	285–290	0.105
101 (0.011)	0.40	0.10		93	304–308	0.138
102 (0.0136)	0.40	0.15		94	315–320	0.140
103 (0.0193)	0.40	0.25		79		0.205
104 (0.0235)	0.40	0.335		97	310–316	0.175
105 bis (0.0165)	0.66	0.15		98	326–332	0.248
106 (0.0056)	0.40	0.05	0.18	97		0.120
107 (0.011)	0.40	0.10	0.34	90	326–336	0.216
108 (0.0136)	0.40	0.15	0.44	63		0.183
109 (0.0193)	0.40	0.25	0.62	87		0.195
110 (0.0235)	0.40	0.355	0.70	91		0.201
111 (0.0245)	0.40	0.42	0.20	96	322–328	0.241
112 (0.032)	1.60	0.305	0.25	96		0.234
113 (0.0058)	0.70	0.05		99		0.211
114 (0.0090)	0.70	0.08		98		0.194
115 (0.011)	0.70	0.10		94		0.307
116 (0.0155)	0.70	0.15		97	330	0.331
117 (0.0195)	0.70	0.20		96		0.256
118 (0.0263)	0.70	0.30		95	317–327	0.595
119 (0.0365)	0.70	0.50		90	310–315	0.195
120 (0.0508)	0.70	0.70		87		0.279
121 (0.0263)	0.70	0.30		96		0.135
122 III (0.0263)	0.70	0.30		90		0.154
123 IV (0.0263)	0.70	0.30		88		0.143
124 (0.0263)	0.70	0.30	0.85	89		0.175

[a] Equimolecular amounts of amine and acid chloride were always used. Total amounts of solvents, 125 ml. [b] Laurylsulfonate. [c] $\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/100 ml.

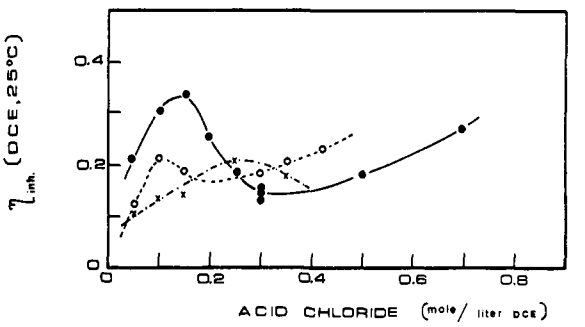

Figure 1. Interfacial polycondensation of (±)-*trans*-1,2-cyclohexanedicarbonyl chloride with *trans*-2,5-dimethylpiperazine as a function of reactant concentration: (●) 0.7 mol of amine/l. of H_2O, (○) 0.4 mol of amine/l. of H_2O, (×) 0.4 mol of amine/l. of H_2O plus soap (10% with respect to reactant amount).

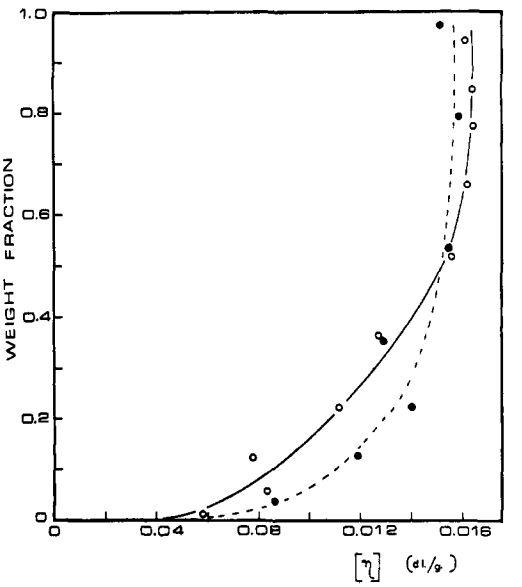

Figure 2. Distribution curves for two racemic samples of *trans*-1,2-CHDCA-DMP polyamide: (○) sample 121, $\bar{M}_w/\bar{M}_n = 1.04$; (●) sample 119, $\bar{M}_w/\bar{M}_n = 1.015$.

