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Synthesis of Poly(3,7-N-Alkylphenothiazinyl Methylene)

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SUMMARY

Polymers containing phenothiazine nuclei in the main chain were prepared by the reactions of a seriese of N-alkylphenothiazines with formaldehyde under acid conditions in dioxane. In the case of lower alkyl groups such as methyl or ethyl, significant amounts of gel accompanied the resulting polymers. ^{13}C-NMR spectroscopy established the chemical structures of the polymers and UV spectroscopic studies indicated π-electron interaction due to homoconjugation between neighboring phenothiazine nuclei. The polymers were readily oxidized to give colored products by photoirradiations in $CHCl_3$.

INTRODUCTION

Polymers containing pendant donative groups such as carbazole groups have been widely investigated in view of their unique physicochemical properties such as photoconductivity and CT complex formation. However, few studies on polymers having phenothiazine groups as pendant have so far been reported (KLÖPFFER et al. 1968, GEBUS et al. 1969; LITT et al. 1973). It is of interest to synthesize polymers having phenothiazine nuclei in the main chain in view of exploring new materials. In this study, the reactions of N-alkylphenothiazines with formaldehyde should be carried out and establish their chemical properties.

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EXPERIMENTAL

A series of N-alkylphenothiazines was prepared according to the procedure described in the literature (LITT et al. 1973). A typical procedure for the preparation of the polymer is described below. A solution of 2.41g (0.01 mole) of N-propylphenothiazine and 0.03g (0.01 mole) of paraformaldehyde in 15 ml of dioxane containing 0.1g of concentrated sulfuric acid was sealed in a glass tube. This was heated at 90°C for 3 hr with shaking. The reaction mixture was poured into 1 liter of well-stirred methanol to precipitate the polymer. The polymer was reprecipitated from N-methylpyrrolidone (NMP)-methanol; 58.3% yield. A series of poly(3,7-N-alkylphenothiazinyl methylene) was similarly prepared, and the results listed in Table 1. Solutions of the polymer in $CHCl_3$ were irradiated with a high pressure mercury lamp (100W) at a distance of 20 cm in a quartz cell. Spectroscopic data were obtained using a Hitachi EPS-3T (UV) and a JEOL JNM-FX 100 (^{13}C-NMR) spectrometer.

Table 1

Products of the Reaction of N-alkylphenothiazines with Formaldehyde

Sample	R	Conversion %	Gel fraction[a] %	PMP[b] °C	$[\eta]$[c] dl/g
1	CH_3	77	11.2	48-78	0.07
2	C_2H_5	65	58.4	45-89	0.11
3	C_3H_7	58	0	44-88	0.07
4	C_4H_9	34	0	79-91	0.08
5	C_6H_{13}	7	0	30-42	0.07

[a] Gel fraction of the yielding polymer.

[b] Polymer melting point.

[c] Intrinsic viscosity of a polymer solution in NMP at 30°C.

RESULTS and DISCUSSION

The effect of the N-alkyl group on the polymerization reaction was identical in the case of N-alkylcarbazoles (WATARAI, 1979), that is, polymers prepared from N-methyl and N-ethyl derivatives contained gel product, whereas polymers having higher alkyl groups were soluble. These results can be explained as steric effect of higher alkyl groups. The synthesized polymers were identified as poly(3,7-N-alkylphenothiazinyl methylene) based on the data of the IR, UV, and ^{13}C-NMR spectra, and the elemental analysis. The assignments of the individual carbons in ^{13}C-NMR spectra were carried out by off-resonance spectroscopy and by comparison with the literature values for phenothiazine (ISBRANDT et al. 1973), and the results are summarized in Table 2. The UV absorption band for the polymer is red-shifted relative to the corresponding monomeric compound, which bears out the existence of π-orbital interaction between neighboring phenothiazine nuclei in the polymer chain (Figure 1).

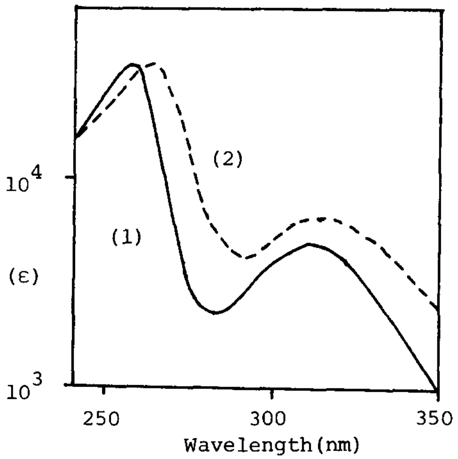


Figure 1. UV absorption spectra of phenothiazine derivatives; (1) [N-ethylphenothiazine] = 4.7 x 10^{-5}mole/liter; (2) poly-(3,7-N-ethylphenothiazinyl methylene), [monomer unit] = 3.4 x 10^{-5}mole/liter. In dichloroethane at 25°C.

