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ESR Study of Intramolecular Energy Transfer in the Radiolysis of Cellulose Thenoates

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Synopsis

The substitution of 2-thenoyl, 5-methyl-2-thenoyl, 2-thiopheneacryloyl, 5-bromo-2-thenoyl, and 5-bromo-2-thiopheneacryloyl groups on fibrous cotton cellulose increased the radiation resistance of cellulose, as indicated by the retention of the breaking strengths of the modified fibrous celluloses at high dosages of γ-radiation, as compared with that of irradiated, unmodified fibrous cellulose. The presence of electropositive or electronegative substituents on the thiophene groups did not reduce the radioprotective effects of these groups for cellulose. Crosslinking of the cellulose thenoates in 1,3-di(4-pyridyl)-propane did not significantly reduce the radiation resistance of the thenoates. Examination of the ESR spectra of irradiated cellulose and cellulose thenoates indicated that the site of the long-lived free radicals on the irradiated cellulose molecules was not changed by the chemical modification. However, the concentration of long-lived free radicals in irradiated cellulose thenoates, at a given radiation dosage, was less than that in irradiated cellulose. The localization of energy on carbon C_1 or C_4 of the cellulose molecule, which leads to depolymerization and loss in breaking strength of fibrous cellulose, was decreased. The radioprotective effects of thiophene groups for cellulose were similar to those of furan and benzenoid groups.

INTRODUCTION

When cotton cellulose in the solid state is exposed to ionizing radiation, such as γ-radiation from ^{60}Co, oxidative degradative reactions are initiated, particularly depolymerization reactions. The depolymerization reactions result primarily from energy transfer in the cellulose molecule and localization of energy on carbon C_1 or C_4. Depolymerization of the cellulose molecule is initiated, and a decrease in breaking strength of fibrous cellulose is observed.[1] We have reported that the substitution of benzenoid[2–12] or furan [13,14] groups on the cellulose molecule decreased the localization of energy in the cellulose molecule and thereby decreased the initiation of oxidative degradative reactions of the cellulose molecule. The radioprotective effects of these groups were shown to extend over several cello-

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biose units.[2] These radioprotective effects were attributed to the selective absorption of the incident energy and/or secondary electrons (produced by the interaction of high-energy radiation with cellulose) by the groups due to their π-electron-type structures. The energy was then dissipated by reemission as heat or light. In the case of benzoylated cellulose, the dissipation of the energy of incident light without initiation of depolymerization of cellulose was demonstrated.[4] That is, a weather-resistant cotton cellulose was prepared.

In further work on the control of energy transfer and localization in cellulose by chemical modification with groups containing π-electron-type structures, we have prepared cellulose thenoates.[15] Experimental data are presented in this report which indicate that the substitution of thiophene groups on cellulose also radioprotect the cellulose molecule, as in the case of benzenoid and furan groups. The ESR spectra and physical properties of irradiated cellulose thenoates are compared with those of irradiated cellulose.

EXPERIMENTAL

Materials

Cotton cellulose of the Deltapine variety, spun into 7s/3 yarn, was purified.[16] The purified cellulose was then allowed to condition at 21°C and 65% R.H. The product had a moisture content of about 7% and a viscosity-average molecular weight of about 700,000.[17]

Cellulose thenoates were prepared by the reaction of purified cotton cellulose with 2-thenoyl chloride, 5-methyl-2-thenoyl chloride, 2-thiopheneacryloyl chloride, 5-bromo-2-thenoyl chloride, or 5-bromo-2-thiopheneacryloyl chloride in pyridine as the acid scavenger at 80–85°C with N,N-dimethylformamide (DMF) as the solvent. The bromo-substituted cellulose thenoates underwent nucleophilic displacement reaction with pyridine, N,N-dimethylcyclohexylamine, or triethylamine to give the corresponding quaternary salt. Crosslinked heterocyclic cellulose esters were prepared by the reaction of bromo-substituted heterocyclic acid chlorides with purified cotton cellulose at 80–85°C in 1,3-di(4-pyridyl)propane as the acid scavenger with dry DMF as the solvent.[15]

