and is by a transxanthation with water to form an unstable orthocarbonate.

2. Free cellulose xanthic acid (λ_{max} *ca.* 285 mμ) is the initial product of the reaction between cellulose xanthate and acid.

3. The absorption characteristics of a thin viscose film in acid quickly changes. The absorbance maximum is shifted to a lower wavelength as the free xanthic acid associates with excess hydrogen ions forming a protonated xanthic acid.

4. It is suggested that the protonated cellulose xanthic acid (λ_{max} *ca.* 270 mμ) is an oxonium-type compound.

5. Forty-five reactions, including redistribution of xanthate groups, describe the acid decomposition of cellulose xanthate.

Acknowledgments. The authors acknowledge the work done by Eugene Hollick, the helpful comments of Dr. W. B. Swann and J. W. Schappel and the drawings of Mrs. M. Upton.

Polyisonitriles. III. Synthesis and Racemization of Optically Active Poly(α-phenylethylisonitrile)[1]

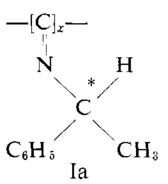
Frank Millich and G. Keith Baker[2]

Polymer Section, Chemistry Department, University of Missouri-Kansas City, Kansas City, Missouri 64110.

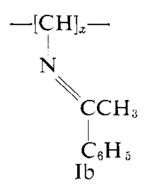
Received September 30, 1968

ABSTRACT: The homopolymerizations of *d*- and of *l*-α-phenylethylisonitrile have been successfully achieved with retention of configuration employing the catalyst system of Millich and Sinclair. The respective polymers of high molecular weight show specific rotations of the same sign yet tenfold greater magnitude than the monomers (*i.e.*, polymer samples, $[\alpha]^{27}\mathrm{D}$ $\sim$400°, $M^{27}\mathrm{D} = 500$ deg cm^2/g). The results tend to support one of two tentative assignments for the structure of the mer, although cautious interpretation shows the results not to be conclusive. Thermal racemization of the optically active polymer in refluxing toluene gives evidence of more than one process taking place, and reveals the generation of chromophores which absorb in the range of 310—390 nm. Nmr spectra of *d*-poly(α-phenylethylisonitrile), at 27 and 128°, are given.

The polymerization of α-phenylethylisonitrile and *n*-hexylisonitrile has been reported[3] using a unique catalytic system to form linear, soluble polymers having number-average molecular weights in the range of 25,000–150,000. Evidence for two possible structures of poly(α-phenylethylisonitrile) Ia and Ib has also been published.[4] Structure Ia appears to be the most reasonable on the basis of physical evidence and the known chemistry of isonitriles. Space-filling Leybold molecular models of four repeating units of Ia show that the polymer chain assumes the configuration of a tightly coiled helix. Furthermore, it appears very likely that the polymerization chain growth is stereoregular with regard to the conformation of the nitrogen substituent relative to the direction of chain growth.[4] That is, the possibility that the chain of repeating imine mer units can accomodate both *syn* and *anti* geometric isomeric forms is precluded by the large relative size of the nitrogen substituent and the inevitable spacial requirements of packing such units in a helical chain.



Ia



Ib

The infrared absorption of the polymer at 1625 cm^{-1} is assignable to a conjugated-imine chromophore. Conjugation in structure Ia can be attributed to planar *cis* and *trans* alignments of neighboring –C=N– groups providing steric restrictions allow such a conformation of the polymer chain. On the other hand, structure Ib, which might arise from Ia by a γ-hydrogen shift, is a possibility worth consideration. In this case the imine is conjugated with the phenyl group making it thermodynamically more favorable relative to Ia. In addition, structure Ib is consistent with some chemical and physical evidence exhibited by the polymer.[4] Millich and Sinclair had allowed that rearrangement conceivably could take place in a stereoregular fashion in a stereoregular polymer, by cooperative γ shifts of hydrogen atoms in a constant direction along the chain axis. Examination of molecular models shows this to be conceptually possible without any shift in the nuclear position of the transferring hydrogen atom, although a rearrangement of bonding and a change of bond angles would be necessary.

To test the possibility of a tautomeric rearrangement, and to attempt to establish additional information regarding the polymer structure, optically active

---

(1) Presented at the International Symposium on Macromolecular Chemistry, I.U.P.A.C., Sept 3, 1968, Toronto, Ontario, Canada.

(2) Predoctoral Research Fellow, Petroleum Research Fund 1777-A1.

(3) F. Millich and R. G. Sinclair, *Polym. Preprints*, **6**, 736 (1965); *J. Polym. Sci., Part A-1*, **6**, 1417 (1968).

(4) F. Millich and R. G. Sinclair, International Symposium on Macromolecular Chemistry, I.U.P.A.C., Brussels-Louvain, June 13, 1967; *J. Polym. Sci., Part C*, **22**, 33 (1968).

