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Polyacrylonitrile with Reactive End Groups

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ABSTRACT: Low molecular weight polyacrylonitriles with hydroxyl, carboxyl, chloride, thiol and thiosulfate end groups have been prepared. Polymers initiated with β,β'-azobis(β-cyanopropanol) have two alcohol end groups but no success was had in extending these polymers with diisocyanates. Polymers initiated by H_2O_2/Fe^{3+} can be obtained with two reactive end groups. Two-thirds of the end groups are hydroxyl functions, one-third are carboxyl functions. After reaction with 0.5 mol of phthalic anhydride, a polymer with two carboxyl groups results. Polymers initiated with Fe^{2+}/H_2O_2 contain mainly hydroxyl end groups. These polymers are very polydisperse. Polymers initiated by 1,1′-dichloro-1,1′-diphenyl(1,1′-azoethane) cannot be extended with hexamethylenedithiol because of elimination (instead of substitution) of the chlorine. Polymers (η_{inh} 0.31) initiated with 1,1′-dichloro-1,1′-di(*m*-chloromethylphenyl)(1,1′-azoethane) can be easily chain extended by heating with excess dithiol and subsequent oxidation, or by treatment with sodium thiosulfate and subsequent oxidation with iodine. This last method yielded white products (even after condensation) with inherent viscosities of ~1.

The end groups of polymers obtained with free radical initiators are determined by the initiators used and by chain transfer and chain termination reactions. At low initiation rates, using a nontransfer solvent and with an initiator not undergoing induced decomposition, the number of initiator fragments incorporated in one polymer chain is determined by the ratio of disproportionation to addition termination. Polyacrylonitrile is reported to terminate by addition of two growing chains.[2,3] When a functional group is incorporated in a free radical initiator, a polymer with reactive end groups is expected to form.

The intention of this work was to prepare a low molecular weight polyacrylonitrile with active end groups which could be easily converted into a higher molecular weight polymer by condensation reactions. Similar work has been done by Bamford[2-4] with γ,γ'-azobis(γ-cyanovaleric acid) and δ,δ'-azobis(δ-cyano-*n*-pentanol).

Polymers with Hydroxyl End Groups. To achieve our intentions we first prepared low molecular weight polymers of acrylonitrile for which β,β'-azobis(β-cyanopropanol) was used as the initiator in dimethylformamide solution. This gave a polymer with an inherent viscosity of 0.14 which gives a calculated molecular weight of 2300 using the Mark–Houwink equation.[5] The equivalent weight calculated from the nmr spectrum (Figure 1) by comparing the intensity for methyl groups with those of methylene protons is 1100. A gel permeation chromatography (gpc) curve shows that $\overline{M}_w/\overline{M}_n = 1.8$.

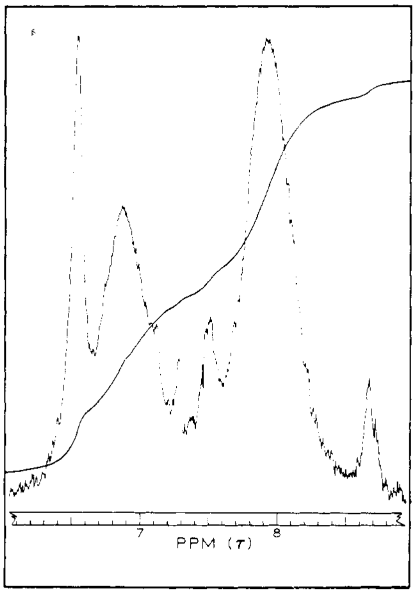
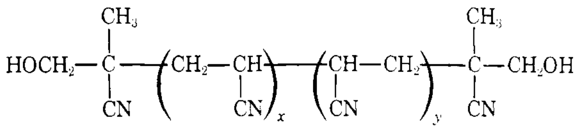


Figure 1. Nmr spectrum of the structure shown below in DMSO-d_6 (external reference, TMS). Resonance at τ 6.55 and 7.50 is attributed to the solvent. Resonance at τ 6.88, 7.92, and 8.68 is attributed, respectively, to methine, methylene, and methyl protons of the polymer.



$$\mathrm{HOCH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}\left(CH_2{-}\underset{CN}{CH}\right)_x\left(\underset{CN}{CH}{-}CH_2\right)_y{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2OH}$$

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[1] Postdoctoral Research Associates supported by Textile Fibers Department of E. I. du Pont de Nemours and Co., Inc., 1966–1967.