In general, dry DMF (200 ml) was placed in a wide-mouthed, round-bottomed flask (500 ml), and then the desired amount of acid chloride was added. Dry pyridine (or other base), twice the amount of acid chloride, was added rapidly. The mixture was thoroughly shaken until a homogeneous solution was obtained. Cotton cellulose in the form of yarn (4–6 g) which had been dried in air at 60°C for 2 hr was placed in the reaction flask. The contents of the reaction flask, with continuous stirring, were heated in an oil bath at 80–85°C; moisture was excluded from the reaction flask by use of a drying tube. After the desired time of reaction, the yarns were removed from the solution and washed twice with DMF (100 ml each time) and immersed in methanol at 50°–60°C for 30 min. The yarns were then kept in 10% $KHCO_3$ solution for 30 min and then washed thoroughly with distilled water. The yarns were stretched overnight to 80–85% of their original lengths. The yarns were equilibrated for 24 hr at 25°C and about 50% R.H. The extent of the reaction was determined by measuring the increase in weight (add-on) of these samples over that of the control yarn.

Methods

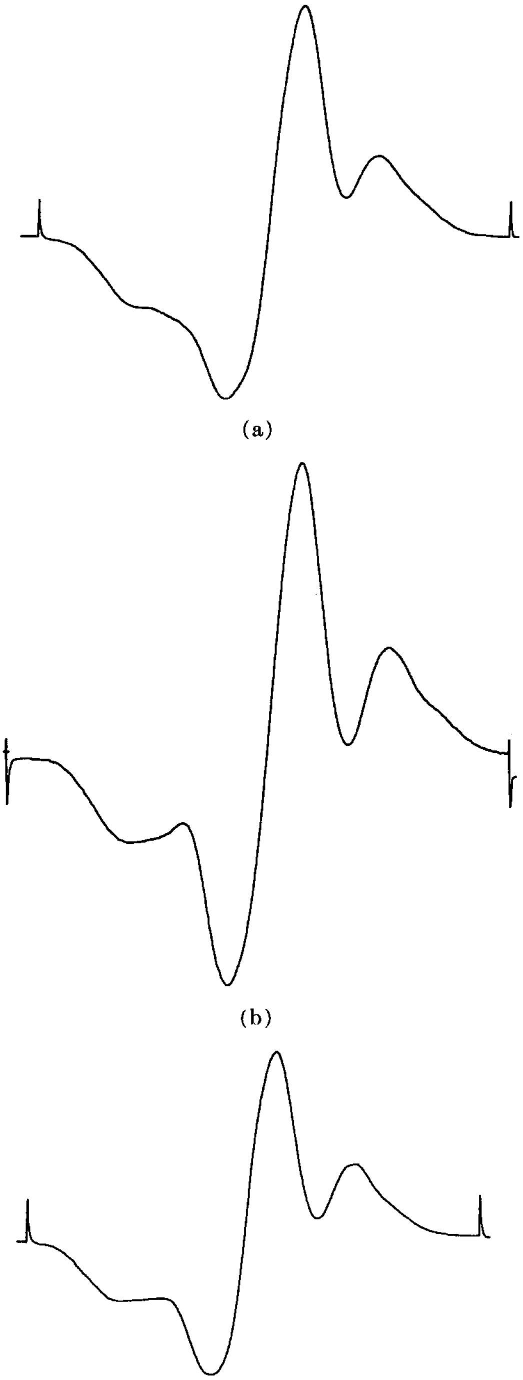
Samples of cellulose, cellulose thenoates, and crosslinked cellulose esters were irradiated in glass containers in air at ambient temperature (about 25°C) to a dosage of about 1.3×10^{21} eV/g. The SRRL ^{60}Co radiation source previously described[18] was used. The dose rate, determined by ferrous–ferric dosimetry,[19] was about 5.3×10^{19} eV/g-hr over the experimental volume irradiated.

