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New Phenothiazine-containing Monomers and Polymers

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SUMMARY

Three new phenothiazine-containing electrono-donor monomers : methacryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate (i) acryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl) propionate (ii) and 2-(N-phenothiazinyl)propionic acid vinyl ester (iii) were synthesized and radically polymerized. The ionization potentials of poly(i), poly(iii) and of the model for the structural unit of the acrylic polymers : acetyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate determined with two small acceptors were discussed in terms of sterical hindrances.

INTRODUCTION

Following our interest in acetylenic (1), vinylic (2) and heterocyclic (3) monomers and polymers with electrono-donor and electrono-acceptor aromatic substituents and in inter- and intramolecular macromolecular charge transfer complexes (CTC) (4), in this paper we shall present the synthesis of three new vinylic monomers and polymers which contain N-phenothiazinyl groups.

The first phenothiazine-containing monomer, N-vinylphenothiazine, was synthesized only in 1956 by Reppe (5). Then, the interest in phenothiazine monomers and polymers increased (6-12). This is due to the multiple possibilities to use these polymers as antioxidants, redox polymers (13), pharmacologically active polymers and CTC with photochromic (14-16) or special electric properties (15, 17, 18).

The importance of the distance between the electrono-donor or electrono-acceptor substituent and the polymer chain was already evidenced, both in intermolecular (19) and intramolecular (20, 21) CTCs. When this distance is sufficiently large, the optimum complexation can be realized in each configuration. This is the reason we propose the synthesis of some monomers having long distances between the vinylic group and the electrono-donor substituent, namely methacryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate, acryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate and 2-(N-phenothyazinyl) propionic acid vinyl ester.

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EXPERIMENTAL

^{1}H-NMR spectra were registered on a Jeol C-60HL spectrometer, IR spectra on a Perkin Elmer 577, and electronic spectra on a Unicam SP 800 spectrophotometer. Phenothiazine was purified by chromatography on carbo animalis (eluent acetone) and then recrystallized from xylene. Monomers were synthesized according to the reactions presented in scheme 1.

2-(N-phenothyazinyl)propionitrile (II)

Was synthesized according to Smith's (22) method by phenothiazine (200 g, 1 mol) cyanethylation with acrylonitrile (300 ml) in the presence of triton B (3.0 ml 40% aqueous solution) at reflux. After recrystallization from acetone, 212 g (84%) white crystals were obtained, m.p. 158-159. IR (KBr): 2240 cm^{-1} (ν C≡N), 760, 745, 729 cm^{-1} (ν CH aromatic out of plane), NMR ($CDCl_3$): 2.78 ppm (t, CH_2CN) 4.23 ppm (t, CH_2N), (8 aromatic protons).

2-(N-phenothiazinyl)propionic acid (III)

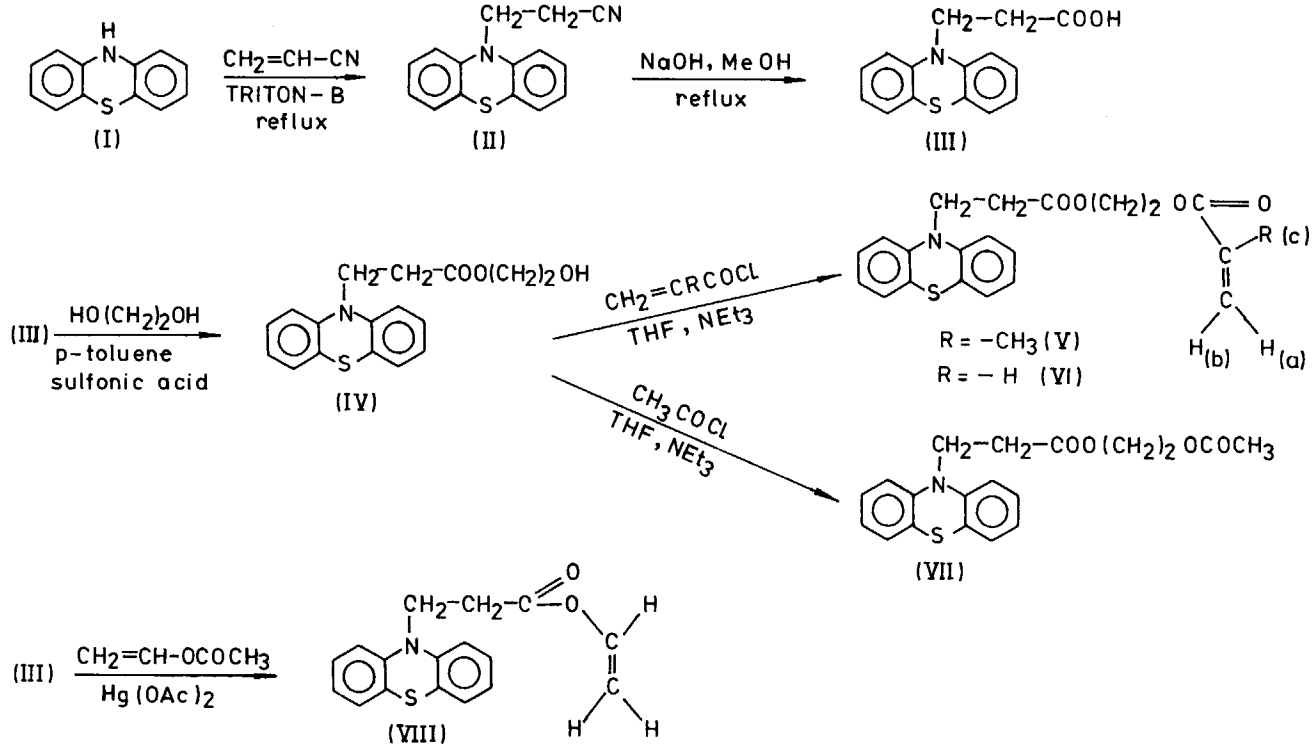
Was obtained by nitrile (II) hydrolysis. A mixture of 181 g (0.72 moles) (II), 1800 ml methanol, 181 g NaOH and 550 ml H_2O was stirred at reflux until all reaction mass was dissolved (ca. 16 hours). The product obtained was poured in ice-water and acidified with HCl. The precipitate was filtered, dried and recrystallized from methanol, yielding 114.5 g (59%) crystals with m.p. 160-163°C. IR (KBr): 1695 cm^{-1} (ν C=O) 755, 748, 728 cm^{-1} (ν CH aromatic out of plane). NMR ($CDCl_3$): 2.93 ppm (t, CH_2CO), 4.31 ppm (t, CH_2N), 6.8-7.5 ppm (8 aromatic protons), 9.92 ppm (OH).

