Cellulose Xanthic Acid.[1] II. Studies of Cellulose Xanthate

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ABSTRACT: Evidence that several forms of cellulose xanthic acid can exist has been obtained from studies of the reaction between cellulose xanthate and acid. Initially (in aqueous solution), cellulose xanthic acid ($\lambda_{\max}$ 285 mμ) is quickly formed by an ionic reaction followed by a slower addition reaction with excess hydrogen ions to give a protonated xanthic acid of an oxonium-type structure ($\lambda_{\max}$ 273 mμ). The acidic forms of cellulose xanthate are in pseudoequilibrium with the xanthate ion ($\lambda_{\max}$ 303 mμ). Decomposition was by a transxanthation with water and, as with the model systems, was retarded in strong acid by formation of the protonated xanthic acid. The redistribution of xanthate groups by transxanthation that occurs during viscose ripening, and can occur during the decomposition of cellulose xanthate in dilute acid, has been considered and an interpretation of the acid decomposition reactions is presented. The mechanism is identical with that proposed for the simple xanthates.

Although the existence of cellulose xanthic acid in the mechanism of acid decomposition of viscose has been postulated for many years, observations (by uv) of the acid products of cellulose xanthate have only been made relatively recently. Phifer, in 1965,[2] published an ultraviolet spectrum of the product of hydrochloric acid and cellulose xanthate in an aqueous methanol solution. Since the product decomposed rapidly in aqueous solutions, methanol was used to stabilize the acid. Using a thin film technique,[3] Jost and Ludwig confirmed that a product having an absorption maximum at 273 mμ was present in acidic solution and identified this product as cellulose xanthic acid. They obtained curves when they attempted to make first-order plots of the decomposition data and at the same time claimed that the data followed reaction mechanism 1. No explanation was given for the curves and no

$$\mathrm{Na^+CX^-} + \mathrm{H^+} \rightleftharpoons \mathrm{HCX} \longrightarrow \mathrm{ROH} + \mathrm{CS_2} \qquad (1)$$

measurements were made in very strong acid.

The curvature in pseudo-first-order plots of the acid decomposition of cellulose xanthate was first noted by Philipp and Fichte,[4] who suggested that the curve represents the sum of two exponentials (decomposition of the C_6 and C_{2-3} species independently). In acid systems, however, most decomposition curves cannot be resolved into two straight lines.[5] Arkhangelski[6] reported that the curvature was related to changes in pH during the decomposition. This idea was rejected by Cichowski,[7] who dismissed the whole problem with the statement that it stems from the complex structure of the compound. Tornell[8] attempted to explain the curvature on the basis of a complex second-order reaction mechanism with the suggestion that cellulose xanthate behaves as a polyelectrolyte.

In general, the mechanisms proposed by these authors are incomplete or inconsistent with the results which have been cited in part I of this paper.[9] In this part, evidence will be presented that the mechanism of acid decomposition of cellulose xanthate is identical with that of the model systems.

The understanding of data taken on the cellulose xanthate system is complicated by the multiplicity of reactions which are occurring simultaneously. In previous papers, evidence has been presented that freshly prepared viscose has most of the xanthate groups substituted in one hydroxyl position,[10] and, as the viscose ages, redistribution occurs toward all three hydroxyl positions with the result that aged viscose contains C_2-, C_3-, and C_6-substituted xanthates. In addition, redistribution has been observed in acidic solutions of cellulose xanthate with the rates being the same order of magnitude as the decomposition rate.[11] Consequently transxanthation must also be included in the interpretation.

Experimental Section

Materials. Viscose having the composition 7.5% cellulose, 7.0% NaOH and 31.5% CS_2 was prepared in a small-scale pilot plant. When "new" viscose was used in the experimentation, it was taken directly from the mixer. The "old" viscose was aged a minimum of 72 hr at 18° to permit redistribution of xanthate groups to approach an equilibrium status. Before use, the viscoses were passed through an ion exchange column containing Amberlite IRA400 to remove the by-product compounds.[12]

The sulfuric acid solutions were prepared from sulfuric acid and water and were standardized against standard sodium hydroxide solutions.

Apparatus. A Cary Model 14 spectrophotometer was used for the slower rate studies and for determining the spectra of relatively stable species. The instrumental modifications which are necessary for the film technique have been previously described.[2]

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(1) Presented in part at the Second International Dissolving Pulps Conference of the Technical Association of the Pulp and Paper Industries, New Orleans, La., June 3–6, 1968.