[2] (a) B. E. Bailey and A. D. Jenkins, *Trans. Faraday Soc.*, **56**, 903 (1960); (b) C. H. Bamford, A. D. Jenkins, and R. P. Wayne, *ibid.*, **56**, 932 (1960).

[3] C. H. Bamford, A. D. Jenkins, and R. Johnston, *ibid.*, **55**, 179 (1959).

[4] C. H. Bamford and A. D. Jenkins, *Nature*, **176**, 78 (1955).

[5] C. H. Bamford, A. D. Jenkins, R. Johnston, and E. F. T. White, *Trans. Faraday Soc.*, **55**, 168 (1959).

Table I
Polymerization of Acrylonitrile to Give Active End Groups

Compd	Acrylonitrile, mol	H_2O_2, mol	$FeCl_3$, mol	Temp, °C	Reaction time, hr	Yield, %	$[\eta]_{inh}$[a]	E_h	E_a	Ratio of carboxyl to hydroxyl end groups
I	1	0.1	0.008	30	6	94	0.46	2,995	9,200	0.45
II	1	0.2	0.008	30	18	74	0.28	1,860	5,328	0.50
III	1	0.4	0.008	30	18	66	0.18	1,430	4,516	0.41
IV	1	0.6	0.008	30	18	60	0.16	1,416	3,924	0.50
V	1	0.8	0.016	10	6	50	0.31	2,425	6,230	0.59
VI	1	0.8	0.048	10	2	52	0.16	1,460	4,160	0.50
VII	1	0.8	0.48	−15	12	40	0.39	4,403	13,900	0.45
VIII[b]	0.33	0.4	0.008	10	5	50	0.13	1,203	3,156	0.54

[a] Determined in dimethylformamide (0.5 g/100 ml) at 30°. [b] The values for VIII were obtained using 40% MeOH as solvent.

Condensation of this polymer with methylene bis-(4-phenylisocyanate) proved unsuccessful. It is probable that the alcohol group is sterically hindered to isocyanate attack by the methyl and cyano group α to the methylene group. A similar effect is noted in neopentyl alcohol and is believed to be responsible for its lack of reactiveness.

We next tried to initiate acrylonitrile polymerization with H_2O_2/Fe^{3+} as recommended by Parts.[6] The mechanism of initiation by this system has been discussed by others.[7-11] The polymers which we obtained (see Table I) contained both hydroxyl and carboxyl end groups. The equivalent weight (E_a) in carboxyl groups was determined by titration with base. The polymers were then condensed with phthalic anhydride to give acid phthalates in the hydroxyl function and again titrated to give the equivalent weight in both carboxyl and hydroxyl groups (E_h). The ratio of carboxyl end groups to hydroxyl end groups was very constant over a wide variety of conditions and the average ratio was 0.49. Merz and Waters[12] have indicated that the radicals $-CH_2O\cdot$ and $\cdot$CHOH may be produced in this initiation process. This could lead to carboxyl and hydroxyl end groups.

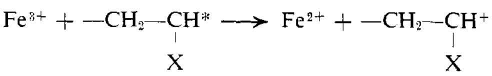
The molecular weight distribution, $\overline{M}_w/\overline{M}_n = 2.15$, as shown by gpc was quite normal.

A third method of preparing short-chain polyacrylonitriles with active end groups was tried using Fenton's reagent.

The use of Fenton's reagent as a free radical initiator has been extensively studied.[13-16] Polymers are reported to have two alcohol end groups[13] (end group analyses were performed on polystyrene).

The reaction occurs only at low Fe^{2+} and H_2O_2 concentration. At high Fe^{2+} concentrations, the hydroxyl radical is reduced instead of initiating a polymer chain.