TABLE I

RESULTS OF POLYMERIZATION OF *dl*-, *d*-, AND *l*-α-PHENYLETHYLISONITRILE IN HEPTANE

Polymer prepn[a]	Monomer[b]	Free radical cocatalysts	Acid cocatalyst[c]	Reaction temp, °C	Reaction time	Yield,[d] %	$\overline{M}_n \times 10^{-4}$[e]	$[\eta]$, dl/g[f]	$[\alpha]^{27}$D, deg cm²/g[g]
1	*d*, *l*	2.0% DBP[h] + O_2	1% $NaHSO_4$ soln	50	14 days	60		0.204	
2	*d*, *l*	2.0% DBP + O_2	10% $NaHSO_4$ soln	85	24 hr	37		0.168	
3	*d*, *l*	O_2	10% $NaHSO_4$ soln	85	24 hr	Nil			
4	*d*	2.0% DBP + O_2	10% $NaHSO_4$ soln	50	120 hr	19		0.198	+298
5	*d*, *l*	2.0% DBP + O_2	10% $NaHSO_4$ soln	50	120 hr	28		0.175	0
6	*d*	O_2	6 *N* H_2SO_4 = A	60	68 hr	80	8.8		+324
7	*d*, *l*	O_2	A	60	68 hr	60	6.4		0
8	*d*	2.5% DBP + O_2	A	60	2 days	70	4.8		+365
9	*d*, *l*	2.5% DBP + O_2	A	60	2 days	55	4.3		
10	*d*	2.5% DBP	A	27	7 days	23		1.26	
11	*d*, *l*	2.5% DBP	A	27	7 days	9		1.16	
12	*d*, *l*	None	A	27	7 days	16		1.38	
13	*d*	O_2	A	50	3 days	55	11.5	0.824	+329
14	*l*	O_2	A	50	3 days	60	14.9	0.973	−382
15	*d*, *l*	O_2	A	50	3 days	47	11.2	0.940	
16	*d*, *l*	2.5% DBP	A	27	19 days	28	18.0	1.84	
17	*d*, *l*	2.5% DBP	A	27	19 days	36		1.74	
18	*d*, *l*	None	A	27	19 days	20		1.97	
19	*l*	2.5% DBP + O_2	A	27	19 days	32		1.93	−356
20	*d*	2.5% DBP + O_2	A	27	19 days	30		1.08	+328
21	*d*	10.0% DBP + O_2	A	60	68 hr	60		0.305	+325

[a] Each number represents a single preparation. [b] The notation *d* and *l* refers to dextro- and levorotatory α-phenylethylisonitrile, respectively. [c] Purified ground glass was treated with the listed solutions and then dried under vacuum. [d] Yield not corrected for recoverable, unused monomer. [e] Determined by dynamic membrane osmometry, in toluene at 30°, and extrapolated to infinite dilution. [f] Determined in toluene at 30°. [g] Determined in toluene. [h] The notation 2% DBP means 0.02 g of dibenzoyl peroxide per gram of monomer.

α-phenylethylisonitrile isomers were prepared and polymerized. This paper reports the results of such polymerizations as well as the racemization of the optically active polymers.

Experimental Section

1. Synthesis of *d*- and *l*-α-Phenylethylisonitrile. Resolution of a racemic mixture of *d*- and *l*-α-phenylethylamine was accomplished by a reported method,[5] by the fractional crystallization of the salts *d*-α-phenylethylamine 1-malate and, subsequently, 1-α-phenylethylamine *d*-tartrate. The free amines were liberated with excess 20% sodium hydroxide at room temperature. The specific rotations of the *d*- and *l*-amines, observed neat in a 1-dm length cell using a Reichert Wien polarimeter, were found to be $[\alpha]^{27}$D+39.5 and −40.4°, respectively. The boiling point of either epimer is 184–186° (745 mm). Ingersoll[5] reported similar values. The average yield of either pure, optically active amine was about 50% of the theoretical maximum.

The optically active amines were converted into the corresponding formamides with better than 90% yields by the reaction of the amines with ethyl formate[6] at 66° for 24 hr, and collection of the distillate fraction boiling at 142–145° (1 mm). The formamides exhibited no rotation of plane polarized light from a sodium lamp.