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(3) H. Jost and J. Ludwig, *Faserforsch. Textiltech.*, **17**, 29, 194 (1966); **18**, 274 (1967).

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(8) B. Tornell, *Svensk Papperstid.*, **70**, 268, 303 (1967).

(9) J. Dyer and L. H. Phifer, *Macromolecules*, **2**, 111 (1969).

(10) J. Dyer and L. H. Phifer, *Svensk Papperstidn.*, **71**, 385 (1968).

(11) J. Dyer and L. H. Phifer, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract E30.

(12) J. P. Dux and L. H. Phifer, *Anal. Chem.*, **29**, 1842 (1957).

For the fast reaction studies, a Beckman DU spectrophotometer was modified so that the output of the photomultiplier tube could be fed through two Model 450A Hewlett-Packard amplifiers in series to a Model 130A Hewlett-Packard oscilloscope. A Polaroid land camera was used to record the oscilloscope trace, using a Dumont adaptor on the oscilloscope. A horizontally slotted (0.25 × 0.001 in.) slider was used in the light path of the cell holder to narrow the vertical band of light. The voltage on the photomultiplier tube was increased to 910 V to compensate for the decrease in light intensity. To permit the injection of solution directly into the cell, a hole was drilled in the cell compartment cover in such a position that a hypodermic syringe needle could be inserted into the cell without being in the light path. Using this equipment, the triggering circuits on the oscilloscope could be set so that the scope would begin to sweep when the meniscus of the injected solution crossed the light path. With a thin film of viscose on an optical flat placed in the cell, perpendicular to the light path, the oscilloscope would record the absorbance changes which occurred in the film from an extremely short time up to a few seconds after the solution which was injected into the cell crossed the light path. With some practice in injecting the solution, the meniscus of the solution would cross the light path in approximately 0.02 sec and absorbance changes after this time could be recorded.

Procedure. The thin film technique for studying viscose reactions using the Cary Model 14 spectrophotometer has been previously described.[2] The basic technique was also used for the fast reaction studies. Using the modified DU spectrophotometer, the procedure was as follows.

1. With the camera shutter closed, the dark current control was used to adjust the oscilloscope trace on the grid to read 0% transmission.
2. Three matched 1-cm^2 cells containing matched optical flats were placed in the cell compartment. One of the cells was filled with the acid solution to be used. In the second cell, a thin film of ion-exchanged viscose was cast on the optical flat. The third cell contained only an optical flat.
3. The wavelength was set at 303 mμ and, with the dry cell and flat in the light path, the oscilloscope was adjusted to read 100% transmittance on the grid. The camera shutter was opened and the scope manually triggered to record this transmittance.
4. The cell containing the optical flat with the viscose film was then moved into the light path and the transmittance of the xanthate film recorded.
5. The wavelength was then set to whatever wavelength the decomposition was to be studied. The cell containing the acid solution was moved into the light path and the oscilloscope again adjusted to read 100% transmittance on the grid.
6. The cell containing the optical flat with the viscose film was returned to the light path and the oscilloscope sweep, set at 0.2 sec, was adjusted to trigger when a change occurred in the light intensity.
7. The camera shutter was opened and the acid solution injected into the cell from a syringe with a long needle which reached the bottom of the cell. As the solution crossed the light path, the oscilloscope sweep triggered and the transmittance was recorded. Generally, multiple sweeps were recorded for the first 10 sec. The camera shutter was then closed.
8. The sample cell transmittance was then observed visually on the oscilloscope grid until a constant value was reached. The camera shutter was opened and the scope manually triggered to record this leveling-off transmittance.
9. The cell containing the acid solution was replaced into the light path and the 0 and 100% transmittance settings were rechecked.

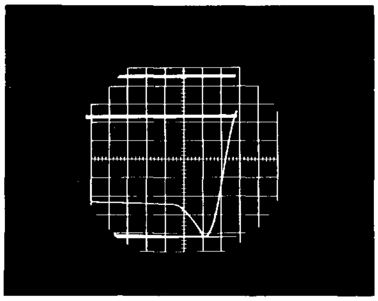


Figure 1. Typical oscilloscope trace of the acid decomposition of cellulose xanthate (scan from right to left).

Typical results obtained are shown in Figure 1. The lower line represents the transmittance of the xanthate film at 303 mμ. The middle is the scan as the acid solution crosses the light path and decomposition starts, and the initial hump is caused by the solution crossing the light path. (The time for this to occur is in the vicinity of 0.02 sec.) The top scans represent the background after the decomposition is completed and 100% transmittance. The absorbance was calculated from these transmittance figures.