TABLE II
d,l COPOLYMERS FROM OPTICALLY ACTIVE *trans*-1,2-CYCLOHEXANEDICARBONYL DICHLORIDE AND *trans*-2,5-DIMETHYLPIPERAZINE

Sample	(+), mol %	$[\alpha]_D$[a]	$[\eta]_{DCE}$[b]	$[\eta]_{MeOH}$[b]	$[\eta]_{MeOH,C_6H_6}$[b,c]	$\bar{M}$[d]
133	97.0	−114.6	0.168	0.248	0.273	25,000
134	89.5	−91.6	0.267	0.295	0.455	35,000
135	80.0	−71.6	0.314	0.329	0.459	38,000
138	75.5	−63.8	0.318	0.352	0.489	38,500
136	71.2	−50.8	0.320	0.348	0.463	39,000
139	64.7	−41.7	0.339	0.371	0.526	42,000
140	60.1	−29.3	0.378	0.399	0.597	44,000
137	55.7	−13.8	0.334	0.377	0.555	41,000
141	50.0	0	0.166	0.198	0.270	24,700

[a] Measured in methanol at 25°. [b] At 25°. [c] Volume ratio benzene/MeOH = 4:1. [d] Computed from the $[\eta] = KM^a$ relationship.

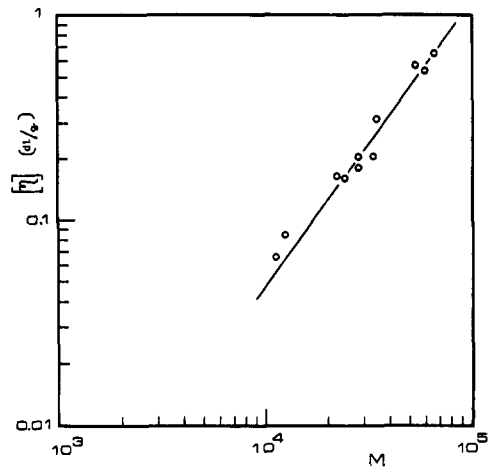

Figure 3. $[\eta]$–M relationship for fractions of racemic *trans*-1,2-CHDCA–DMP polyamide.

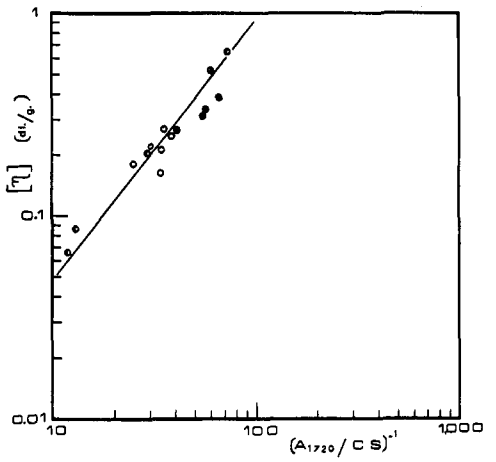

Figure 4. Relationship $[\eta]$–end group infrared absorbance for *trans*-1,2-CHDCA–DMP polyamide (concentration in grams per liter): (○) racemic whole samples, (◑) racemic fractions, (●) optically active whole samples.

TABLE III
FRACTIONATION DATA FOR RACEMIC *trans*-1,2-CHDCA–DMP POLYAMIDE

Fraction[a]	Weight, g	Cumulative wt fraction	Corr cumulative wt fraction	$[\eta]$,[b] dl/g	M[c]
121 A	0.08	0.021	0.011	0.058	11,600
121 B	0.26	0.087	0.054	0.083	15,000
121 C	0.27	0.156	0.122	0.077	14,200
121 D	0.51	0.286	0.221	0.111	18,500
121 E	0.60	0.439	0.363	0.126	20,200
121 F	0.57	0.585	0.512	0.156	23,600
121 G	0.55	0.726	0.655	0.162	24,300
121 H	0.33	0.810	0.768	0.164	24,500
121 I	0.29	0.885	0.847	0.164	24,500
121 J	0.45	1.000	0.943	0.160	24,000
119 A	0.31	0.070	0.035	0.086	15,300
119 B	0.44	0.170	0.120	0.119	19,500
119 C	0.44	0.270	0.220	0.141	22,000
119 D	0.72	0.434	0.352	0.129	20,800
119 E	0.92	0.643	0.539	0.154	23,500
119 F	1.37	0.955	0.799	0.158	24,000
119 G	0.20	1.000	0.978	0.150	23,000

[a] 121 (whole sample), η_{inh} = 0.135; 119 (whole sample), η_{inh} = 0.20. [b] Measured in DCE at 25°. [c] Calculated from $[\eta] = 1.35 \times 10^{-7} M^{1.39}$.

