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SYNTHESIS AND CHARACTERIZATION OF ACETONE-TEREPHTHALALDEHYDE POLYMER AND ITS OLIGOMERS.

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ABSTRACT

We report the synthesis of several oligomers of defined structure and the polymer arising from the base-catalyzed condensation of acetone and terephthalaldehyde. We have characterized these materials by IR, NMR, and elemental analysis. The preparation of oligomer ATA requires an acetone/terephthalaldehyde ratio ~ 50:1; otherwise, only polymer results. We explain this observation on the basis of enolate equilibria. The interaction of these compounds with Lewis acids produces oxonium ions.

INTRODUCTION

The reaction of acetone and terephthalaldehyde was first reported by Loew [5] in 1885. This reaction yields a cross-conjugated system. In acetone-

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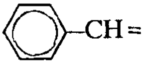
[*] For convenience we have used the following notation:

A = acetone residue: $CH_3COCH=$, $=CHCCH=$

T = terephthalaldehyde residue:  or

B = benzaldehyde residue: 

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terephthalaldehyde-based oligomers and polymer the carbonyl groups are separated by a fixed conjugated system of two vinylene and one phenylene units. Although Loew claimed to prepare the fully dehydrated polymer, he did not publish any characterization. The target polymer $(AT)_n$* is intractible and difficult to characterize. To aid us in its characterization, we have prepared oligomers ATA, TAT, ATATA, and TATAT. We employed both acid- and base-catalysts and characterized the products by IR, and NMR spectroscopy. We also investigated the acid-treatment of these materials by H_2SO_4, HCl, and BF_3 Et_2O and examined the chemistry of this acid treatment through NMR spectral studies on H_2SO_4 solutions.

EXPERIMENTAL

Chemicals and Solvents. Acetone (Mallinckrodt, AR grade) was distilled and kept over molecular sieves (3 A) prior to use. Terephthalaldehyde (Aldrich, 98%) was crystallized from methanol-water prior to use. Other chemicals such as sodium hydroxide, methanol, ethanol, chloroform, hydrochloric acid, sulfuric acid (98%) (all Fischer Scientific), and boron trifluoride etherate (Fluka), 40% were used as received. Deuterated solvents ($CDCl_3$ or DMSO-d_6) (Aldrich) were used as ^1H NMR or ^{13}C NMR solvents. TMS (Aldrich) was used as an internal standard. All chemical shifts are expressed as ppm.

Characterization and Chemical Analysis. Characterization of these compounds was carried out by chemical and spectral - IR, ^1H NMR, and ^{13}C NMR -analyses. Chemical analyses were performed by Desert Analytic, Tucson, Arizona. The ^1H NMR spectra were recorded on a JOEL FX-90, an IBM Bruker, or a Varian EM 360-A Spectrometer. The ^{13}C NMR spectra were obtained on a JOEL FX-90 Spectrometer. The IR spectra were obtained on a Beckman model FTIR-1100 instrument.

Acetone-Terephthalaldehyde Polymer [2,3]. The following general procedure was followed for the synthesis of all the AT oligomers and polymers. Only the molar ratios were changed.

In a one-liter flask fitted with a dropping funnel and a magnetic stirrer was placed 23 mL 10% NaOH (0.058 mole) and 25 mL EtOH. To this solution was added dropwise a solution of 25 mL EtOH, 3.7 g (0.027 mole) terephthalaldehyde, and 2.0 mL (0.027 mole) acetone at room temperature. The solution turned yellow a few minutes after addition, and stirring was continued for 2 hours. The solution was poured into a mixture of 400 mL water and 20 mL acetic acid resulting in the formation of a bright yellow precipitate. After washing the precipitate with water, EtOH, and ether, it was dried overnight under vacuum. Yield: 4.0 g (90%); Tm > 360°C; insoluble in all common solvents. IR (KBr pellet) 3500 (OH stretch), 3050 (C-H