Best results are obtained in acid media. In this way H_2O_2/Fe^{3+} initiation is avoided. Generated Fe^{3+} acts as chain terminator.[17,18]



$$\mathrm{Fe^{3+}} + -\mathrm{CH_2}-\underset{\overset{|}{\mathrm{X}}}{\mathrm{CH}}{}^{*} \longrightarrow \mathrm{Fe^{2+}} + -\mathrm{CH_2}-\underset{\overset{|}{\mathrm{X}}}{\mathrm{CH}}{}^{+}$$

In kinetic studies of this reaction, ferrous perchlorate is often employed. Although most other anions form complexes with the ferrous ion, these complexes are often reported to give even faster initiation.[19] We found that these polymers, prepared in this system, contained both carboxyl and hydroxyl end groups, and when condensed with diisocyanate, gave insoluble materials.

Polymers with Active Chlorine Ends. A polymer formed in the system $Bz_2O_2/CCl_4/AN$ is reported to have –Cl and $-CCl_3$ end groups.[20] Such a polymer was treated with excess sodium sulfide in DMF solution. Upon oxidaton with air, the polymer became insoluble. This indicates reaction at the chloride ends and prompted us to make a study of chlorine containing initiators. These initiators are not easily accessible because of the reactivity of the chloride group in nucleophilic substitution and reduction reactions.

1,1′-Dichloro-1,1′-diphenyl(1,1′-azoethane) is easily formed by addition of chlorine to the corresponding azine.[21] The azo compound gives, upon heating in benzene, 2,3-dichloro-2,3-diphenylbutane.

The decomposition of 1,1′-dichloro-1,1′-diphenyl-(1,1′-azoethane) was carried out in DMAC at 80°. From this reaction there was isolated 25% yield of acetophenone (in the form of its dinitrophenylhydrazone). This indicated a deviating reaction pattern. Polymerization experiments in DMAC with acrylonitrile gave, accordingly, poor results. Consequently, the polymerizations shown in Table II were carried out in benzene.

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(16) J. F. Baxendaele, S. Bywater, and M. G. Evans, *J. Polym. Sci.*, **1**, 237 (1946).

(17) F. S. Dainton and P. H. Seaman, *ibid.*, **39**, 279 (1959).

(18) F. S. Dainton, P. H. Seaman, D. G. L. James, and R. S. Eaton, *ibid.*, **34**, 209 (1959).

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(21) S. Goldschmidt and B. Ackersteiner, *Ann.*, **618**, 173 (1958).

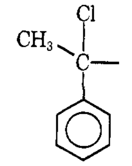
TABLE II
POLYMERIZATION OF ACRYLONITRILE WITH ABOVE AZO INITIATOR CONTAINING ACTIVE CHLORINE

Compd	AN, mol	Initiator, mol	Temp, °C	Time, hr	Yield, %	η_{inh}	Cl, %
I	2.5	0.125	50	2	73	0.33	1.77
II	2.5	0.125	70	0.75	45	0.2	

TABLE III
POLYMERIZATION OF ACRYLONITRILE WITH ABOVE AZO INITIATOR

AN, mol	Initiator, mol	Temp, °C	Time, hr	Yield, %	η_{inh}	Cl, %
2.5	0.125	50	1	75	0.31	2.56

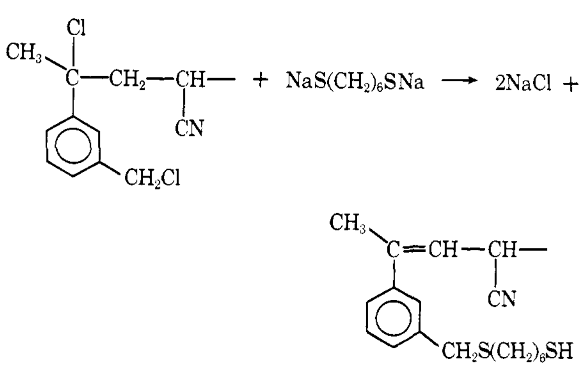
These polymers should have the end groups



When these polymers (I) were heated with an equivalent amount of the sodium salt of hexamethylenedithiol (several hours at 110°), the viscosity remained constant. The chlorine content of the polymer dropped to 0.42%. This indicates that the chlorine atom was removed by elimination instead of substitution.

Polymers Initiated with 1,1′-Dichloro-1,1′-di(*m*-chloromethylphenyl)(1,1′-azoethane). This initiator can be prepared by chlorination of *m*-chloromethylacetophenone azine. Upon decomposition in benzene the azo compound yielded 2,3-dichloro-2,3-di(*m*-chloromethylphenyl)butane. Polymerizations in benzene were carried out with this new initiator. The reaction conditions and results are given in Table III. During the reaction, the polymer precipitated as a white powder.