2'-hydroxyethyl-2-(N-phenothiazinyl)propionate (IV)

A mixture of 13.6 g (0.05 moles) III, 0.3 g p-toluene sulfonic acid and 30 ml ethylenglycol was stirred 8 hours at 115°C. Afetr cooling, a yellow product crystallized and was filtered. A sufficient quantity of water was added to the solution in order to precipitate all the reaction product, which was filtered together with the crystalline one, and dried. After one recrystallization from methanol and one from 1:1 cyclohexane:benzene mixture, 11.1 g (70.2%) crystals are obtained. m.p. 91-93°C. IR (KBr): 3420 cm^{-1} (ν OH), 1710 cm^{-1} (ν C=O), 760, 752, 730 cm^{-1} (ν CH aromatic). NMR ($CDCl_3$): 2.41 ppm (s, OH), 2.86 ppm (t, CH_2CO), 3.73 ppm (t, CH_2O), 4.25 ppm (t, CH_2N, CH_2OCO), 6.7-7.4 ppm (8 aromatic protons).

Methacryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate (V)

A mixture of 7.84 g (0.075 moles) methacryloyl chloride and 10 ml tetrahydrofuran (THF) was added dropwise during 20 minutes under strong stirring to a solution of 15.8 g (0.05 moles) IV and 10.5 ml (0.075 moles) triethylamine (TEA) in 100 ml THF (cooled at 6°C). The mixture was stirred one hour at 6°C and 6 hours at room temperature, then NEt_3.HCl was filtered. The solution was concentrated to about 40 ml on a rotovapour (below 35°C) and then poured into water. The oleum product was washed with $NaHCO_3$ aqueous solution and water until it became solid, then was recrystallized from methanol yielding 13 g (68%) crystals with m.p. 52-54°C.


(I)
CH2=CH-CN
TRITON-B
reflux
(II)
NaOH, MeOH
reflux
(III)
HO(CH2)2OH
p-toluene
sulfonic acid
(IV)
CH2=CRCOCl
THF, NEt3
R = -CH3 (V)
R = -H (VI)
R (c)
H(b)
H(a)
CH3COCl
THF, NEt3
(VII)
CH2=CH-OCOCH3
Hg(OAc)2
(VIII)

Scheme 1

IR (KBr): 1700 cm^{-1} (ν C=O), 1625 cm^{-1} (ν C=C), 875 cm^{-1} (νCH out of plane), 754, 741, 725 cm^{-1} (ν CH phenothiazine). NMR ($CDCl_3$): 1.95 ppm (s, CH_3), 2.83 ppm (t, CH_2CO), 4.20 ppm (t, CH_2N), 4.30 ppm (s, OCH_2CH_2O), 5.51 ppm (=CHa), 6.04 ppm (=CHb), 6.6-7.3 ppm (m, 8 aromatic protons).

Acryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate (VI)

Was synthesized like V with acryloyl chloride instead of methacryloyl chloride. From 15.8 g (0.05 moles) IV, 10.5 ml (0.075 moles) TEA, 6.8 g (0.075 moles) acryloyl chloride in 100 ml THF, 9 g (48.8%) crystals were obtained, m.p. 48-51°C. IR (KBr): 1726, 1710 cm^{-1} (ν C=O), 1610 cm^{-1} (ν C=C), 1400 cm^{-1} (ν =CH in plane), 980 cm^{-1} (ν =CH out of plane I), 880 cm^{-1} (ν =CH out of plane II), 764, 751, 729 cm^{-1} (ν CH aromatic). NMR ($CDCl_3$): 2.85 ppm (t, CH_2CO), 4.22 ppm (t, CH_2N), 4.32 ppm (s, OCH_2CH_2O), 5.6-6.6 ppm (m, $CH=CH_2$), 6.7-7.3 ppm (m, 8 aromatic protons).