The formamides were converted into the optically active isonitriles by a modification of the method of Ugi and coworkers.[7] The introduction of gaseous phosgene into the reaction mixture in the original procedure was found to be an unsatisfactory technique because the gas inlet frequently became clogged with reaction products. The procedure was modified by first dissolving 30 g of cooled liquid phosgene (bp 8°) in 50 ml of methylene chloride at about −70°. This solution was slowly added during 1 hr to the reaction mixture of 39 g of N-formyl-α-phenylethylamine, 79 g of anhydrous pyridine and 250 ml of reagent grade methylene chloride, by means of a pressure-compensated dropping funnel, refrigerated with Dry Ice packs. Stirring was maintained for 1 more hr at −20°, and then 20 ml of distilled water was added in small portions. When the effusion of gas into a trap of sodium hydroxide solution ceased the flask contents were allowed to cool to room temperature and 200 ml of distilled water was added with stirring and a stream of nitrogen gas was blown through the entire system to clear the apparatus of phosgene. The organic phase was separated, washed with water and with 5% aqueous sodium bicarbonate, and again with water. After drying over magnesium sulfate for 20 hr, the solution was distilled, and α-phenylethylisonitrile was collected as the fraction boiling at 55–57° (1 mm), in a yield of 65%. The specific rotations, observed neat, were found to be $[\alpha]^{27}$D +37.2 and −35.8° for the optically active isonitriles, and corresponded in sign to their respective precursor amines.

The ultraviolet spectra of the optically active monomers in chloroform exhibited a single maximum at 2575 Å. The molar absorptivity at this wavelength was found to depend on the concentration of α-phenylethylisonitrile. For

---

(5) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1946, p 506.

(6) J. Moffat, M. V. Newton, and G. J. Papenmeier, *J. Org. Chem.*, **27**, 4058 (1962).

(7) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem.*, **77**, 492 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 472 (1965).

Table II

Optical Rotation Data as a Function of Concentration in Toluene at 27°

Sample[a]	Concn, g/ml	α, deg[b]	$[\alpha]^{27}\text{D}$, deg cm^2/g
A	0.0407	−14.5 ± 0.4	−356
	0.0306	−11.1 ± 0.1	−363
	0.0204	−7.3 ± 0.2	−358
	0.0153	−5.4 ± 0.1	−353
	0.0076	−2.7 + 0.1	−353
B	0.0350	+11.5 ± 0.2	+328
	0.0262	+9.0 ± 0.1	+344
	0.0175	+6.0 ± 0.1	+343
	0.0131	+4.2 ± 0.1	+321
	0.0066	+2.0 ± 0.1	+303

[a] The sample designation refers to that used in Figure 1. Samples A and B are referenced as no. 19 and 20, respectively, in Table I. [b] The variance indicated is calculated as the standard deviation of eight determinations of each angle.

example, samples which were 3.87×10^{-3}, 3.01×10^{-3}, and 1.61×10^{-3} *M* in monomer had molar absorptivities of 185, 189 and 198 l. mol^{-1} cm^{-1}, respectively, from which an expression of $\epsilon = 208 - 6000 \times$ molarity l. mol^{-1} cm^{-1} may be derived from a linear extrapolation to infinite dilution and from the slope of the curve.

2. Polymerization of *d*- and *l*-α-Phenylethylisonitrile. Primarily, procedures previously reported for the polymerization of α-phenylethylisonitrile were employed.[8] The polymerization involves (a) a solid surface (*i.e.*, ground glass) which contains a very light coating of an acid, (b) either oxygen or dibenzoyl peroxide, and (c) a solvent for the monomer, *e.g.*, heptane. The results of the polymerizations are summarized in Table I. Some variations from the original procedure by Millich and Sinclair were made. First, it was found that a less acidic ground glass than used in early studies gave better yields. The glass used in this work had about 4×10^{-2} mequiv of titratable protons per gram of glass. Second, it has been found that high molecular weight polymer can be obtained using sodium bisulfate coated on ground glass. An aqueous solution of sodium bisulfate was poured over clean ground glass. The glass was partially dried by suction filtration, and then thoroughly dried at 50° (1 mm) for 10 hr. As seen in Table I, a better yield of polymer was obtained when the aqueous solution used for coating the glass was of 1% concentration of sodium bisulfate than when it was 10%. Titration of the cocatalyst preparations showed 2.1×10^{-2} and 3.7×10^{-2} mequiv of titratable protons per gram of 1 and 10% $NaHSO_4$-coated ground glass, respectively.

Another variation from the standard polymerization procedure[8] was examined. It was observed that rather high molecular weight polymer was obtained, but at reduced rate of polymerization, in a procedure in which both oxygen and dibenzoyl peroxide were excluded from the reaction mixture (polymer preparations 12 and 18, Table I).

3. Molecular Weight Determinations. The number-average molecular weights were determined using a Model 502 Mechrolab Hi Speed membrane osmometer. All determinations were made at 30° in toluene and using Schleicher and Schuell Co. gel cellophane membranes, designated O-8, which have pores of 50 Å average diameter. The intrinsic viscosity values shown in Table I were determined at 30° in toluene and using a Cannon-Ubbelohde dilution viscometer.