Results and Discussion

Experiments Using the Modified DU Spectrophotometer. From the studies of simple xanthates, described in part I,[9] it was expected that, in the acid decomposition of cellulose xanthate, the absorbance of at least three different species—xanthate ion, xanthic acid and protonated xanthic acid—would be obtained. The xanthic acid was considered to be present as a short-lived intermediate. For the fast reaction experiments using the modified Beckman DU spectrophotometer, an aged viscose was used since it was recognized that measurements must be made at a rather large number of wavelengths over several hours. Thus the effects on the experiments of the relatively rapid changes which are occurring in the viscose composition when the viscose is "new" were minimized. Since it is known[11] that redistribution of xanthate groups can occur in dilute acid media, an acid concentration of 0.4 *N* was used. At this acid concentration, redistribution is at a relatively low level. Measurements were made at 2-mμ intervals from 320 to 260 mμ. The decomposition curve at each wavelength was extrapolated to zero time and corrected by subtracting the background. The ratio of this absorbance to that of the original xanthate absorbance times the molar absorbtivity of the xanthate ion at 303 mμ, 15,900,[12] gave a value of the "apparent" absorbtivity at that wavelength. When the "apparent" absorbtivity was plotted against the wavelength, curve a of Figure 2 was obtained. The curve, the average of five measurements at each wavelength, had absorption maxima at 273 and 283 mμ and evidence of a peak at 303 mμ.

Curve b of Figure 2 illustrates the "apparent" absorptivity 5 sec after the reaction started. The plot was similar to that of curve a except that the peak at 283 mμ had almost disappeared and the peak intensity at 273 mμ had increased. The half-life of the 283-mμ peak was approximately 0.7 sec. The 303-mμ peak was attributed to xanthate ion, the 273-mμ peak was due to the species which has been previously identified as being present in acid solutions of cellulose xanthate,[2] and the

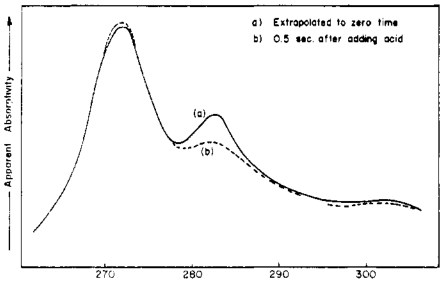


Figure 2. Apparent absorptivity of cellulose xanthate in 0.4 N H_2SO_4.

283-mμ peak was similar to that observed in model systems and discussed in part I of this paper. The initial reaction between xanthate ion and acid was more rapid than the time that it took the solution to cross the light path (in less than 0.02 sec). This conclusion was reached by setting the wavelength at 303 mμ and running the acid decomposition experiment. These results are shown in Figure 3. The intensity of the xanthate peak decreased to the equilibrium value as soon as the solution crossed the light path. The implication was that the initial reaction was an ionic reaction and did not involve a rearrangement. From Figure 2, the intensity of the 273-mμ peak after 5 sec was actually higher than the extrapolated zero time plot indicating that the 283-mμ peak was disappearing to form the 273-mμ peak. The relative slowness of the reaction suggested a rearrangement or addition compound formation. These observations were completely consistent with the behavior of the model systems.

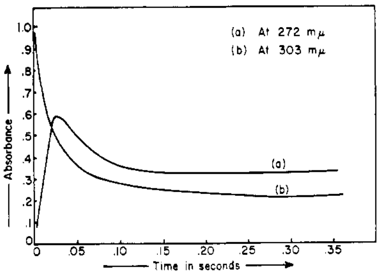


Figure 3. Uv absorbance of cellulose xanthate in 0.4 N H_2SO_4.

There was no evidence that decomposition of the xanthate system occurred more rapidly in the initial reaction stages when the acid intermediate was at a higher concentration. This indicated that the intermediate was not itself decomposing to give the alcohol and CS_2 and that the concentration of the intermediate was not a rate-controlling factor in the decomposition.

Experiments with the Cary Spectrophotometer. To simplify the interpretation of the results, specific conditions were chosen to study the 273-mμ species which occur in the acid reactions with cellulose xanthate. These were, first, a new viscose (since the xanthate groups are mostly in one position, and, under suitable experimental conditions, the decomposition curves would be pseudo first order), and second, strong acid conditions were used wherever possible to prevent redistribution of the xanthate groups during decomposition.