Condensation Experiments. Condensation with Dithiols. The following condensation reaction was attempted.



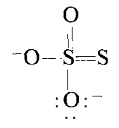
$$2HS-R + I_2 \longrightarrow 2HI + RS-SR$$

The polymer was treated with the sodium salt of hexamethylenedithiol, acidified and oxidized with iodine. The oxidation was very fast and accordingly the rise in viscosity was spectacular: initial η_{inh} 0.31; after condensation η_{inh} 0.86.

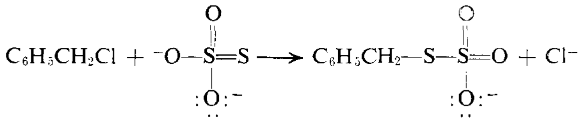
Because of the strong basic properties of the thiol salt, the polymer became brown. To obtain a cleaner condensation, a weaker base was chosen.

Condensation with Sodium Thiosulfate. Thiosulfates have special properties in substitution reactions. They are very weak bases (pK = 1.4, 2.5) but, nevertheless, they are very reactive to carbon–X in the sp^3 configuration (X = leaving group). On the other hand, they show very little reactivity if the carbon is in the sp^2 configuration (acyl halides).

Furthermore, the nucleophilic center is different from the basic center, *i.e.*, the center of greatest basicity is on the oxygen, while the center of greatest nucleophilic reactivity is on the sulfur atom. Benzyl thiosulfate gives dibenzyl disulfide by iodine oxidation.[22]



$$^{-}O-\overset{O}{\underset{:\ddot{O}:^{-}}{S}}=S$$



$$C_6H_5CH_2Cl + {}^{-}O-\overset{O}{\underset{:\ddot{O}:^{-}}{S}}=S \longrightarrow C_6H_5CH_2-S-\overset{O}{\underset{:\ddot{O}:^{-}}{S}}=O + Cl^{-}$$

The chlorine-containing polymer was allowed to react with sodium thiosulfate. The mixture was separated and the polymer solution was oxidized with iodine. The oxidation was instantaneous and the resulting polymer was white: initial η_{inh} 0.31 (mol wt ~7000); after condensation η_{inh} 0.98 (mol wt ~33,500).

This reaction was very clean, involved fast reactions at room temperature and did not require a stoichiometric balance in reactive groups. The fact that all of the obtained condensed polymers were completely soluble illustrates that the chlorine on the tertiary carbon was removed by elimination, not by substitution.

Experimental Section

β,β′-Azobis(β-cyanopropanol). In a 2-l. screw-capped bottle were added 15.4 g (0.32 mol) of sodium cyanide, 20.5 g (0.16 mol) of hydrazine sulfate and 400 ml of ice water. The bottle was capped to prevent loss of hydrogen cyanide. To the cooled mixture was added 22.2 g (0.3 mol) of α-hydroxyacetone. The bottle was capped and held at 0° for 15 min and then allowed to warm to room temperature. The bottle was occasionally shaken for 6 hr and then allowed to stand for an additional 15 hr. The contents of the bottle were transferred to a 2-l. three-necked flask equipped with a stirrer, thermometer, and dropping funnel. The flask was cooled to less than 10° and bromine was added dropwise to the stirred solution until a slight orange color persisted. Excess bromine was destroyed with aqueous sodium bisulfite. The white precipitate was filtered, washed with cold water and dried, mp 145° dec (recrystallized from EtOH). The yield was 60% of theory.

Anal. Calcd for $C_8H_{12}N_4O_2$: C, 48.98; H, 6.12; N, 28.57; O, 16.38. Found: C, 49.26; H, 6.19; N, 28.37; O, 16.63.

Polymerizations were performed in capped bottles under a nitrogen atmosphere. The polymers were precipitated in water or methanol. Indicated viscosities are always inherent and obtained on 0.5 g/100 ml of DMF at 30°.

Reactions in Fe^{2+}–Fe^{3+}/H_2O_2 Systems. H_2O_2/Fe^{3+} Poly-

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[22] T. S. Price and A. Jacques, *J. Chem. Soc.*, 105, 1140 (1914).

merizations. Nitrogen was bubbled through the appropriate quantity of water and hydrogen peroxide and acrylonitrile were then added along with a corresponding quantity of a ferric chloride solution. The reaction mixture turned deep brown (FeOOH^{2+}) and the polymer started to precipitate almost immediately. If oxygen was not removed, long induction periods occurred.