TABLE IV
VISCOSITY–MOLECULAR WEIGHT DATA FOR FRACTIONS OF RACEMIC *trans*-1,2-CHDCA–DMP POLYAMIDE

Fraction	$\bar{M}_n$	$[\eta]$,[c] dl/g
125 K	22,350[a]	0.162
112 A	24,400[a]	0.160
112 B	28,250[a]	0.180
117 A	28,250[a]	0.205
117 B	33,800[a]	0.207
116 A	34,300[a]	0.318
118 A	53,550[a]	0.580
118 B	59,800[a]	0.535
118 C	66,800[a]	0.650
103 A	11,200[b]	0.066
119 A	12,100[b]	0.086

[a] Measured in methanol by membrane osmometry at 30°. [b] Measured by infrared. [c] Measured in DCE at 25°.

TABLE V
DIPOLE MOMENT DATA IN BENZENE AT 25° FOR RACEMIC AND OPTICALLY ACTIVE SAMPLES OF *trans*-1,2-CHDA–DMP POLYAMIDES AND RELATED MODEL COMPOUNDS

Compound	n[a]	M	a_ϵ[b]	a_n[b]	μ,[c] D	$(\mu^2/n)^{0.5}$
$C_6H_{11}CONC_5H_{10}$		195.3	8.22	0.032	3.84 ± 0.04	
$C_6H_{10}(CONC_5H_{10})_2$[d] (II)		306.4	1.56	0.102	2.03 ± 0.06	
126 B[e]	34.0	8,500[g]	2.61	0.112	14.0	2.40
126 A[e]	37.2	9,300[g]	2.35	0.155	13.7	2.25
118 D[e]	240	60,000[g]	1.88	0.107	31.4	2.02
137[f]	164	41,000[g]	1.74	0.101	24.9	1.94
140[f]	176	44,000[g]	2.54	0.081	31.6	2.38
139[f]	168	42,000[g]	2.12	0.069	28.2	2.17
136[f]	156	39,000[g]	2.11	0.081	27.0	2.16
138[f]	154	38,500[g]	2.25	0.078	27.7	2.24
135[f]	152	38,000[g]	1.95	0.143	25.2	2.04
133[f]	100	25,000[g]	2.81	0.124	24.8	2.49

[a] $n = M/M_0$; $M_0 = 250$. [b] $a_\epsilon = [(\epsilon_{12} - \epsilon_1)/W_2]_{W_2 \to 0}$, $a_n = [(n_{12}^2 - n_1^2)/W_2]_{W_2 \to 0}$, ϵ_1 is the dielectric constant of the solvent, ϵ_{12} is the dielectric constant of the solution, W_2 is the weight fraction of solute, n_1 is the refractive index of the solvent, and n_{12} is the refractive index of the solution. [c] Calculated according to Guggenheim: $\mu^2(D^2) = 9.208(a_\epsilon - a_n)M \times 10^{-3}$. [d] Racemic. [e] Racemic fractions. [f] *d,l* copolymer (whole sample); see Table II. [g] Calculated from the $[\eta]$–M relationship.

(f_c) expected for our polymers of molecular weight M. It is easily recognized that a critical frequency below 10^6 Hz is expected only for polymer fractions having molecular weights above 30,000. The molecular weights of samples reported in Table V fall below this value or slightly above, except for sample 118 D (M = 60,000). (The use of a spherical model (eq 1) to estimate f_c is, in principle, incorrect, since we conclude (see below) that polyamide I has a rigid-rod type of conformation. More sophisticated equations are available for rigid rods (H. Block and A. M. North in "Advances in Molecular Relaxation Processes," Elsevier, Amsterdam, 1970, p 323), but relaxation times calculated through them come very close to those predicted for the random-coil molecules. Given the relatively low molecular weights of our samples, our estimates may be considered sufficiently approximated.)