4. Specific Rotation Determinations. The angle of rotation, α, of plane polarized light produced by the optically active monomers and polymers were determined using a Reichert Wien polarimeter, No. 2396. The light source was a sodium lamp (George W. Gates & Co.). All measurements were made at ambient temperatures. In the case of polymers, measurements were made on solutions of polymer in toluene. The variation of the angle of rotation as a function of concentration of both the dextro- and levorotatory polymers in toluene is shown in Figure 1. The data for these plots are given in Table II. In the concentration range shown, the rotation varies linearly with the concentration. The polymer solutions are red-brown, and solutions above about 6.0×10^{-2} g/ml were too concentrated to transmit enough light through cells of 1-dm light path length for satisfactory measurements.

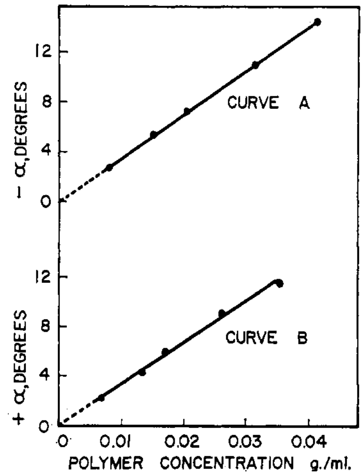


Figure 1. Dependence of optical rotation on the concentration of poly(α-phenylethylisonitrile) in toluene at 27° (*cf.*, Table II).

5. Thermal Racemization of Polymers of *d*- and *l*-α-Phenylethylisonitrile. Thermal racemizations of the optically active polymers were conducted with stirring, at the reflux temperature of the polymer solutions (concentration = 2 g/100 ml) and in the absence of any catalysts. These temperatures were near the reported boiling points of the pure solvents: benzene (80°), toluene (111°), and chlorobenzene (132°). The optical rotation was determined periodically, directly on each solution, at which time the heating was interrupted, the solution was cooled to 27° and adjusted to the original volume. The optical rotation was observed in a cell of 10 cm path length, and the solution was

---

(8) F. Millich, R. G. Sinclair, II, and G. K. Baker, "Macromolecular Synthesis," Vol. 4, John Wiley & Sons, Inc., New York, N. Y., in press.

TABLE III

THE EFFECT OF THERMAL TREATMENT ON THE OPTICAL ACTIVITY OF SOLUTIONS OF *d*- AND *l*-POLY(α-PHENYLETHYLISONITRILE)

Expt	Solvent	Temp, °C	Time lapsed, hr	α, deg	$[\alpha]^{27}_{\mathrm{D}}$, deg cm^2/g	Polarimeter cell concn, g/ml
1[a]	Benzene	80	0	-7.3 ± 0.1	-376	0.0194
			24	-7.0 ± 0.2	-360	0.0194
			168	-5.3 ± 0.1	-273	0.0194
2[b]	Chlorobenzene	132	0	$+8.9 \pm 0.1$	$+334$	0.0266
			6	$+1.0 \pm 0.1$	$+187$	0.0066
3[b]	Toluene	111	0	$+7.5 \pm 0.1$	$+325$	0.0231
			1	$+7.0 \pm 0.1$	$+303$	0.0231
			2	$+6.6 \pm 0.1$	$+286$	0.0231
			4	$+3.4 \pm 0.1$	$+271$	0.0125
			8	$+3.0 \pm 0.1$	$+239$	0.0125
			20	$+2.8 \pm 0.1$	$+225$	0.0125
			44	$+1.4 \pm 0.1$	$+225$	0.0063
4[a]	Toluene	111	0	-9.2 ± 0.1	-382	0.0242
			1.2	-8.7 ± 0.1	-363	0.0242
			2.2	-8.4 ± 0.1	-348	0.0242
			11.5	-3.9 ± 0.1	-323	0.0121
			27.5	-3.8 ± 0.1	-315	0.0121

[a] The polymer used in this experiment is that designated as no. 14 in Table I. [b] Polymer preparation no. 21, Table I.

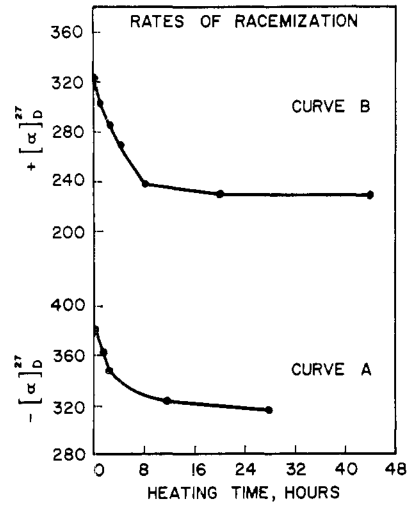


Figure 2. Changes of specific rotation of *d*- and *l*-poly(α-phenylethylisonitrile) as a function of heating time in refluxing toluene (*cf.*, Table III, expt 3 and 4); concentration = 2 g/100 ml.

then returned to the reaction flask with the aid of small amounts of solvent rinses of the cell. The original volume was reestablished by evaporation of solvent and then the heating was resumed.