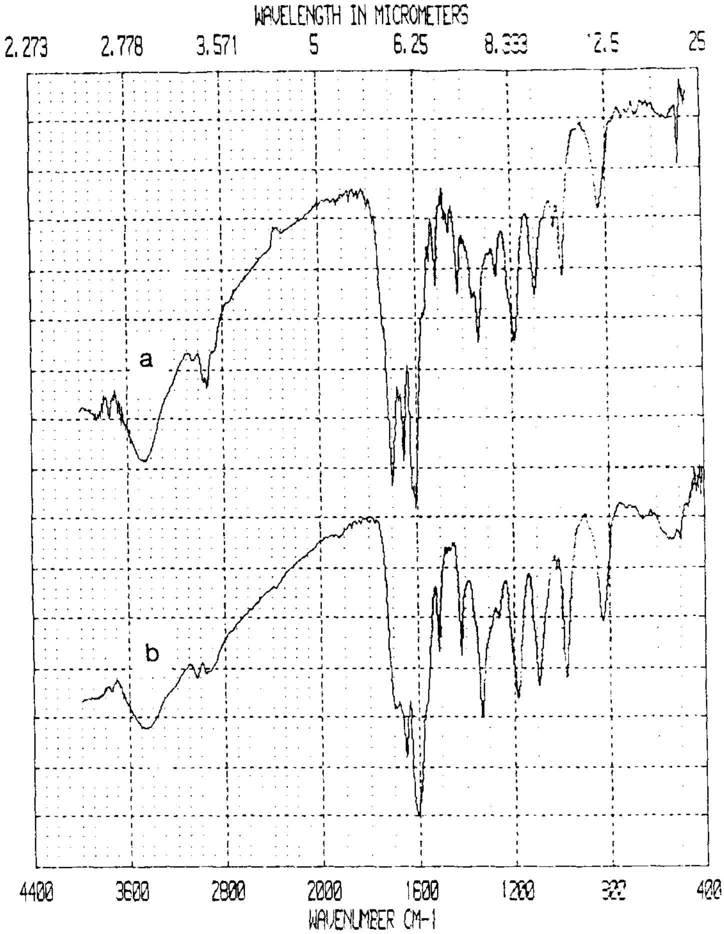


Figure 1. IR spectra of (a) extracted portion and (b) insoluble portion of AT polymer

stretch), 2950(satd. C-H stretch), 1700(terminal C=O stretch), 1648 (conj. C=O stretch) cm^{-1}. The polymer was extracted with methanol (Soxhlet Extraction) and two fractions were obtained, an extracted or soluble fraction and an insoluble fraction (Figure 1).

Synthesis of A T A [1]. NaOH (40 g, 1.0 mole), 402 mL water (to make a 10% solution), 736 mL (582 g, 10 moles) of acetone, 25 mL methanol, and

10% NaOH (1.3 mM), and 30 mL methanol. Yield: 0.17 g (73%); Tm: 360°C; Elem. Anal. Calcd. for TATAT: C, 80.71; H, 4.93; Found: C, 80.46; H, 5.08; IR (KBr pellet) 3050 (=CH stretch), 2850, 2750 (CH stretch, -CHO), 1692 (terminal C=O stretch), 1648 (conj. C=O stretch,) cm^{-1}; ^1H NMR (DMSO/60-70°C) δ 10 (s, 2H, CHO), δ 7.4-8.0 (m, 20H, olefinic and ring).

Synthesis of B A T A B. Reaction of 0.23 g (2.2 mM) of benzaldehyde in 5 mL of methanol with a solution of 0.093 g (0.43 mM) of ATA, 0.52 mL 10% of NaOH (1.3 mM), and 7 mL of methanol yielded: 0.076 g (45%)of crystals; Tm: 360°C; Elem. Anal. Calcd. for BATAB: C, 86.15; H, 5.64; Found: C, 85.94; H, 5.74; IR (KBr pellet) 3050 (=CH stretch), 1648 (conj. C=O stretch), 753, 694 (CH bending, benzene ring) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7-8 (m, ring and olefinic protons).

Reaction of T A T A T with Acetone. TATAT (1.1 g, 2.2 mM) 60 mL (0.67 mole) acetone, 20 mL 10% of NaOH (0.050 mole) and 100 mL methanol was refluxed for 20 hours. Work-up yield: 0.38 g (34%); Tm 300°C; Elem. Anal. Calcd. for ATATATA: C, 82.13; H, 5.70; found C, 80.24; H, 5.95. IR (KBr pellet) 3500 (-OH stretch), 1700 (terminal C=O stretch), 1650 (conj. C=O stretch), 1600 (C=C aromatic ring) cm^{-1} This product is insoluble in DMSO and burns slowly (2-3 minutes) on an open Bunsen burner flame leaving no residue.

Reaction of A T A with T A T. A similar procedure using 0.15 g (0.70 mM) ATA, 0.20 g (0.69 mM) TAT, 0.70 mL, 10% of NaOH (1.8 mM) and 50 mL of methanol, after work-up, yielded: 0.34 g of yellow crystals; Tm: 300°C; Elem. Anal. Calcd. for ATATAT: C, 81.99; H, 5.38; found: C, 77.69; H, 4.87; IR (KBr pellet) 3500 (-OH stretch), 3029 (=CH stretch), 2930 (satd. -CH stretch), 2828, 2730 (aldehydic CH stretch), 1694 (terminal C=O stretch), 1648 (conj. C=O stretch), 825 cm^{-1}.

Reaction of A T A T A with Benzaldehyde. Reaction of 0.34 g (0.92 mM) ATATA, 0.99 g (9.3 mM) benzaldehyde in 10 mL of methanol, and 1.1 mL (10%) NaOH (2.8 mM), yielded: 0.35 g (70%)of yellow crystals; Tm 300°C; IR (KBr pellet) 3500 (OH stretch), 3050 (=CH stretch), 1648 (conj. C=O stretch), 818 (CH bending, benzene ring), 760, 694 (CH bending, monosubstituted benzene ring) cm^{-1}. The presence of a hydroxyl band and CH aliphatic absorptions at 2900 cm^{-1} in the IR spectrum suggest that dehydration of the aldol product is incomplete. For this reason we did not obtain an elemental analysis of this compound.