TABLE VI
DIELECTRIC CONSTANT (ϵ_{12}) AND LOSS (ϵ'') FOR RACEMIC AND *d,l* COPOLYMERS OF *trans*-1,2-CHDCA–DPM POLYAMIDE AS A FUNCTION OF THE FREQUENCY

Sample (W_2)	Measuring frequency, Hz	ϵ_{12}[a]	ϵ''[a]	μ_1,[b] kHz	μ_2,[c] MHz
126A	10,000	2.176	0.0019		
(7.80×10^{-3})	5,000	2.176	0.0036		
	2,000	2.176	0.0089	14.8	13.7
	1,000	2.176	0.0170		
	500	2.176	0.0352		
	400	2.176	0.0550		
	200	2.178	0.0870		
138	10,000	2.169	0.0005		
(7.36×10^{-3})	5,000	2.169	0.0009		
	2,000	2.169	0.0021	24.01	27.7
	1,000	2.169	0.0042		
	500	2.169	0.0082		
	400	2.169	0.0101		
	200	2.169	0.0200		
133	10,000	2.184	0.0006		
(11.90×10^{-3})	5,000	2.184	0.0010		
	2,000	2.184	0.0020	25.5	29.1
	1,000	2.184	0.0039		
	500	2.184	0.0078		
	400	2.184	0.0089		
	200	2.184	0.0170		

[a] Measured in *trans*-1,2-dichloroethylene at 25°. [b] Calculated in *trans*-1,2-dichloroethylene at 25° according to Guggenheim: μ^2 (D^2) = $(6.766 \times 10^{-3})(a_\epsilon - a_n)M$. [c] Calculated in benzene; see Table V.

The optical rotatory properties of the sterically pure polyamide I have been already reported.[1] We have measured the ORD curves for the series of *d,l* copolymers reported in Table II. The curves are quite similar to that of the optically pure polymer, except for the intensity, showing a peak at 208 mμ and a trough at 224 mμ. The molar rotation values of the peaks *vs.* those of the troughs for each copolymer are reported in Figure 5.

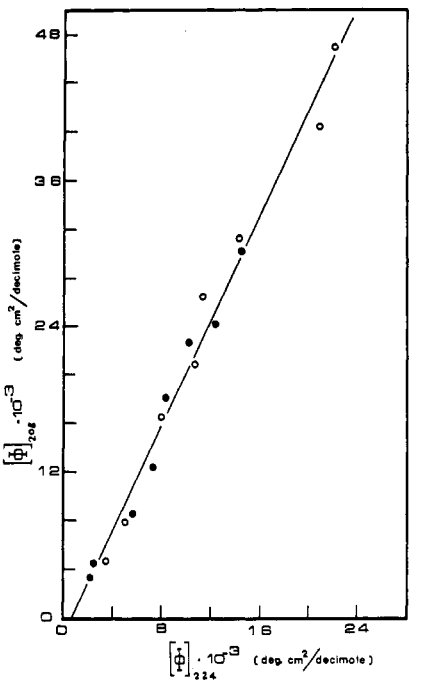

Figure 5. Plot of the molar rotation $[\phi]_{208}$(peak) *vs.* $[\phi]_{224}$(trough) for the series of *d,l* copolymers described in Table II: (●) TFE, (○) MeOH.

Discussion

The experimental evidence available for the discussion comes mainly from four sources of information:[8] (a) conformational preference of the model compounds, (b) hydrodynamic measures, (c) dipole moments, and (d) optical rotatory properties.

The results described in the preceding paper[8b] have shown that *trans*-2,5-dimethylpiperazine diamides are biased in the form with the methyl groups in the diaxial positions and that diamide II exists in solution in an extended molecular conformation. These data may directly provide a molecular model for the conformation of polyamide I. In fact, in order to generate the polymeric chain starting from diamide II, one need only replace the piperidine side rings with dimethylpiperazine rings. Since the latter are rigid units (see above) possessing the same chairlike shape of piperidine units, the chain may be continued without introducing new internal rotation angles with respect to diamide II.

Assuming that the extended conformation of diamide II is preserved in the polymer, the polyamide model results in a rigid rod in the cases of both racemic and optically active polymers, although the rods may be different in the two cases. The optically active polymer may, in fact, possess a definite sense of spiralization due to the configurational purity of the substituted cyclohexane rings, while this is unlikely in the case of the racemic polymer. (However, these differences are expected to play a minor role, since the dimethylpiperazine units allow cis and trans amide rotamers to be accommodated with equal ease in the structure.[8b])

This *a priori* molecular model must now be compared with the experimental results. The main conclusion from the hydrodynamic data is that racemic and optically active polymers both fit the same $[\eta]$–M equation with an exponent of 1.4 (membrane osmometry, Figure 3) or 1.3 (infrared end groups, Figure 4).