Within 10–20 min after removal from the radiation source, samples of each of the irradiated and control celluloses (60–80 mg) were transferred in air to quartz tubes. Then the ESR spectra of the celluloses were recorded at 25°C with a Varian 4502-15 EPR spectrometer system. The breaking strengths of the fibrous celluloses were determined in accordance with ASTM methods with the Instron tester.[20]

RESULTS AND DISCUSSION

The effects of γ-irradiation on the breaking strengths of fibrous purified, thenoylated, and crosslinked thenoylated cotton celluloses are shown in Tables I and II. The breaking strengths of the control, unirradiated yarns were dependent on the base used, on the extent of chemical modification, and whether the yarns were treated under slack or tension conditions. The substitution of thiophene groups on cellulose increased the radiation resistance of fibrous cellulose. As the degree of substitution or add-on of the thiophene groups on cellulose increased, the radiation resistances of the celluloses increased, as shown by the increased retention of the breaking strengths of the irradiated thenoylated fibers. Crosslinked thenoylated and furoylated cottons also showed radiation resistance.

The ESR spectra of irradiated purified cellulose and thenoylated celluloses are shown in Figure 1. The ESR spectrum of irradiated cellulose (Fig. 1a) indicates that the long-lived free radical generates a triplet spectrum which is asymmetric and has limited resolution. For cellulose I, it has been suggested that localization of the energy on carbon C_5 of the glucupyranoside ring initiates dehydrogenation, followed by resonance stabilization of the free-radical site on carbon C_5. The approximately equivalent protons on carbon C_6 then interact with the free radical to generate a triplet spectrum.[21] The ESR spectra of the irradiated thenoylated celluloses (Figs. 1b to 1f) indicate that the long-lived free radicals in these irradiated celluloses also generate similar spectra. This would suggest that modification of cellulose by substitution of thiophene groups did



(a)

(b)

(c)

Fig. 1 (*continued*)