Synthesis of Dibenzalacetone Using HCl Gas [4]. Hydrogen chloride gas was passed into a solution of 0.79 g (14 mM) acetone and 3.1 g (29 mM) benzaldehyde. Work-up yielded: 0.91 g (28%)of brownish-yellow crystals; Tm:

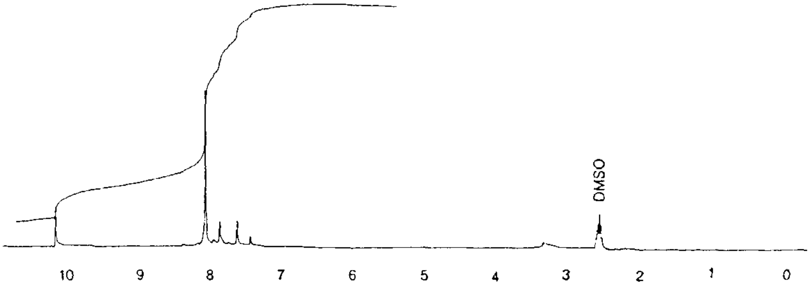


Figure 4. ^1H NMR spectrum of TAT

a solution of 6.5 g (0.048 mole) terephthalaldehyde and 75 mL MeOH. Yield: 8.7 g (81%). Recrystallization from MeOH-water mixture yielded 6.3 g; Tm 140-145°C (Lit. [1]: 146°C); Elem. Anal. Calcd. for ATA: C, 78.50; H, 6.54; found: C, 78.86; H, 6.49; IR (KBr pellet) 3037(=C-H stretch), 2950(satd. C-H stretch), 1664 (C=0 stretch, conj. CO), 825 (C-H bend, ring) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36(s, 6H, CH_3), δ 6.73(d, 2H, vinylic H_a, J = 16.1 Hz), δ 7.49(d, 2H, vinylic H_b, J = 16.4 Hz), δ 7.55(s, 4H, Arom.) (Figure 2). ^{13}C NMR(DMSO) δ 27.36(CH_3), δ 197.95(C=O), δ 128.01, 142.04(C_3, C_4), δ 136.25(ring ipso), δ 128.83(ring ortho) (Figure 3).

Synthesis of T A T. Terephthalaldehyde (8.0 g, 0.06 mole) in 100 mL methanol, to which was added a solution of acetone (0.9 mL, 0.72 g, 0.012 mole), 12.3 mL 10% NaOH (0.031 mole) and 20 mL methanol. Yield: 3.0 g (86%), Tm: 228-233°C. Elem. Anal. Calcd. for TAT: C, 78.62; H, 4.83; Found: C, 78.95, H, 4.97; IR (KBr pellet) 3150 (=CH stretch), 2850, 2750 (-CH stretch, -CHO), 1692 (C=O stretch, -CHO), 1651 (C=O stretch, ketonic C=O), 825 (CH bending, benzene ring) cm^{-1}; ^1H NMR (DMSO) δ 10 (s, 2H), δ 7.3-8.0 (m, 12H, olefinic and ring) (Figure 4).

Synthesis of A T A T A. Acetone (48 mL, 38 g, 0.65 mole) 26 mL 10% NaOH (0.065 mole), and 200 mL methanol, to which was added pinchwise 0.94 g (33 mM) TAT. Yield: 1.1 g (93%); Tm ZY242-250°C; Elem. Anal. Calcd. for ATATA: C, 81.08; H, 5.70; Found: C, 81.23; H, 5.80; IR (KBr pellet) 3050 (=C-H stretch), 2950 (satd. -CH stretch), 1687 (terminal C=O stretch) 1656 (internal C=O stretch), 825 (CH bending, benzene ring) cm^{-1} ^1H NMR (DMSO/ 60-70°C) δ 6.7-8.0 (m, 16H, olefinic and ring), δ 2.3 (s, 6H, methyl).

Synthesis of T A T A T. Terephthalaldehyde (0.34 g, 2.5 mM) in 25 mL methanol, to which was added a solution of 0.11 g (0.51 mM) ATA, 0.60 mL