The value of this exponent is known to be highly indicative of the rigidity or flexibility of a polymer chain in solution.[9] To our knowledge, this is the highest exponent among all polymers thus far investigated, with the exception of polypeptides in helical form.[9,10] Polyisocyanates, which have recently been found to behave as stiff chains in solution, have an exponent of about 1.2.[11] Our viscosity data have been subjected to the usual treatment to differentiate between a randomly coiled and a stiff chain,[12] and severe deviations from the random statistics have been found. It seems rational, therefore, to conclude that polyamide I in solution behaves approximately as a stiff chain. The result is confirmed by dipole moment data.

(8) (a) Although nmr was extensively used for the investigation of the model compounds[8b] and work in this area is in progress in our laboratory for polymers as well, no relevant nmr data are available at the present time for polyamide I. (b) See G. Montaudo, P. Finocchiaro, P. Maravigna, and C. G. Overberger, *Macromolecules*, **5**, 197 (1972).

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(10) P. Doty, J. H. Bradbury, and A. M. Holtzez, *J. Amer. Chem. Soc.*, **78**, 947 (1956).

(11) N. S. Schneider, S. Futusake, and R. W. Lenz, *J. Polym. Sci., Part A-1*, **3**, 933 (1965).

(12) M. Kurata and W. H. Stockmeyer, *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).

The experimental value of the mean dipole moment per residue,[13–15] $(\mu^2/n)^{0.5}$, is independent of the molecular weight and is essentially constant both for racemic and optically active polymers (2.0–2.5 D, Table V). This value is considerably lower with respect to that calculated (~3.8 D) from eq 3 when a statistical cancellation of amide group moments is assumed[15]

$$\mu^2 = 0.92n\mu_0^2 \quad (3)$$

(μ is the dipole moment of a polymer chain of n units and μ_0 is the amide group moment (3.84 D, Table V)). The experimental value of $(\mu^2/n)^{0.5}$ comes very close to that measured for the model diamide II (2.03 D, Table V), and it may be obtained by introducing in eq 3 the dipole moment of diamide II (2.03 D) as μ_0.

This fact may be understood considering that the resultant moment of the diamide unit in its preferred (extended) conformation is oriented nearly perpendicular to the major chain axis[8b] and considering also that a random arrangement of the diamide units along the chain is likely to occur in the present case because the dimethylpiperazine rings allow cis and trans amide rotamers to be accommodated with equal ease in the polymer structure.[8b] Under these circumstances, the individual moment (μ_0) to be used in eq 3 is not the amide group moment but the experimental dipole moment of diamide II, and a statistical cancellation of these moments (eq 3) does not imply the flexibility of the polymer chain but only the absence of sizeable portions of the rod in perfectly helical conformations (*i.e.*, with a definite sense of spiralization of diamide II units in the rod). (It is interesting to note that a referee was puzzled at how we can conclude that a $(\mu^2/n)^{0.5}$ value independent of the chain length can be compatible with a rod-like structure rather than proving the existence of a random coil. We interpret our results as indicating that the structural repeat unit has a resultant dipole moment *perpendicular* to the main polymer axis with *no component parallel to it*. Under these circumstances, the $(\mu^2/n)^{0.5}$ value *must* be independent of the chain length (no parallel component) and *must* come close to the value found for diamide II. The absence of a sense of spiralization causes the random cancellation of the *perpendicular* components, so the overall dipole moment of the polymer will be given, approximately, by $\mu^2 = 0.9\mu_0^2 n$, where μ_0 is 2.03 D, *i.e.*, the diamide II dipole moment.) The stiff-chain model also accounts for the optical rotatory properties of the *d,l* copolymers (Figure 5). If a polymer is composed of conformationally rigid monomer units, portions of the polymer chain will have a fixed geometry. This allows coupling of identical chromophores to take place with consequent enhancement of the rotatory strength.[16] Optical properties result from short-range interactions, and provided that the chain is stiff, it is not necessary to have perfectly ordered sequences in order to get exciton interaction.[16–18] Accordingly, if optically active units are progressively introduced into a racemic stiff chain, the rotatory strength is expected to increase about linearly with the percentage of optically active material.