Table 2

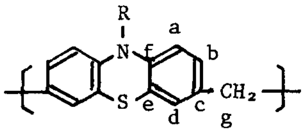
25-MHz ^{13}C-NMR data of Poly(3,7-N-alkylphenothiazinyl methylene)

R	Chemical shifts of each carbone[1] (Multiplicity[2])												
	a	b	c	d	e	f	g	1	2	3	4	5	6
$\overset{1}{\mathrm{C}}\mathrm{H}_3$	113.9	(127.3)	135.1	(127.7)	123.2	144.0	39.7	35.1					
	(D)	(D)	(S)	(D)	(S)	(S)	(T)	(Q)					
$\overset{1}{\mathrm{C}}\mathrm{H}_2\overset{2}{\mathrm{C}}\mathrm{H}_3$	114.8	(127.2)	134.9	(127.5)	124.1	143.0	39.6	41.6	12.9				
	(D)	(D)	(S)	(D)	(S)	(S)	(T)	(T)	(Q)				
$\overset{1}{\mathrm{C}}\mathrm{H}_2\overset{2}{\mathrm{C}}\mathrm{H}_2\overset{3}{\mathrm{C}}\mathrm{H}_3$	115.2	(127.1)	135.0	(127.5)	124.6	143.4	39.7	49.0	20.0	11.3			
	(D)	(D)	(S)	(D)	(S)	(S)	(T)	(T)	(T)	(Q)			
$\overset{1}{\mathrm{C}}\mathrm{H}_2\overset{2}{\mathrm{C}}\mathrm{H}_2\overset{3}{\mathrm{C}}\mathrm{H}_2\overset{4}{\mathrm{C}}\mathrm{H}_3$	115.1	(127.1)	135.0	(127.5)	124.6	143.4	39.8	47.0	28.9	20.2	13.8		
	(D)	(D)	(S)	(D)	(S)	(S)	(T)	(T)	(T)	(T)	(Q)		
$\overset{1}{\mathrm{C}}\mathrm{H}_2\overset{2}{\mathrm{C}}\mathrm{H}_2\overset{3}{\mathrm{C}}\mathrm{H}_2\overset{4}{\mathrm{C}}\mathrm{H}_2\overset{5}{\mathrm{C}}\mathrm{H}_2\overset{6}{\mathrm{C}}\mathrm{H}_3$	115.1	(127.1)	135.0	(127.5)	124.6	143.4	39.8	47.3	31.4	26.7	26.9	22.6	14.0
	(D)	(D)	(S)	(D)	(S)	(S)	(T)	(T)	(T)	(T)	(T)	(T)	(Q)

[1] in parts per million downfield from Me_4Si.

[2] by off-resonanced spectra.

b and d carbons are tentative assignments.



CT complex band of the polymer (Sample 5) with bromanil as an acceptor was observed at 830 nm in ClC_2H_4Cl. The chemical structure of the polymer which consists of diarylmethane units is predictable for giving of colored polymeric dye by hydrogen abstraction. Irradiation of the polymer in $CHCl_3$ resulted in color formation. Figure 2 shows the spectral changes of the polymer in $CHCl_3$ after photoirradiation. A new absorption appeared at ca. 600 nm due to oxidation of the diarylmethane sites to the corresponding colored carbonium ions.

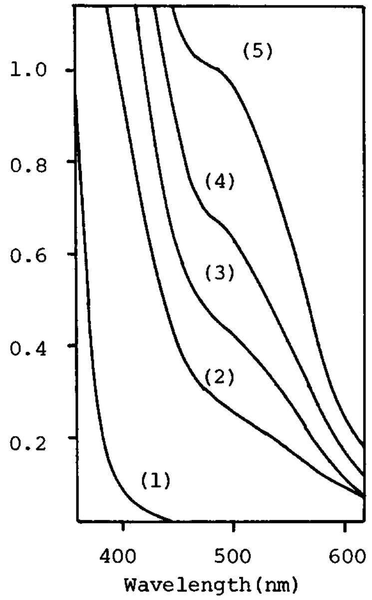


Figure 2. Spectral change of poly(3,7-N-butylphenothiazinyl methylene) on photoirradiation. In $CHCl_3$ [monomer unit] = 10^{-3} mole/liter, by 100W high pressure mercury lamp. (1); 0, (2); 0.5, (3); 1, (4); 2, (5); 2 hr.

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