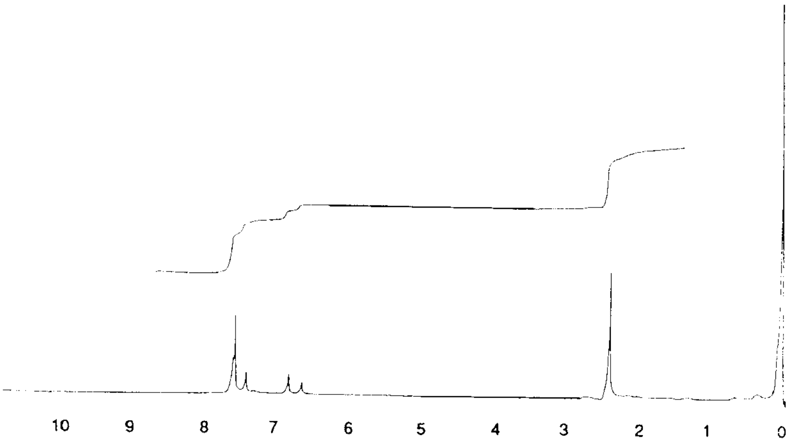


Figure 2. ^{1}H NMR spectrum of ATA

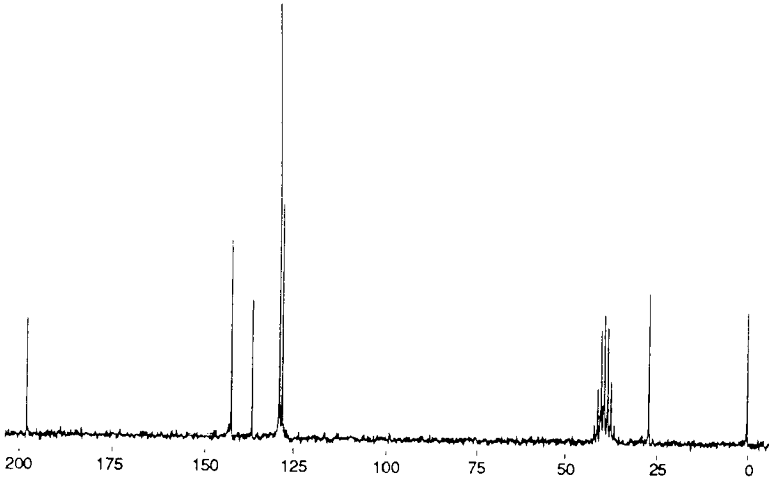


Figure 3. ^{13}C NMR spectrum of ATA

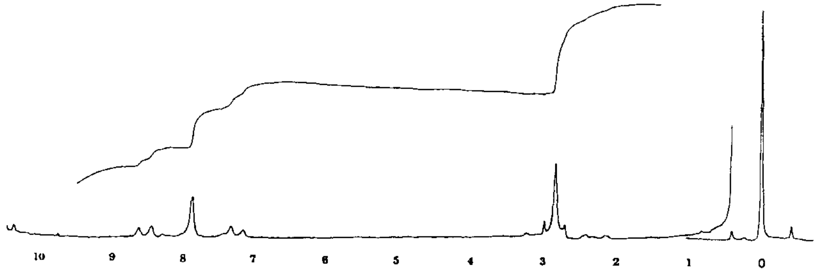


Figure 5. ^1H NMR spectrum of ATA in H_2SO_4

108-111°C (Lit.: 110-111°C); IR (KBr) 3050 (=C stretch), 1648 (conj. C=O stretch), 1600 (conj. C=C stretch), 753, 694 (CH bend, benzene ring) cm^{-1}.

Reaction of Acetone with Terephthalaldehyde Using HCl Gas. The above procedure was repeated using 0.60 g (4.5 mM) terephthalaldehyde and 2.6 g (50 mM) acetone. Work-up yielded: 0.50 g (72%); Tm: 300°C; Elem. Anal. Calc. for $C_{11}H_8O$: C, 84.61; H, 5.13. Found: C, 79.46; H, 5.38; Cl, 2.31; IR (KBr) 3050 (=CH stretch), 2950 (satd. CH stretch), 1710 (C=O stretch, terminal acetone group), 1689 (terminal C=O stretch), 1653 (conj. C=O stretch), 1600 (conj. C=C stretch), 818 (CH bend, benzene ring) cm^{-1}.

Sulfuric Acid Study. Sulfuric acid treatment of the AT polymer was accomplished by mixing 0.001 mole of the polymer with 5 mL of 96% sulfuric acid and allowing the mixture to stand for 2 hours. The H_2SO_4-treated polymer was obtained by adding 100 mL ether to the mixture followed by filtration and washing the product at least four times with an additional 100 mL ether. The polymer, dark violet in color, was dried overnight under vacuum at 50-60°C.

ATA, ATATA, and the AT polymer were separately stirred in conc. sulfuric acid until most of the material in each case appeared to dissolve. ATA gave a clear solution after 15 minutes, whereas the sulfuric acid solution of ATATA and the AT polymer had to be filtered through a sintered glass funnel to obtain a clear solution. A part of the solution was transfered into an NMR tube for NMR studies, and a part of it was precipitated with water. The precipitate was filtered, washed with water until it was free of acid, dried under vacuum at 60°C, and saved for IR analysis. A sealed capillary containing DMSO d_6 (for deuterium lock) and TMS (internal standard) was put into the NMR tube.