In our case, as already reported,[1] the sterically pure polymer shows a marked enhancement of rotatory strength, compared to the model compound diamide II, but data in Figure 5 show no abrupt changes in the ORD curves of *d,l* copolymers, therefore supporting the stiff-chain model.

Additional evidence in favor of the latter model is that the uv maxima are found shifted toward the red (210 mμ; MeOH) in both racemic and optically active polymers with respect to the model diamide II (204 mμ; MeOH). In fact, this red shift is usually interpreted[16,17] as indicating exciton splitting of the amide $\pi \rightarrow \pi^*$ transition.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer 237 infrared spectrophotometer, uv spectra were recorded on a Hitachi Perkin-Elmer EPS-3T spectrophotometer, and ORD spectra were measured with a Jasco ORD/CD/UV-S spectropolarimeter with 0.1–1.0-mm cell width and a concentration of $1–2 \times 10^{-2}$ mol of residue/liter.

Melting points (uncorrected) were obtained in glass capillary tubes sealed under vacuum and checked with a Kofler hot-stage microscope.

Polycondensation Procedure. (±)-*trans*-1,2-Cyclohexanedicarbonyl chloride was obtained according to the procedure described previously,[2] starting from *cis*-1,2-cyclohexanedicarboxylic anhydride. *trans*-2,5-Dimethylpiperazine available commercially was recrystallized twice from ethyl acetate; colorless plates were obtained, mp 117–118° (lit.[19] mp 118°).

Methylene chloride, obtained commercially, 1500 ml, was washed three times with 150 ml of concentrated sulfuric acid, once with 150 ml of water, twice with 150 ml of 0.5 *N* sodium hydroxide, and finally once with 150 ml of water. After drying over calcium chloride overnight, it was distilled into a flask which contained phosphorus pentoxide and allowed to stand overnight. It was then distilled and kept cold over activated 4A molecular sieves in the dark.

The polymerizations were carried out by the method of interfacial polymerization.[4] A typical example is described. In a Waring Blendor container precooled in a refrigerator were placed 2.68 g (0.0235 mol) of *trans*-2,5-dimethylpiperazine, 16.2 ml of methylene chloride, and 58.8 ml of cold water containing 0.047 mol of sodium hydroxide. To the rapidly stirred system was added all at once 4.90 g (0.0235 mol) of (±)-*trans*-1,2-cyclohexanedicarbonyl chloride in 50 ml of methylene chloride. The mixture was stirred for 10 min and poured into 500 ml of water. Methylene chloride was removed with gentle warming. The polymer which precipitated was filtered, washed with water, and dried *in vacuo* at 50°; the yield was 4.7 g (97%). The crude polymer was dissolved in chloroform at a concentration of 10%. The solution was filtered through a medium sintered-glass funnel and slowly dropped into 500 ml of *n*-hexane. After standing overnight, the polymer was filtered, washed with *n*-hexane, and dried *in vacuo* at 50°: η_{inh} = 0.175 (DCE, 25°).

Anal. Calcd for $C_{14}H_{22}O_2N_2$: C, 67.16; H, 8.86; N, 11.12. Found: C, 67.43; H, 8.65; N, 11.31.

Viscometry. Viscosities of polymers were measured in a Desreux-Bishoff suspended-level viscometer with such a capillary diameter as to give a flow time of 261 sec for DCE. The viscometer contained a coarse sintered-glass filter attached just below the reservoir so that the solutions were filtered as they rose into the capillary. The temperature was maintained at 25.00 ± 0.02°. The intrinsic viscosity was determined as the common intercept of linear plots of η_{spec}/C against concentration; the values of η_{spec}/C followed a strictly linear dependence on concentration.

Fractionation. The polymer was precipitated from a 5% DCE solution into the finely divided support material of a column.