It was observed that the polymer solution became darker in the red-brown color as time elapsed. For this reason it was sometimes necessary to make dilutions of the sample taken for the determination of the optical rotation.

The results of these experiments are summarized in Table III. The data show several interesting points. There is a loss of optical activity of both the *d* and *l* polymers of α-phenylethylisonitrile with increasing time of heating, and the loss of optical activity occurs more readily in the higher boiling solvents. Polymer heated at the reflux temperature in chlorobenzene exhibited a 44% loss in optical rotation after only 6 hr. Of course, for any determination of activation energies of the processes, the rates studied at different temperatures are confined to a single solvent.

A graphical plot of the specific rotation as a function of time for the data of experiments 3 and 4 of Table III is shown in Figure 2. As can be seen a nonzero limiting value of the specific rotation is approached with each polymer sample.

One might expect the loss of optical activity to follow first-order kinetics. As a test of this possibility, graphical plots of log $([\alpha] - [\alpha]_\infty)^{27}_{\mathrm{D}}$ as a function of time were made and are given in Figure 3. The values of $[\alpha]_\infty$ for the *d* and *l* polymers were taken as +225 and −310°, respectively. The dextropolymer exhibits a reasonably good straight line for the first few hours, and then exhibits curvature.

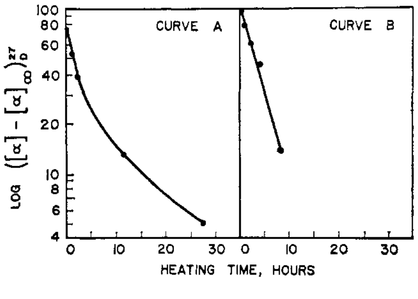


Figure 3. First-order plots of the loss of specific rotation of poly(α-phenylethylisonitrile) in excess of the asymptotic values observed in Figure 2, *i.e.*, $[\alpha]^{27}_{\mathrm{D}}{}^{\infty}$ were taken as −310 and +225° for curves A and B, respectively.

Infrared analysis shows that the spectra of polymer before and after the thermal treatment are nearly identical. The only prominent difference in the spectra of both polymer samples taken after the thermal treatment is that they no longer have an originally weak absorption band at 8.2 μ (1220 cm^{-1}).

The changes in the ultraviolet spectra of the optically active polymers as a result of the thermal treatment are illustrated in Figure 4. During the first 27 hr of heating only small change is evident in the 3000–4000-Å spectral region. During this first period the specific optical rotation has been shown to diminish rapidly. Thereafter, the specific rotation diminished slowly, but an appreciable development occurs of chromophores absorbing in this range, centered about 3700 Å, there is also an intensification of a more strongly absorbing shoulder at 2440 Å and a very strong band lies below the transparency limit of the solvent. At a polymer concentration of 1 g/l. in tetrahydrofuran the absorbance values observed at 3700 Å in a 1.0-mm path length sample cell are 0.06, 0.10 and 0.30 for, respectively, 0-, 27.5- and 44-hr periods of heating in refluxing toluene.

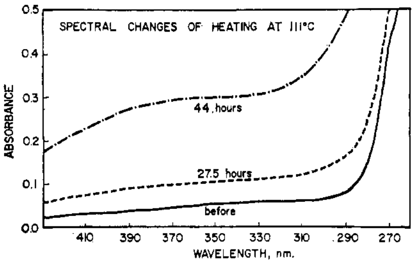


Figure 4. The effect on the ultraviolet absorption of poly(α-phenylethylisonitrile) by heating in refluxing toluene; concentration = 0.73 g/l.

Three weeks of heating did not effect further changes in the shape of the absorption spectrum in this region. Presently, efforts are being made to resolve the ultraviolet spectra by means of polarized light, and the kinetics of the separate phases of racemization can be subjected to more quantitative study.

During the course of thermal treatment the intrinsic viscosities of the two polymers heated in toluene were determined in a Ubbelohde viscometer at 30°. The levo polymer had an initial intrinsic viscosity, [η], equal to 0.973 dl/g, and after 27.5 hr [η] equal to 0.342. In the case of the dextro polymer, initially [η] was equal to 0.305, and after 44 hr [η] was equal to 0.153 dl/g. These results show the molecular weight, which is proportional to the intrinsic viscosity, decreased during the thermal treatment.

The following procedure was followed to prove that degradation of the polymer did not take place by a depolymerization, *i.e.*, a reversion to monomer. The polymeric material employed in the thermal racemization experiments was recovered by slowly adding the toluene solution to 300–400 ml of vigorously agitated methyl alcohol. The polymer which precipitated was collected by filtration, washed with methyl alcohol and dried at room temperature. The filtrate was observed to be nearly clear, with a very slight yellow color, and only a trace of residue could be isolated as a result of evaporating the methyl alcohol filtrate.