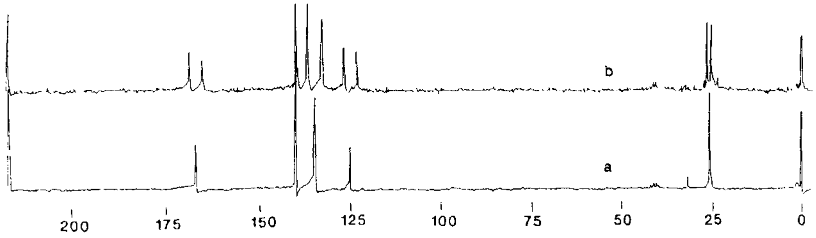


Figure 6. (a) ^{13}C NMR spectrum of ATA in H_2SO_4 (completely decoupled)

(b) ^{13}C NMR off-resonance spectrum of ATA in H_2SO_4

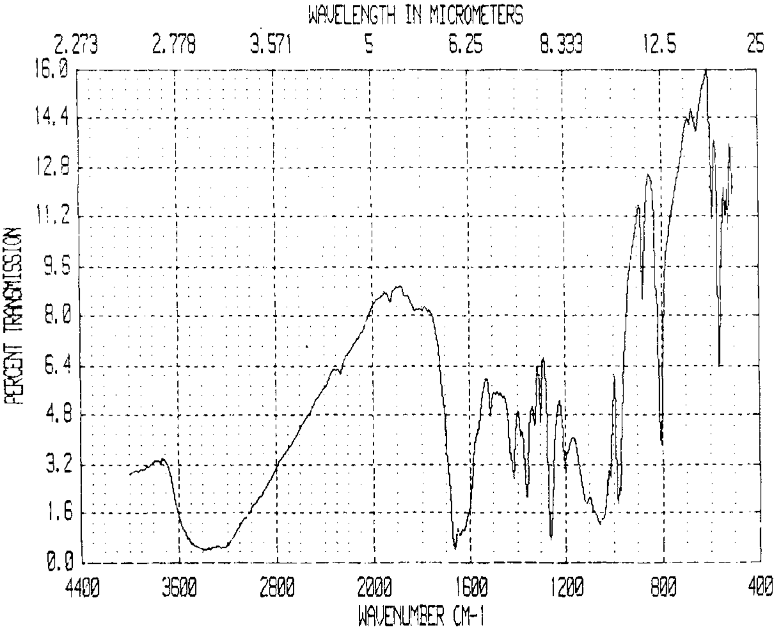


Figure 7. IR spectrum of BF_3-treated ATA

ATA: ^{1}H NMR(H_2SO_4) δ 2.79(s, 3H, $CH_3$with satellite signals at δ 2.68 and δ 2.99), δ 7.27(d, 2H, vinylic H_a, J = 18.9 Hz), δ 8.51(d, 2H, vinylic H_b, J = 16.2 Hz), δ 7.84(s, 4H, arom.), δ 10.37(s, $=OH^+$) (Figure 5). ^{13}C NMR (H_2SO_4) δ 25.06(CH_3), δ 217.78(C=O), δ 124.52, δ 166.59(C_3, C_4 vinylic), δ 139.34 (ring ipso), δ 134.16(ring ortho) (Figure 6).

Exposure of a sample of AT polymer or oligomer to gaseous HCl or to the vapor over a conc. HCl solution causes the sample to turn red immediately. Upon removal of the sample from the HCl vapor, it reverts to its original yellow color within a few seconds. Similar exposure of AT polymer and oligomers to the vapor of BF_3 Et_2O in a previously evacuated chamber for 5-24 hours yielded products whose IR spectra contain a strong band near 100 cm^{-1} (B–O–C stretch). The spectrum of ATA thus treated with BF_3•Et_2O is illustrative (Figure 7).

RESULTS AND DISCUSSION

Synthesis and Characterization. To throw some light on the structure of the acetone-terephthalaldehyde polymer, we synthesized several compounds of definite structure - ATA, TAT, ATATA, TATAT, BATAB - which would allow us to correlate their properties with those of the polymer. The reactions leading to these oligomers are shown in Scheme 1.

Lebsadze et al. [2] reported the AT polymer to be fully dehydrated but did not provide corroborating evidence. Our IR and elemental analyses suggest the presence of aldol units in our product. The AT polymer as well as other compounds synthesized are yellow in color. The infrared spectrum of the polymer shows the presence of both dehydrated (C=C) and aldol (OH) units. The polymer was extracted with methanol (Soxhlet extraction) and two

T + excess A ——> ATA
A + excess T ——> TAT
ATA + excess T ——> TATAT
ATA + excess B ——> BATAB
TAT + excess A ——> ATATA
ATATA + excess T ——> TATATAT
ATATA + excess B ——> BATATAB
TATAT + excess A ——> ATATATA
ATA + TAT ——> ATATAT
A + T ——> AT Polymer

SCHEME 1 Reactions of Terephthalaldehyde, Acetone and Benzaldehyde fractions were obtained. The unextracted fraction has twice the ($A_{int.\ C=O}/A_{ter.\ C=O}$) ratio that the extracted fraction has, where $A_{int.\ C=O}$ is the absorbance of the internal carbonyl groups (1648 cm^{-1}) and $A_{ter.\ C=O}$ is the absorbance of the terminal carbonyl groups (1700 cm^{-1}). Also the ($A_{int.\ C=O}/A_{OH}$) of the unextracted fraction is 1.6 times that of the extracted fraction, where A_{OH} is the absorbance of the hydroxyl groups (3500 cm^{-1}). This result is expected because the insoluble fraction would have more internal carbonyl groups and fewer hydroxyl groups than the soluble fraction.