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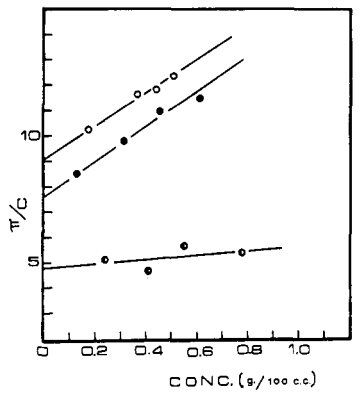

Figure 6. The reduced osmotic pressure π/C of three racemic *trans*-1,2-CHDCA–DMP samples as a function of the concentration at 30° in methanol: (○) sample 117 A, (●) sample 117 B, (◐) sample 118 A.

Polymer fractions were then eluted isothermally (30°) from the column with progressively better solvent liquids (200 ml of a mixture of DCE and cyclohexane) under nitrogen. The optimum ratio of DCE to cyclohexane was determined through calibration of the solubility curves. The time of contact of the solvent with the support material was 30 min; after this time, the polymer solution was dropped slowly into 700 ml of *n*-hexane. After standing overnight, the polymer was filtered, washed with *n*-hexane, and dried *in vacuo* at 50°.

Osmometry. Osmotic pressure measurements were carried out using Hellfritz-type osmometers[20] in methanol at 30 ± 0.02° using "allerfeinst" membranes previously conditioned in MeOH. Osmotic heads were measured by a cathetometer. The value $(\pi/C)_{C=0}$ was determined as the common intercept of linear plots of π/C against concentration; the values of π/C followed a linear dependence on concentration (Figure 6).

Infrared End Group Determinations. The end group (–COOH) analysis was carried out by measuring the adsorbance at 1720 cm^{-1} of 1% $CHCl_3$ polymer solutions, using a double-beam Perkin-Elmer 237 infrared spectrophotometer in a 1-mm NaCl cell. The absorbance per unit concentration (grams per liter) and unit cell width was assumed to be inversely proportional to the molecular weight of the polymer.

Dipole Moments. The dielectric constants were measured in benzene solution at 25 ± 0.02° with a DM 01 Dipolmeter WTW working at 2 MHz. Benzene (99.9%, Merck) was dried over molecular sieves. The dielectric constant of benzene was taken[21] to be 2.2725 at 25°. Attainable measuring sensitivity is about two units in the fourth decimal place in the dielectric constant. For measurement of refractive indices, a differential refractometer, BP 2000 V Brice-Phoenix, was used, which measured the difference in refractive index between a solution and benzene as the solvent, at 25°. Since this apparatus is equipped with a mercury vapor lamp, Δn measured at 436 and 546 mμ were reported at the sodium line values using the Chauchy dispersion formula and refractive indices of benzene[21] as 1.51979 at 436 mμ, 1.5021 at 546 mμ, and 1.49722 at 589 mμ, at 25°. The differences between Δn values measured at 546 mμ and reported at 589 mμ were very small, sensible only at the fifth decimal place. Use of the above instrument, although time consuming, allows a measurement having a sensitivity of about three units in the sixth decimal place of a refractive index difference. The dipole moments were calculated as described by Guggenheim.[22] The final formula obtained in benzene at 25° is $\mu^2(D^2) = 0.009208M \cdot (a_\epsilon - a_n)$, with a probable error of ±0.05 D. The dielectric constant and loss were measured in the range 10^2–10^4 Hz, with a General Radio Bridge Type 1311 A audiooscillator, which provided sine-wave signals with an accuracy of ±1%. The measuring cell was a cylindrical gold-plated condenser having an air capacitance of about 85.6 pF and a volume of about 10 ml. The instrument was calibrated with air and benzene (ϵ_1 = 1.000 and 2.2725, respectively, at 25°), and the calibration was checked with other liquids. The uncertainties were ±0.002 in ϵ_{12} and ±1% in ϵ''.

Measurements were also made in *trans*-ClCH=CHCl (99.9%), previously dried over molecular sieves (ϵ_1 = 2.145).[21] No sensible variation of ϵ_{12} was observed in the range of frequency investigated, as can be seen from Table VI.

The loss observed, ϵ'', is clearly due only to the dc conductance, as indicated from the data in Table VI.

The value of ϵ'' begins to increase sharply at low frequency and does not show a maximum, as one should expect if a relaxation process if operating.[5] Furthermore, the product of ϵ'' times the frequency is nearly constant, clearly indicating that the increase in ϵ''_{obsd} is due only to the conductance of the solution.[5]

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