The precipitated polymers were then analyzed for optical rotatory power by redissolving the polymers in fresh toluene. The specific rotations of the thermally racemized *d* and *l* polymers gave values of $[\alpha]^{27}\mathrm{D}$ equal to +208 and −298°, respectively, which are nearly the same values observed for the polymer solutions before isolation of the polymers by precipitation.

The nmr spectra of a dextrorotatory polymer sample, dissolved in tetrachloroethylene (10% w/v), were obtained at room temperature and at 128° with tetramethylsilane as the internal standard at 100 MHz. The peaks are broad and show some slight change with 100° increase in temperature. Figure 5 shows peaks centered about 6.82, at 5.00, and (apparently a doublet) at 1.30 and 0.86 ppm, which are attributable to phenyl, methinyl, and methyl hydrogens, respectively. The absorption areas are in the ratio of 5:0.9:3, respectively.

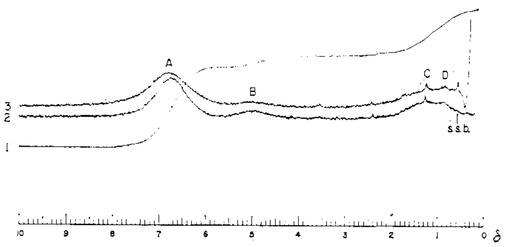


Figure 5. Nuclear magnetic resonance spectra of *d*-poly(α-phenylethylisonitrile) in tetrachloroethylene at room temperature (curve 3), and at 128° (curve 2) at 100 MHz. Curve 1 integrates area under curve 2. Concentration is 10% w/v. S.s.b. is the position of the spinning side bands of the tetramethylsilane internal reference sample.

Discussion

The results provide some interesting information regarding the structure of poly(α-phenylethylisonitrile). With our catalyst system each optically active monomer yields optically active polymer having a specific rotation of the same sign as the monomer, but of tenfold greater magnitude, (*i.e.*, *M*D >500 deg cm^2/g). Such enhanced optical activity can occur in an arrangement in which the transition dipoles of the absorbing chromophores are coupled, and provides experimental support for a previous assumption that poly(α-phenylethylisonitrile) assumes a preferred conformation in solution.[4] Presumably, a continuous section of the main chain of the stereoregular polymer exists in a helical conformation of predominately one screw sense. Arcus and West were among the first to conclude that enhanced optical rotation could be due to the presence of helical sections of a stereoregular polymer in solution.[9] More recently other workers have made similar statements.[10–15]

The specific rotations of both the levo- and dextrorotatory polymers were comparable. The average of eight values is 338 ± 22 deg cm^2/g. Although the two levorotatory polymers (*cf.*, preparations 14 and 19, Table I) show slightly greater values of specific rotation, molecular weight, and yields than comparable dextrorotatory polymers (*cf.*, preparations 13 and 20), it is felt that the synthetic control of the heterophasic polymerizations is not yet precise enough to attach significance at this time to such slight differences. The conclusion one may draw is that both epimeric forms allow a chain conformation of analogous packing. Furthermore, the fact that a racemic mixture of monomers yields a racemic polymer product or more prob-

(9) C. L. Arcus and D. W. West, *J. Chem. Soc.*, 2699 (1959).

(10) T. M. Birshtein, Y. Y. Gotlib, and O. B. Ptitsyn, *J. Polym. Sci.*, **52**, 77 (1961).

(11) P. DeSantis, E. Giglio, A. M. Liguori, and A. Ripamonti, *J. Polym. Sci., Part A*, **1**, 1383 (1963).

(12) M. Takada, K. Timura, A. Yamada, and Y. Imamura, *Bull. Chem. Soc. Jap.*, **33**, 1219 (1960).

(13) M. Goodman, K. J. Clark, M. A. Stake, A. Abe, *Makromol. Chem.*, **72**, 131 (1964).

(14) M. Goodman, A. Abe, and Y. L. Fan, "Macromolecular Reviews," Vol. 1, Interscience Publishers, New York, N. Y., 1967, p 1.

(15) I. N. Topchieva, *Russ. Chem. Rev.*, **35**, 741 (1966).

ably a racemic mixture of optically active polymers supports the conclusion that one optically active form is substantially not specifically favored. The possible resolution of racemic polymer product into optically active polymeric antipodes by means of optically active resolving substrates, similarly to the work of Pino, *et al.*,[16] has not yet been attempted.

At first glance, it might appear that the results resolve the ambiguity with regard to the choice between structures Ia and Ib for the mer unit. The source of optically activity of structure Ia is obvious since the pendent group contains an asymmetric carbon.