Of the oligomers prepared, ATA, TAT, ATATA, TATAT, and BATAB are fully dehydrated; that is, there is no evidence of a hydroxyl stretching band in the IR spectra of these compounds. The solubility of these compounds drops quite rapidly with increasing molecular weight after TAT. The compounds with terminal aldehydic groups are less soluble than the compounds with methyl groups.

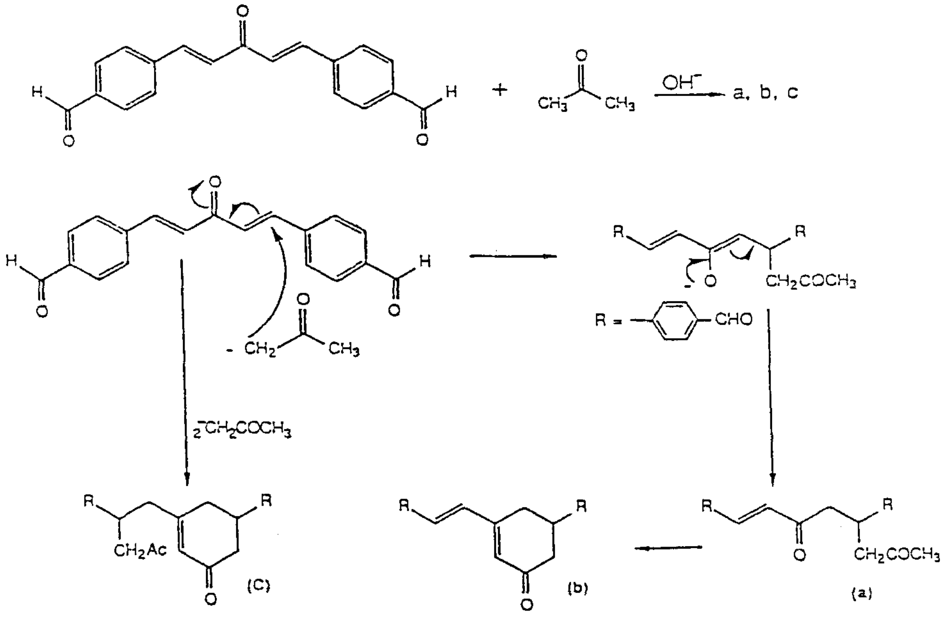
The molecules with chains longer than TATAT cannot be prepared directly because of their very low solubilities. When TATAT was reacted with acetone using the above procedure, even after two days of reaction, fully dehydrated product could not be obtained. The IR spectrum of this product is similar to that of the polymer obtained from the acetone-terephthalaldehyde polymerization.

To overcome solubility problems, we attempted polymerizations at higher dilution, but these attempts led only to recovery of starting material, terephthalaldehyde. Attempts to prepare BATATAB, ATATATA and ATATAT gave products that show a broad IR band around 3500 cm^{-1}. This suggests that, in higher oligomers and polymer, as soon as the aldol product is formed, it precipitates out before it has a chance to dehydrate. The products of the reactions, benzaldehyde with ATATA, TATAT with excess acetone, and TAT with ATA, do not show the typical aldehydic C-H stretch at 2750 cm^{-1} and 2850 cm^{-1} but show a broad band at 3500 cm^{-1} in the IR spectrum. This indicates that the terminal CHO groups have reacted to form aldol products. The aldol reactions can be conducted under acidic conditions using dry HCl [5,6] to produce a halogen-substituted product, which could be more soluble than the dehydrated one. When we applied this reaction to the synthesis of dibenzalacetone, we obtained the fully conjugated dibenzalacetone and not the halogenated derivative, as indictated by the IR spectrum and the melting point of the product, both of which correspond to dibenzalacetone. In case of the acetone-terephthalaldehyde reaction, the product did contain a small amount of Cl, but C, H analysis does not agree with the calculated one probably because of slow combustion during analysis.

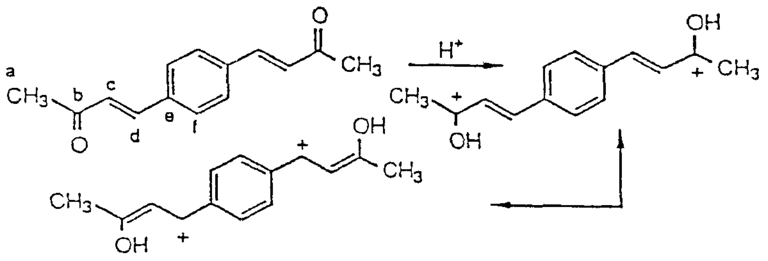
While synthesizing these model compounds we found that ATA could be made only at A:T ratios greater than 50:1. Using 30:1 of A:T, we obtained only polymer. The molar ratio of base to terephthalaldehyde in this latter case was 2.5:1; moreover, the product, ATA, could not be obtained in good yields. Therefore, the use of acetone in 200 molar excess and base in 20 molar excess over terephthalaldehyde was explored. Not only did these extreme molar excesses give ATA in good yield (80% crude, 50% recrystallized), but also the work-up was much easier.