To quench the reaction, a strong acid was added (HNO$_3$) and the mixture turned completely white (the complex FeOOH^{2+} is suppressed). The polymer was filtered and washed several times. For purification, the polymer was dissolved in dimethylformamide and precipitated in methanol.

Phthalation. Polymer (3 g), 3 g of phthalic anhydride, 3 ml of pyridine and 20 ml of dimethylformamide were dissolved and heated for 1 hr at 90°. The polymer was precipitated in MeOH, filtered, dried, redissolved in dimethylformamide and reprecipitated.

Titration. About 1 g of polymer, obtained in reaction under 1 or 2, was dissolved in about 40 ml of DMF. The solution was titrated with 0.1 *N* NaOH and the equivalent point was determined using a potentiometer.

Fe^{2+}/H$_2$O$_2$ Polymerizations. The procedure was essentially identical with the ferric salt. Polymerizations were very fast. Using 1 mol of acrylonitrile, 0.2 mol of hydrogen peroxide, 0.2 mol of FeSO$_4$ and 0.5 mol of sulfuric acid, a polymer with an inherent viscosity of 0.97 was obtained in 40% yield in 20 min at 10°. Titration showed the ratio of carboxyl end groups to hydroxyl end groups was 0.1. The molecular weight distribution determined by gpc was $\overline{M}_{\text{w}}/M_{\text{n}} = 9.1$.

Reactions with Chlorine-Containing Initiators. 1,1′-Dichloro-1,1′-diphenyl(1,1′-azoethane). This azo compound was prepared from acetophenone azine and chlorine.[23]

Decomposition of 1,1′-Dichloro-1,1′-diphenyl(1,1′-azoethane) in DMAC. Azo compound (2 g) in 20 ml of DMAC was heated at 80° until nitrogen evolution ceased. An equivalent amount of 2,4-dinitrophenylhydrazine dissolved in 75 ml of MeOH with addition of 2 ml of H$_2$SO$_4$ was added. A hydrazone compound (1 g) separated. This product was acetophenone 2,4-dinitrophenylhydrazone (25%). It was identical with a sample prepared from acetophenone and 2,4-dinitrophenylhydrazine, mp 237°.[24]

Polymerization with 1,1′-Dichloro-1,1′-diphenyl(1,1′-azoethane) in Benzene. Recipes are indicated in the theoretical part and need no further comments.

Preparation of the Disodium Salt of Hexamethylenedithiol. Sodium was dissolved in methanol, titrated and added to an equivalent amount of dithiol. The solution was evaporated under vacuum and heated for 1 hr at 100° under 0.3 mm pressure. A white powder resulted.

Condensations with Polymers from the Above Initiation. Polymer (2 g) dissolved in 10 ml of DMAC was heated with a calculated amount of dithiolsodium salt (the molecular weight of the polymer was estimated from chlorine analysis and viscosity). The mixtures were heated as high as 110° for 6 hr. After the reaction was finished, the polymer was precipitated in MeOH.

Reactions for the Preparation of 1,1′-Dichloro-1,1′-di(*m*-chloromethylphenyl)(1,1′-azoethane). Methyl chloromethyl ether was prepared from formaldehyde, MeOH and hydrochloric acid.[25] *m*-Chloromethylacetophenone was prepared by chloromethylation of acetophenone.[26]

m-Chloromethylacetophenone Azine. Ketone (15.012 g) was dissolved in 45 ml of acetic acid and an equivalent amount of hydrazine hydrate was added (2.17 ml). After about 3 hr at room temperature, the reaction mixture was filtered and the azine recrystallized from acetic acid. The yield was 13 g (90%), mp 123–124°.

Anal. Calcd for C$_{18}$H$_{18}$N$_2$Cl$_2$: C, 64.87; H, 5.41; N, 8.41; Cl, 21.32. Found: C, 64.96; H, 5.48; N, 8.31; Cl, 21.51.