One can further argue that if rearrangement in a stereoregular manner occurred, resulting in mer units of Ib, a *reduction* in the magnitude of the specific rotation might be expected since the site of asymmetry then becomes located in the chain backbone. Frisch, Schuerch and Szwarc point out that vinyl homopolymers, with which structure Ib is relatable, cannot exhibit any measurable optical activity.[17] They further state that this is true even if they polymerize through a highly stereoregular mechanism to form isotactic or syndiotactic polymers. The basis for this reasoning is that with the exception of the carbon atoms located near the ends of the polymer chain, the internal carbon atoms have essentially two identical groups (*i.e.*, the polymer chain extending in both directions).

Although *syn–anti* geometric isomerism about the nitrogen is possible, in principle, in poly(α-phenylethylisonitrile), only one of these forms is practically possible in a low energy form of the sterically compressed helix, as presumed by Millich and Sinclair. This means internally symmetric *meso* forms of the rearranged polymer, such as structure a in Figure 6, are very improbable in an unperturbed state. A structure having a regular pattern of one of the geometrically isomeric mers, as in structure b in Figure 6, but in which rotational interconversion between *syn* and *anti* forms is hindered, could have internal symmetry only in the special case in which all the ketimino groups are oriented in a plane orthogonal to the helical chain axis. Molecular models show that this special case also is not likely. Therefore, in the polymer model in the lower half of Figure 6, one can expect a constructively additive, specific rotational contribution from each mer (although it may be small), and this structure represents an exception to the generalization of Frisch, *et al.*,[17] given above, concerning pseudoasymmetry.

Thus the information achieved in these experiments, in which optically active α-phenylethylisonitrile leads directly to optically active polymer, does not of itself preclude structure Ib. It established that if, in fact, a rearrangement is taking place through a γ shift of hydrogen from the benzylic carbon atom of the substituent group to the carbon atom at a vicinal position in the chain backbone, it is taking place in a stereospecific manner. The rearrangement would be seen as being cooperative among successive vicinal groups,[1] and requires that a zipper action take place for extensive lengths of the polymer chain—an exciting idea, but possibly an event not to be awaited.

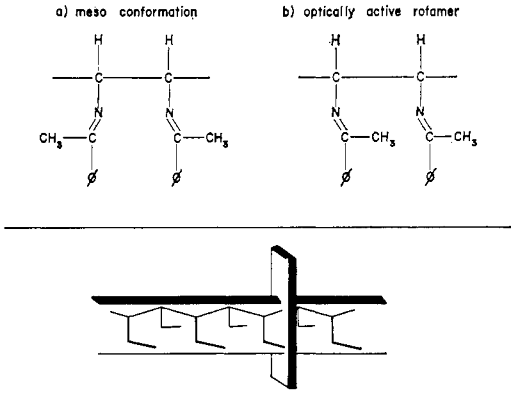


Figure 6. Upper, rotational-isomeric conformations of the hypothetical rearranged poly(α-phenylethylisonitrile); lower, an analytical model of an optically active polymer formed from rotamer b, above.

The practical realization of a highly optically active polymer which is formed by rearrangement depends on (a) a stereoregular chain growth during polymer propagation, (b) a much preferred rotational orientation of the α-ethylbenzyl substituent, (c) steric hindrance to rotation of the substituent with a rather sizable rotational activation energy, and (d) constant conformational integrity over the major length of the chain. Although the first three requirements may be reasonably met by the structure of poly(α-phenylethylisonitrile), the last requirement is not as likely. Figure 7 illustrates how heterogeneity may occur between stereoregular blocks of helical sections, which are joined at points of structural abberations. (Chemical evidence of the existence of weak chain links, occurring on the average of once in every $\overline{DP}$ length of 25, has already been reported.)[3] The conformations in the four segments shown involve a mer of a single optical antipode, from which two helices can be derived which differ in axial screw direction. None of the blocks are mirror images. Since block 1 is obtained by an about-face of block 2 (and similarly, block 3 from block 4), the mixing of these blocks, albeit of various lengths,

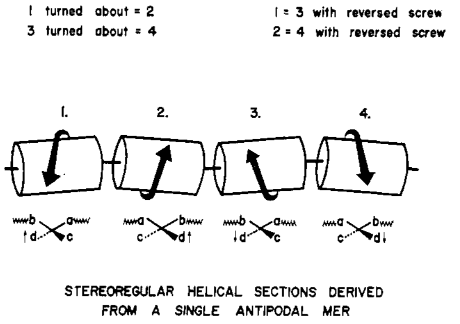


Figure 7. Stereoregular sections of a polymer constructed from an optically active monomer. The arrows on the cylinders and on substituents d, below, trace the positions of successive large lateral substituents: in the hypothetical rearranged polymer structure Ib, c is H, d is $-N{=}C(CH_3)C_6H_5$, and the optically active center is on the chain backbone; in the unrearranged polymer structure Ia, c is nonexistent and d is $=NCH(CH_3)C_6H_5$ (optically pure isomer) with the center of optical activity situated at the benzylic carbon atom.

---

[16] P. Pino, *Advan. Polym. Sci.*, 4, 395 (1965).