We explain these results by assuming that ATA enolate is less basic than acetone enolate and is therefore formed at the expense of the latter, especially at lower OH^- concentrations. When acetone enolate is not present in sufficient amounts, ATA enolate is the only nucleophile present and gives rise to the polymer. The large excess of acetone and base ensure the presence of the more basic and more reactive acetone enolate at all times.

In the preparation of TAT, we found that terephthalaldehyde in at least 5 molar excess over acetone was necessary to get a good product and to have an easy work-up. The need for lower excess of terephthalaldehyde over acetone may be explained by the fact that the intermediate TA anion, formed by the reaction of $CH_3COCH_2^-$ with terephthalaldehyde, regardless of the



SCHEME 2



SCHEME 3

presence of acetone enolate, has no choice but to react with terephthalaldehyde to form the product, TAT, which is insoluble in the reaction solvent (methanol) and therefore is not available for further reaction.

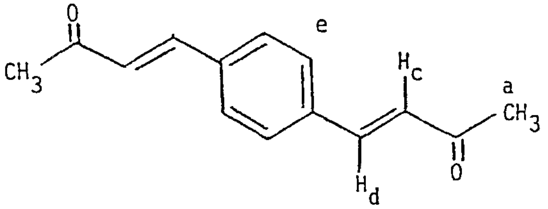
The possibility of a Michael addition during all of these acetone-terephthalaldehyde reactions suggests the possible formation of cyclic products, as shown in Scheme 2 for the reaction of acetone with TAT.

In order to find evidence for such products as a,b and c, the reaction time was increased to 24 hours (in the synthesis of ATATA). We found no evidence in the infrared and NMR spectra for these products. Moreover, none of these Michael addition products could be isolated when the amount of base in these reactions was increased. This suggests that the Michael-addition reaction is not significant under these conditions.

HCl, both dry gas and the concentrated aqueous solution, causes a reversible change in color from yellow to red. This color change strongly suggests that protonation is occurring. Reversible protonation is further supported by the following observation: when water is added to the red sulfuric acid solution of ATA, ATATA and AT polymer, the original yellow material is regained, as evident from the IR spectra. In the case of ATA, the product precipitated from sulfuric acid solution shows a ^{1}H NMR spectrum identical with that of the starting material. The higher oligomers are not sufficiently soluble in sulfuric acid to yield NMR spectra.

Both ^{1}H NMR and ^{13}C NMR in sulfuric acid provide an insight into the reaction with acids. Of ATA, TAT, ATATA, and the AT polymer, the NMR spectrum of only ATA could be obtained. This might be due to the lesser solubility of the other oligomers in concentrated sulfuric acid, although all the oligomers gave a dark reddish color in sulfuric acid. In the reaction with acid, we suggest that the carbonyl oxygen accepts the proton (Scheme 3).

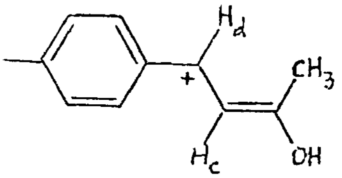
TABLE 1. Proton NMR Chemical Shifts of ATA in DMSO and H_2SO_4



	$CDCl_3$	H_2SO_4	Paramagnetic Shift, Hz
(a) (CH_3)	2.36	2.79	38.70
(c) Vinylic H_c	6.73	7.27	48.60
(d) Vinylic H_d	7.49	8.51	91.80
(e) Aromatic	7.55	7.84	26.10

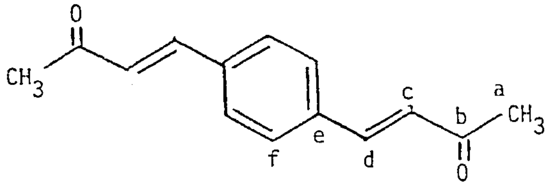
Protonation of the carbonyl oxygen is evidenced by both ^1H NMR and ^{13}C NMR, in agreement with previous observations [7]. The proton NMR spectrum exhibits the paramagnetic shifts shown in Table 1.

The large paramagnetic shift observed for H_d is consistent with oxygen protonation which places a large positive charge on H_d:



That all the shifts are paramagnetic suggests that considerable delocalization of the positive charge has occurred. The signal at δ 10.37 can be assigned to the proton on the oxygen atom. This view is supported by ^{13}C NMR - both off-resonance and completely-decoupled spectra - as shown in Figure 6 and Table 2. The carbonyl carbon atom also experiences a paramagnetic shift, for there is a positive charge on this carbon atom after protonation.