A thin film of ion-exchanged viscose was treated with 16 N H_2SO_4 and the ultraviolet spectrum was plotted. The absorbance at each wavelength was corrected for the decomposition which occurred while the spectrum was being plotted with the results shown in Figure 4. The maximum absorbance, λ_{max}, was at 273.5 mμ. Comparison of this spectrum with that of the 270-mμ species of ethyl xanthic acid (in part I) indicated that they were very similar. The peak position for the cellulose derivative was at a slightly higher wavelength and there was no direct evidence of any shoulder or other peak (around 285 mμ) which could be attributed to cellulose xanthic acid. A simple calculation indicated that a second peak at 280 mμ having an intensity 20% of the 270-mμ peak could be present without showing up as an identifiable shoulder, but would displace the peak maximum of the 270-mμ species to a higher wavelength. If there were two peaks present, there was no obvious way to resolve them and they should be in equilibrium with each other. Further characterization was made considering the total absorbance as that of a single species.

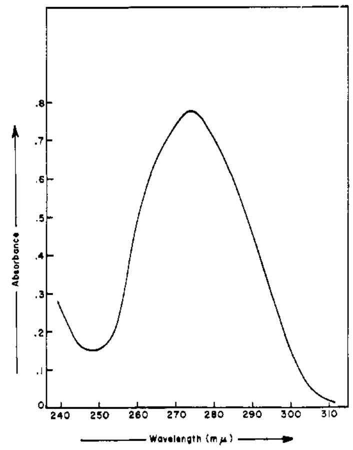


Figure 4. Uv absorbance of "new" cellulose xanthate in 16 N H_2SO_4.

Using the thin film technique, the decomposition of cellulose xanthate was followed in strong acid solution at 273 mμ and in dilute acid at 303 mμ. Typical semilogarithmic plots of the absorbance as a function of time are illustrated in Figure 5. For the strong acid (>0.2 N), the initial portion of the curves systems was linear. In dilute acid, curves were obtained due to transxanthation in the acid media resulting in a continuous change in the composition of the sample. A line, drawn tangent to the initial portion of the curve (see Figure 5), was considered to be representative of the decomposition of the major species present in the new viscose. The slopes of the tangents to the decomposition curves (k_{exp}) were plotted against the acid concentration with the results shown in Figure 6. As in the case of the model compounds, the decomposition rate passed through a maximum at a low pH and continued to decrease as the acidity increased.

The ratio of the absorbance at 273 mμ to that at 303

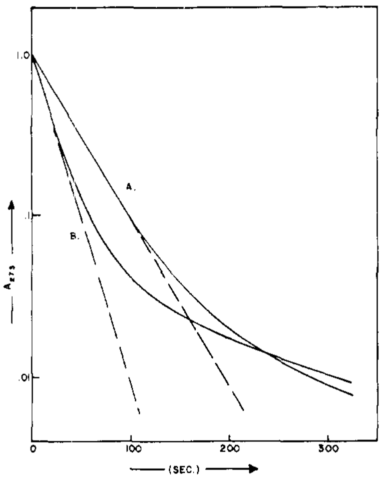


Figure 5. Decomposition curves of "new" cellulose xanthate in (A) 8 *N* and (B) 0.1 *N* H_2SO_4 at 22°.

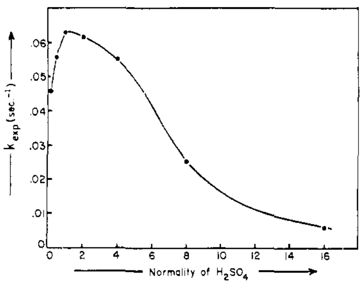


Figure 6. Influence of acidity on the decomposition of "new" cellulose xanthate.

mμ increased with increasing acid concentration as shown in Figure 7. This again was behavior identical with that of the model xanthates and the same conclusion was reached, *viz.*, that the decomposition does not occur through the 273-mμ species.