1,1′-Dichloro-1,1′-di(*m*-chloromethylphenyl)(1,1′-azoethane). Azine (10 g) was cooled at −70° (Dry Ice–acetone) and chlorine was introduced until a visible quantity of liquid chlorine was evident. The excess chlorine was removed by an aspirator and the residual white product was recrystallized from acetone (20 to −20°), mp 103° dec. The yield was quantitative.

Anal. Calcd for C$_{18}$H$_{18}$N$_2$Cl$_4$: C, 53.47; H, 4.46; N, 6.93; Cl, 35.15. Found: C, 53.72; H, 4.49; N, 7.04; Cl, 34.98.

2,3-Dichloro-2,3-di(*m*-chloromethylphenyl)butane. Azo compound (5 g) was heated in 50 ml of benzene at 75° for 1 hr. After cooling, the product separated in crystals, mp 174° (benzene).

Anal. Calcd for C$_{18}$H$_{18}$Cl$_4$: C, 57.48; H, 4.80; Cl, 37.74. Found: C, 57.30; H, 4.60; Cl, 37.65.

Polymers from 1,1′-Dichloro-1,1′-di(*m*-chloromethylphenyl)(1,1-azoethane). Polymerizations. The polymerization recipes are given in the theoretical part. Polymerizations are carried out under nitrogen in pressure bottles. The polymer was purified in the system DMF–benzene.

Condensations with Dithiols. The amount of sodium salt of hexamethylenedithiol was calculated in the chlorine content of the polymer. Thiol salt (1 equiv) was used for 1 mol of chlorine. In order to determine the chlorine content, the results of the analysis plus 0.3% were employed. Polymer (2 g) required 166 mg of NaS(CH$_2$)$_6$SNa.

The polymer was first dissolved in 20 ml of dimethylacetamide. The sodium salt of the dithiol together with 20 ml of dimethylacetamide and some iron balls were put in a high-pressure bottle. The mixture was shaken until a fine suspension was obtained; afterward it was transferred to the polymer solution and heated for 12 hr at 50°. The color of the reaction mixture depends very much upon the quality of the salt suspension. After the reaction, hydrogen chloride was introduced until all sodium salts are neutralized (the color of the mixture turns yellow). Upon addition of an iodine solution in DMAC, the viscosity increased immediately. The polymer was precipitated in water containing some thiosulfate to neutralize excess iodine.

Condensations with Sodium Thiosulfate. Polymer (2 g), 1 g of water-free sodium thiosulfate, 20 ml of DMAC and some iron balls were shaken in a high-pressure bottle for 3 days at room temperature. The mixture was centrifuged and the clear supernatant liquid separated.

An excess of an I$_2$–DMAC solution was added and immediate condensation occurred. The polymer solution was diluted and precipitated in water containing some sodium thiosulfate. The polymer precipitated almost white.

The reagents used are as follows: α-hydroxyacetone, Jefferson Chemical Co., used as received; acrylonitrile, Matheson Coleman and Bell (for purification the monomer is passed through a silica gel column); FeCl$_3$·6H$_2$O, Mallinckrodt AR; FeSO$_4$·7H$_2$O, Mallinckrodt AR; H$_2$O$_2$ (30% solution), Mallinckrodt AR; N,N-dimethylformamide, Matheson Coleman and Bell (the product is distilled under nitrogen); N,N-dimethylacetamide, Baker Analyzed Reagent (this product is dried over P$_2$O$_5$ and distilled under reduced pressure); hexanedithiol, Aldrich, used as received.

Acknowledgment. The financial support of the

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(24) C. F. H. Allen, *J. Amer. Chem. Soc.*, **52**, 2955 (1930).

(25) C. S. Marvel and P. K. Porter, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p 369.

(26) Ya. L. Gol'dfarb and Yu. B. Vol'kenshtein, *Zh. Obschch. Khim.*, **31**, 616 (1961); *Chem. Abstr.*, **55**, 24712 (1961).

Textile Fibers Department of E. I. du Pont de Nemours and Co. is gratefully acknowledged. The gel permeation chromatography determinations were done by Dr. Myer Ezrin of DeBell and Richardson, Inc. Analyses were done by Micro-Tech, Skokie, Ill. Dr. W. Bracke is indebted to the International Exchange Service in cooperation with the Exchange Visitors Program for a travel grant.