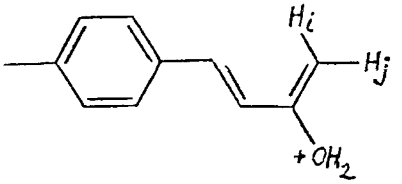
TABLE 2. ^{13}C Chemical Shifts of ATA in DMSO and in H_2SO_4



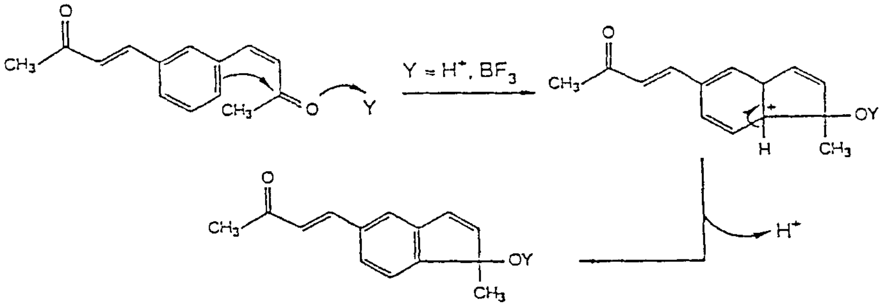
	DMSO	H_2SO_4	Paramagnetic,Shift
(a)	27.36	25.06	-207.00
(b)	197.95	217.28	+1739.70
(c)	128.01	124.52	-314.10
(d)	142.04	166.59	+2209.50
(e)	136.25	139.34	+278.10
(f)	128.83	134.16	+479.70

Delocalization of the positive charge may account for the paramagnetic shift of (d) carbons. It may be argued that the shift could be due to the use of a different solvent, but the proton NMR spectrum of ATA in DMSO d_6 was identical with that of ATA in $CDCl_3$, thereby suggesting that the paramagnetic shift in this case is not solvent-induced.

The coupling constants in the proton NMR spectra are consistent with the trans-structures shown (J 16 Hz in $CDCl_3$ and 17 Hz in H_2SO_4). A final note is made of the satellite signals on either side of the methyl signal in H_2SO_4 solution: These signals, which may be due to side bands, may alternatively be due to a small amount of protonated terminal enol,



in which H_i and H_j give rise to the higher and lower field signals, respectively.



SCHEME 4

There is the possibility of cyclization of these materials through the carbocations produced during acid treatment, as shown for ATA in Scheme 4.

But even after 15 days in conc. sulfuric acid there was no sign of any cross-linking or decomposition of ATA as indicated by its proton NMR spectrum in sulfuric acid. Moreover, the IR spectrum of ATA precipitated from concentrated sulfuric acid solution after 7 days in acid was identical to that of the untreated material.

To determine whether sulfuric acid treatment causes a permanent change in the polymer, doped polymer was triturated with aqueous ammonia and allowed to stand for 2 hours followed by filtration and washing with water and ethanol. The IR spectrum of the dried material was identical with that of the pristine polymer.

An analogous chemistry may be taking place during BF_3-treatment. The incorporation of BF_3 in these compounds can be shown by IR spectroscopy. A band around 1200 cm^{-1} indicates the B-O-C bond [8]. IR spectra of doped materials all show the characteristic trailing off at 1800-4000 cm_{-1}. ATA shows a typical spectrum (Figure 7). After evacuating the treated samples under dynamic vacuum for 24 hours, the broad band around 1100 c^{-1} remains unabated, suggesting the possibility of delocalized positive charge on the carbon atom of the carbonyl group, leading to the stretching absorption of the B-O-C bond at lower frequency (the band in $BH_3 \bullet Et_2O$ occurs at 1200 cm^{-1}). Evacuating a pellet of polyterephthaloyl [9] for 5 hours results in complete loss of the IR band at 1000-1200 cm^{-1} and to a spectrum identical to that of polyterephthaloyl. This suggests that the carbonyl group of polyterephthaloyl does not bond strongly with BF_3, possibly owing to the positive charge accumulated on the adjacent carbonyl carbon atom. In contrast, the carbonyl groups of the AT oligomers can bond to BF_3 to create delocalized positive charges.

The effect of atmospheric moisture on BF_3-treated materials has been ruled out as follows: If there were a reaction between BF_3-treated oligomers and atmospheric humidity during IR spectral studies, the same should be observed for BF_3-treated polyterephthaloyl. In the latter case, no difference was observed between the IR spectra of untreated and that of evacuated, treated sample; thereby suggesting that the band near 1100 cm^{-1} in the IR spectrum of BF_3-treated samples is due to the reaction of the carbonyl oxygen atom and BF_3.

CONCLUSIONS

(1) Formation of AT polymer proceeds with incomplete aldol dehydration.

(2) Oligomers ATA, TAT, ATATA, TATAT, and BATAB have been prepared and characterized.

(3) The base-catalyzed preparation of ATA requires the use of at least 50/1 excess of A/T and large ratios (20/1) of base/T; otherwise, polymer results.

(4) The preparation of TAT requires a T/A ratio of 5/1.

(5) Michael addition is not observed during base-catalyzed synthesis of AT polymer or oligomers or during their reactions with strong acids.

(6) Strong protonic acids react with AT polymer and its oligomers to give O-protonation, and with BF_3 to give O-boronation.

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