Acetyl-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate (VII)

Was synthesized like V using acetyl chloride instead of methacryloyl chloride. From 10 g (0.032 moles) IV, 7 ml (0.05 moles) TEA, 3.57 ml (0.05 moles) acetyl chloride and 50 ml THF, 5.8 g (51%) white crystals with m.p. 31°C were obtained after one recrystallization from methanol. IR (KBr): 1720 cm^{-1} (νC=O) NMR ($CDCl_3$) : 2.03 ppm (s, CH_3), 2.81 ppm (t, CH_2CO), 4.19 ppm (t, CH_2N), 4.21 ppm (s, OCH_2CH_2O), 6.6-7.3 ppm (8 aromatic protons).

2-(N-phenothiazinyl)propionic acid vinyl ester (VIII)

Was synthesized by transesterification of III with vinyl acetate as follows. To a mixture of 25 g (0.092 moles) III, 100 ml vinyl acetate, 0.33 g mercury acetate and a small amount of hydroquinone, 0.15 ml H_2SO_4 100% were added. The solution was refluxed three hours. After cooling, 2.0 g natrium acetate were added and the solution was filtered. The filtrate was evaporated on a rotovapour, the solid product was dissolved in 150 ml benzene and the filtrate was re-evaporated. The solid residue was twice recrystallized from methanol, affording 12.5 g (46%) white crystals with m.p. 48-51°C. IR (KBr): 1745 cm^{-1} (ν C=O), 1635, 1195, 1125 cm^{-1} (ν $CH=CH_2$), 751, 742, 725 cm^{-1} (ν CH aromatic). NMR ($CDCl_3$): 2.89 ppm (t, CH_2CO), 4.22 ppm (t, CH_2N), 4.45-5.0 ppm (m, CH_2=), 6.6-7.3 ppm (m, 8 aromatic protons and =CH).

Monomer polymerization

The monomers were polymerized in dioxan solution (monomer concentration 10%) in the presence of 1% AIBN from monomer weight, under argon, in sealed ampoules, at 60°C. Polymer purification was realized by reprecipitation from methanol. Intrinsic viscosities were measured in THF at 25°C (table 1).

TABLE 1.
Radical polymerization of the monomers

Monomer	Time (h)	Conversion (%)	$[\eta]$ (dl/g)
V	22	84.7	0.09
VI	22	82.3	0.06
VIII	48	43.5	0.06

Ionization potentials

Ionization potentials (I_p) of VII, poly(V) and poly(VIII) were calculated from the absorption maxima values of CTCs with 2,4,7-trinitro-9-fluorenone (TrNF) and chloranil (CA) (in THF solutions) using the equation :

$$h\nu_{CT} = (I_p - c_1) + c_2/(I_p - c_1)$$

where c_1 and c_2 are constants for a given acceptor. Their values are $c_1 = 5.85$ and $c_2 = 0.58$ for CA and $c_1 = 5.61$ and $c_2 = 0.74$ for TrNF (23). CTC solutions were obtained in all cases mixing in different proportions a donor solution having the concentration 0.5 moles/l and an acceptor one having the concentration 0.1 moles/l. CTCs present only one absorption maximum corresponding to the transition from the last occupied molecular orbital of the donor to the first free molecular orbital of the acceptor. The values obtained are presented in table 2.

TABLE 2.
CTC absorption maxima values and ionization potentials of the donors

Donor	TrNF			CA		
	λ_{max}(nm)	$h\nu$(eV)	I_p(eV)	λ_{max}(nm)	$h\nu$(eV)	I_p(eV)
VII	510	2.43	7.6	690	1.80	7.23
poly(V)	510	2.43	7.6	670	1.85	7.30
poly(VIII)	510	2.43	7.6	755	1.64	6.97

DISCUSSION

The syntheses of three phenothiazine-containing monomers having different distances between the vinylic group and the electrono-donor substituent are presented. Their radical polymerization gives white polymers with small molar mass (table 1) and with IR and NMR spectra corresponding to the proposed structures. Radical polymerization of acrylate and methacrylate is faster than that of the vinyl ester. All polymers are soluble in CH_2Cl_2, benzene, $CHCl_3$. The ionization potential values are equal for all compounds studied with TrNF as acceptor but are very different when determined with CA as acceptor (table 2). The same phenomenon was observed by other authors also (14, 17, 18). CA is smaller than TrNF and can give, depending on sterical hindrances of the donor, I_p values apparently different. In this context, poly(VIII) presents a structure giving the lowest I_p value. This polymer class offers the possibility to study "polymer" effect in intermolecular CTCs. Researches in this field are in progress.

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