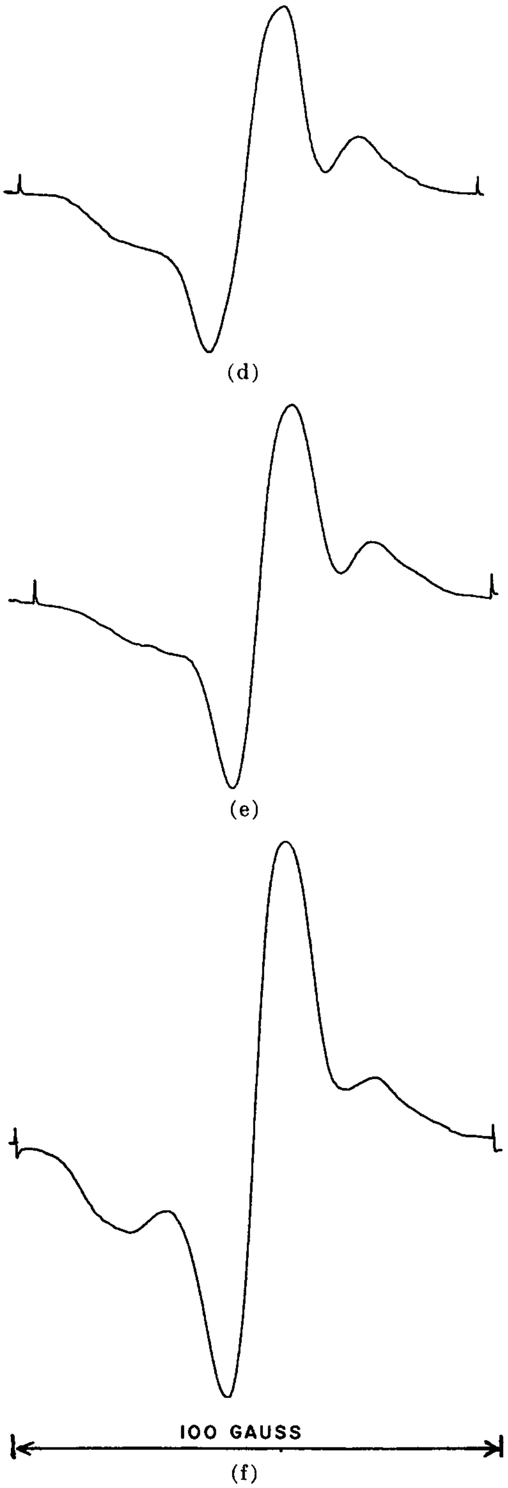


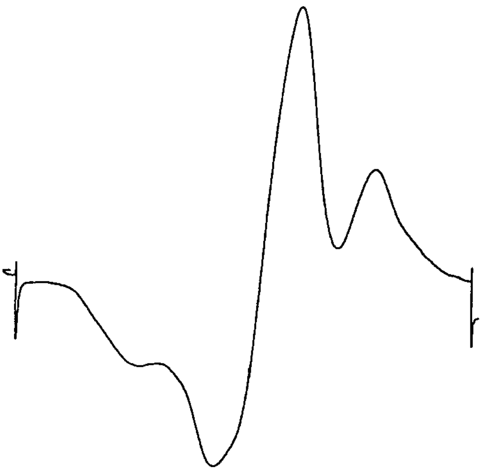
Fig. 1. ESR spectra of irradiated celluloses containing thiophene groups: (a) purified cotton cellulose; (b) 2-thenoyl cellulose, DS = 0.46; (c) 5-methyl-2-thenoyl cellulose, DS = 0.25; (d) 2-thiopheneacryloyl cellulose, DS = 1.43; (e) 5-bromo-2-thenoyl cellulose, 99% add-on; (f) 5-bromo-2-thiopheneacryloyl cellulose, 250% add-on.

TABLE I
Effect of Thenoylation on Radiation Resistance of Cotton Cellulose

Derivative	Degree of substitution	Breaking strength of yarn, lb		Retention of strength, %
		Control	Irradiated[a]	
Purified yarn (7s/3)	0.00	10.42	2.24	21
2-Thenoyl	0.20	8.50	4.56	53
	0.46	5.62	4.40	78
5-Methyl-2-thenoyl	0.25	3.45[b]	2.35	68
	0.56	7.60	6.08	80
2-Thiopheneacryloyl	0.05	4.88	2.87	59
	1.43	9.65	6.05	62
5-Bromo-2-thenoyl	80%[c]	10.53	5.74	55
	99%[c]	3.76	4.66	(100+)
	9.8%[d]	3.41	1.66	48
	12%[e]	4.83	2.10	43
5-Bromo-2-thiophene-acryloyl	250%[c]	4.79	4.03	84
	8.1%[d]	8.21	2.79	34
	11%[e]	7.34	2.93	40

[a] Radiation dosage, 1.3×10^{21} eV/g.
[b] Dried under slack conditions.
[c] Add-on from pyridine.
[d] Add-on from triethylamine.
[e] Add-on from N,N-dimethylcyclohexylamine.

not change the resonance stabilizing effect of the glucopyranoside ring and that the free-radical sites of irradiated thenoylated celluloses are also on carbon C_5. However, it was observed that at the same radiation dosage the concentrations of long-lived free radicals in irradiated thenoylated celluloses were less than in irradiated celluloses. This would indicate



(a)

Fig. 2 (*continued*)