Mechanism of Acid–Cellulose Xanthate Reactions. It has been demonstrated that both cellulose xanthic acid and the protonated xanthic acid are present in the acid–cellulose xanthate system. In addition, it was shown

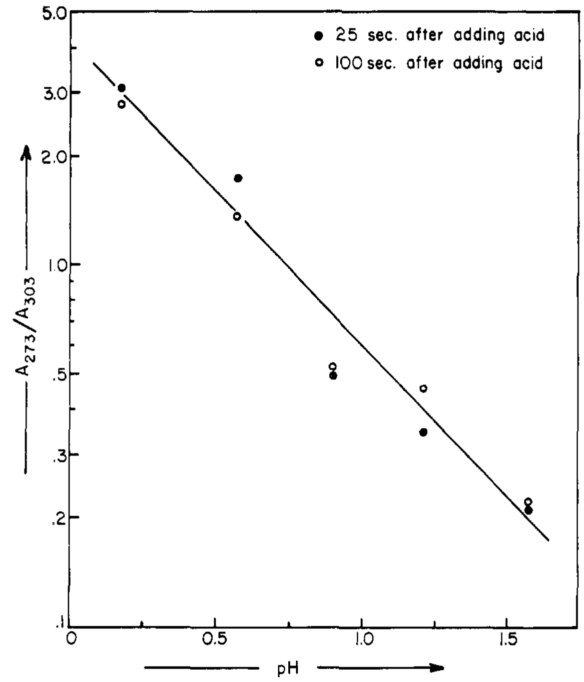


Figure 7. Influence of acidity on the absorbance ratio A_{273}/A_{303} of "new" cellulose xanthate.

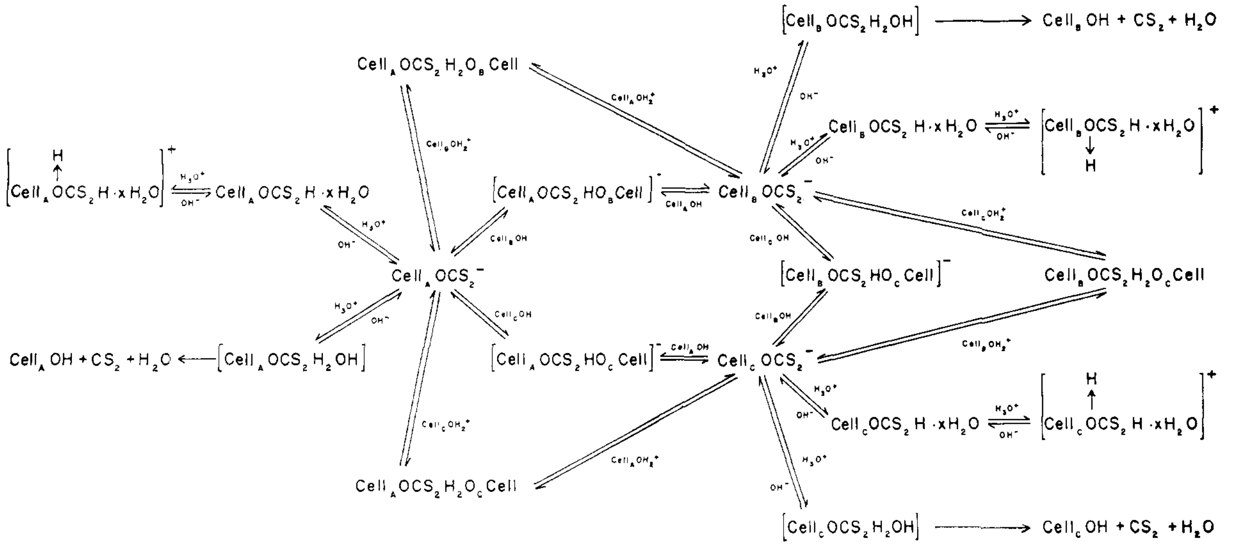
that neither of these species was directly decomposing and, in fact, the protonated acid had a stabilizing effect on the system. This behavior was identical with that observed in the model systems and it was concluded that there was an identical reaction mechanism (Scheme I). The mechanism, including the redistribution of xanthate groups that can occur during viscose aging and acid decomposition, contains 45 reactions. In the reaction scheme shown, the subscripts A, B and C refer to three different alcohol groups of the cellulose molecule (C_2, C_3 and C_6).

Conclusions

1. The mechanism of acid decomposition of cellulose xanthate is identical with that for simple xanthates

SCHEME I

ACID DECOMPOSITION AND SOME REDISTRIBUTION REACTIONS OF CELLULOSE XANTHATE



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.

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

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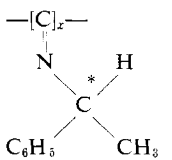
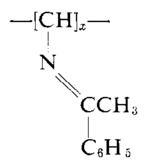
Polymer Section, Chemistry Department, University of Missouri–Kansas City, Kansas City, Missouri 64110. *Received September 30, 1968*

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, $[\alpha]^{27}\text{D}$ ~400°, M^{27}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

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(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).