[17] H. L. Frisch, C. Schuerch, and M. Szwarc, *J. Polym. Sci.*, **11**, 559 (1953).

is equivalent to a simple solution in which the blocks would be unattached, and no reduction in the total rotation results from these interactions. The relation of block 2 with block 3 (similarly, block 1 with 4) represents a "conformational reversal," as described by Pino and Luisi[18] and said to produce an opposite rotational sign for the specific rotation.[19] From the consistently high values of specific optical rotation obtained with the *d*-polyisonitrile and the *l*-polyisonitrile samples one may conclude that very few conformational reversals take place during chain propagation, and that each optical isomer propagates a chain with a preferred screw direction. It is, therefore, predictable that a racemic mixture of optically active monomer produces a mixture of optically active polymers.

It is interesting to reflect on thoughts of what must be taking place on the surface of the acidic catalyst, at the site of polymerization. The hybridized molecular orbitals of the nitrogen atom are of linear sp type in the monomer and of angular sp^2 type in the polymer. One can imagine many trial positionings of associated monomer to the propagating chain until good fitting of the added unit is achieved and the chain propagation advances by degree. This may partly explain the need in this system for catalysis at a surface, may explain the slow over-all rates of conversion, and may explain the previously reported[3] observation of polyisonitrile serving as catalyst for polymerization, possibly as seeding of a supercooled solution serves the onset of crystallization.

Racemization of Optically Active Polymer. If indeed structure Ia is the more reasonable choice for the structure of poly(α-phenylethylisonitrile) then the possibility exists that rearrangement to Ib might be induced, particularly since a resulting gain in conjugation should be thermodynamically favored. To test this prospect, optically active polymer was refluxed in several solvents of differing boiling points. The rates of racemization in refluxing toluene were conveniently followed, and are shown in Figures 2 and 3. The curves do not show a simple first-order decay, but indicate that a relatively rapid initial thermal racemization is superimposed upon one or more slower processes. At the end of 48 hr the specific rotations are still quite large.

During the entire heating period little change is observed in the infrared spectra. Ultraviolet spectroscopy shows the development of absorption bands taking place at 2440 Å and in the range of 3100–3800 Å, especially during the latter phase of the racemization. This is probably indicative of chromophores of a rather high degree of conjugation, such as is possible in the molecular structures suggested by one of the authors in 1965.[3] However, even in the untreated polymer there is evidence of absorption in the near-ultraviolet spectral range, which is responsible for the yellow color of the polymer, and for which assignments are not yet possible.

During the initial, rapid phase of racemization the process is attended by a concurrent decrease in the viscosity of the polymer solutions. There are two general ways the polymer chains could be cleaved as a result of the thermal treatment. One is cleavage at random sites on a given chain. The other is a "zipper" depolymerization of given chains into monomer units or derivatives of the repeating unit. A solution of polymer undergoing either of these processes would exhibit a decrease in viscosity and both could exhibit a loss of optical activity. If cleavage by "zipper" depolymerization occurred, then the residual polymer, isolated from the mixture, should have approximately the original specific optical rotatory power (*i.e.*, prior to the thermal treatment). Since almost all of the material from the racemization is precipitable as a polymeric material, and upon redetermination shows the same loss of specific rotation, the depolymerization must have occurred at random sites on a given chain.

Thus several possible modes exist by which decrease in the value of specific rotation may take place. These are (a) a C–H bond cleavage followed by a recombination in the opposite configuration; (b) formation of *meso* forms in the hypothetical rearranged molecular model, by rotation around the CH–N bond in the substituent (b → a, Figure 6), or in the unrearranged structure Ia, by rotation around the CH–N bond in the lateral substituent; (c) decrease in molecular weight to shorter chain segments which would relieve steric compression in the chain and which would provide sufficient space to allow some *syn–anti* isomerization in the unrearranged molecular model; (d) complete loss of the chain conformation through thermal perturbation, independent of chain cleavage; (e) "conformational reversals"[18] with reversals of helical screw direction. The activation energy for possibility a is probably among the greatest, and is most likely not associated with the initial rapid phase of racemization. Presently, synthetic efforts are being directed toward the preparation of optically active polyisonitriles with molecular weight stability at the temperature at which racemization can be induced.

Acknowledgment. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This paper is taken in part from the doctoral dissertation of G. K. Baker, University of Missouri at Kansas City, Jan 1968. The authors are indebted to Drs. D. N. Matthews and D. Kates, UniRoyal Research Center, Wayne, N. J., for obtaining the nmr spectra.

---

(18) P. Pino and P. L. Luisi, *J. Chim. Phys.*, **65**, 130 (1968).

(19) This deduction by Pino, *et al.*, is based on the application of the semiempirical method of J. H. Brewster, *cf. J. Amer. Chem. Soc.*, **81**, 5475, 5483, 5493 (1959), and in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967.