Poly-9-vinylacridine. Preparation and Some Spectral Properties

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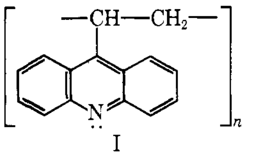
Rehovoth, Israel. *Received July 18, 1968*

ABSTRACT: Poly-9-vinylacridine (9-PVA) was prepared by free-radical initiated polymerization of 9-vinylacridine. Using azobisisobutyronitrile as initiator a fairly high polymer ($n > 25$) was obtained, whereas benzoyl peroxide gave only low molecular weight polymer ($n \sim 5$). The spectrophotometric titration, absorption spectra, fluorescence properties and charge-transfer interactions were studied in comparison with 9-ethylacridine. The apparent $\mathrm{p}K_a$ of the polymer and 9-ethylacridine in 60% dioxane are 2.88 and 4.27, respectively. The absorption spectra of 9-PVA in its two ionization states showed considerable hypochromism and loss of vibrational structure. The fluorescence spectrum of the unprotonated polymer in various anhydrous solvents revealed only an excimer emission band (maximum at 520 mμ) with a relatively high quantum yield of $Q = 0.085 \pm 0.003$. In methanol, however, monomer-type fluorescence was also observed. Aqueous acid solutions of 9-PVA showed only very weak ($Q < 0.01$) monomer-type emission. The two ionization states of the polymer showed less tendency to form charge-transfer complexes than the monomer. On the basis of these observations and structural considerations it is suggested that 9-PVA has a rigid syndiotactic structure in which next nearest neighbors are stacked face to face 3.5 Å apart.

The only reports of the preparation of poly-9-vinylacridine (9-PVA) appear to be as a result of accidental polymerization of salts of 9-vinylacridine in aqueous[2a] or acetone solutions.[2b] Apart from being described as a glassy yellow solid its properties have not been recorded.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9-PVA (I) is a potentially interesting polymer because the bulkiness of the acridine side chains probably severely limits the number of possible conformations, thus providing an excellent system for spectroscopic study of interacting chromophores. The absorption spectra should reflect the ground-state geometry of the acridine, whilst emission spectra should be sensitive to excited state conformations, notably excimer formation which has been observed in polystyrene[3-5] and polyvinylnaphthalene.[4]

The polymer can also be studied as a polycation, and the possibility exists of an intramolecular charge-transfer complex between adjacent protonated and unprotonated acridine residues, as has been observed in acridine–acridinium mixtures.[6] The properties of the array of acridine residues on the polymer may be of help in interpreting the interaction of acridines with polyelectrolytes, especially deoxyribonucleic acid.

Experimental Section

Materials. 9-Vinylacridine. Several routes to 9-vinylacridine appear in the literature.[2,7] The most convenient was found to be that of Fischer[2a] in which 9-methylacridine, prepared from acetic acid and diphenylamine, was converted by a Mannich reaction into 9-(2-dimethylaminoethyl)acridine, which after methylation and a Hofmann degradation yielded 9-vinylacridine. Purification was effected by elution from an alumina column with 1:1 benzene–petroleum ether (bp 30–60°) giving pale yellow crystals on evaporation of the solvent, mp 89° as reported.[2,7]

Poly-9-vinylacridine. Cationic, anionic and free radical initiators were tried. Boiling 9-vinylacridine with dilute hydrochloric acid did not yield any polymeric materials. Neither potassium naphthalene nor butyllithium produced any polymer from solutions of 9-vinylacridine in benzene or in the melt.

Benzoyl Peroxide Initiation. A solution of 9-vinylacridine (500 mg) and benzoyl peroxide (5 mg) in dry benzene (10 ml) with a trace of cobaltous acetate was refluxed under nitrogen for 3 days with occasional addition of more benzene to maintain the volume. The benzene was evaporated and the residue precipitated from chloroform with *n*-heptane, yield 350 mg, mp 200–220° with darkening. This proved to be low molecular weight material of $n \sim 5$ (see below).

Azobisisobutyronitrile (AIBN) Initiation. 9-Vinylacridine (760 mg) and AIBN (0.01 equiv) were polymerized in the melt *in vacuo* for 7 days at 94°. After a few days the melt solidified. Analysis on a Sephadex column (see below) showed that the product contained 20% monomer, the remainder being polymer of $n > 25$. The crude polymer

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