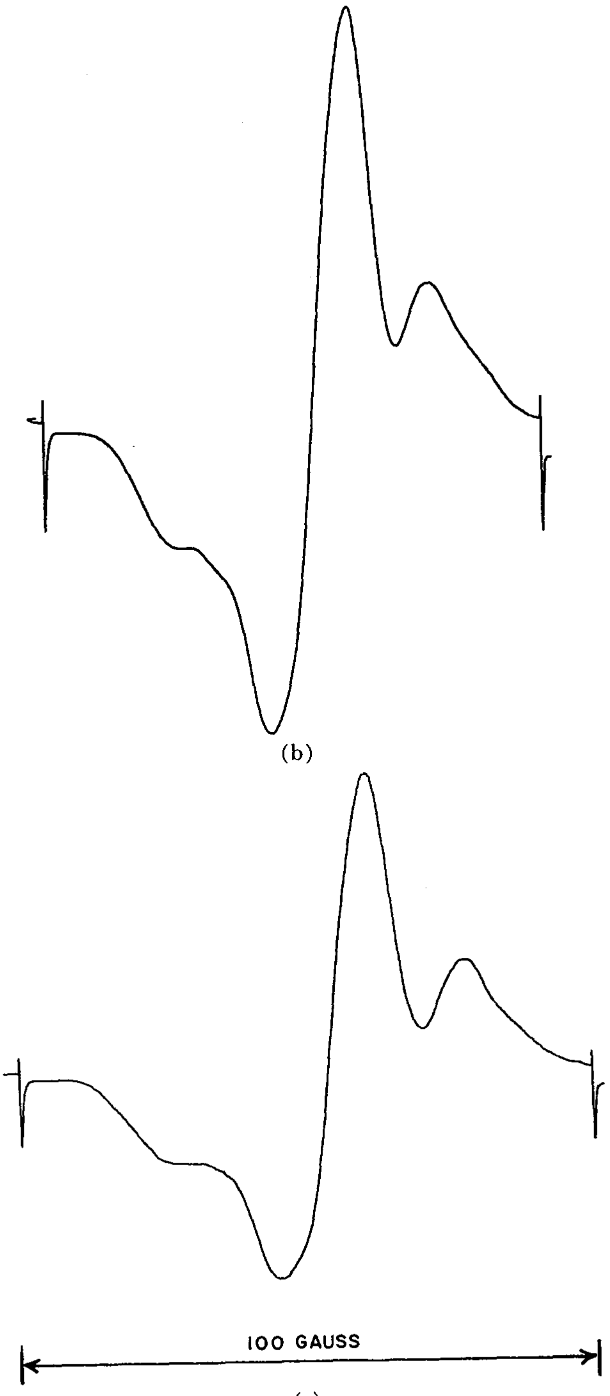


Fig. 2. ESR spectra of irradiated celluloses containing thiophene and furan groups and crosslinked: (a) 5-bromo-2-thenoyl cellulose, 31% add-on; (b) 5-bromo-2-thiophene-acryloyl cellulose, 11% add-on; (c) 5-bromo-2-furoyl cellulose, 35% add-on.

TABLE II
Effect of Crosslinking on Cellulose Thenoates on the Radiation Resistance of the Products

Derivative	Add-on,[a] %	Breaking strength of yarn, lb		Retention of strength, %
		Control	Irradiated[b]	
Purified yarn (7s/3)	0	10.39	2.32	22
5-Bromo-2-thenoyl	31	8.05	2.81	35
5-Bromo-2-thiophene acryloyl	11	7.04	3.91	55
5-Bromo-2-furoyl[c]	35	7.01	3.61	51

[a] Add-on from 1,3-di(4-pyridyl) propane.
[b] Radiation dosage, 1.3 × 10^{21} eV/g.
[c] See Singh and co-workers.[14]

that localization of energy in thenoylated celluloses was decreased as compared with localization of energy in cellulose.

The ESR spectra of irradiated, crosslinked thenoylated and furoylated celluloses are shown in Figure 2. The long-lived free radicals in these irradiated celluloses also generated similar spectra. This would suggest that crosslinking did not affect the site of the localization of energy on the glucopyranoside ring.

As in the cases for benzenoid and furan groups, the radioprotective effects of thiophene groups for cellulose appeared to be related to their π-electron-type structure. Exner and Simon[22] have reported that the relative mobilities of π-electrons in these structures are in the order benzenoid > thiophene > furan groups. We have also reported that benzenoid groups were more effective radioprotectants for cellulose than furan groups.[14] The radioprotective effects of thiophene groups for cellulose were about the same as those of furan groups. The mechanism of interaction of ionizing radiation with cellulose and intramolecular energy transfer and localization in the cellulose thenoates were apparently modified, so that localization of energy on carbon C_1 or C_4, which leads to depolymerization and loss in breaking strength of fibrous cellulose, was minimized. Further investigations on energy transfer and localization in cellulose could lead to the preparation of thermally resistant cottons as well as light- and radiation-resistant cottons. This could lead to the development of molecular protection processes for making these cottons which would have many clothing and other textile product uses where light, radiation, of thermal resistant properties are desired.

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