

# Polymerization of 1-Methyl-2,5-bis[1-(4-phenylurazoly)] Pyrrole with Alkyldiacid Chlorides

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## ABSTRACT

1-Methyl-2,5-bis[1-(4-phenylurazoly)] pyrrole (**3**) from the reaction of 4-phenyl-1,2,4-triazoline-3,5-diones (**1**) with *N*-methylpyrrole (**2**) was reacted with excess acetyl chloride. Acylation reaction occurred at room temperature and led to the formation of diacetylated adduct in quantitative yield. This product was characterized with IR, <sup>1</sup>H NMR, and elemental analysis. Polymerization of monomer (**3**) with suberoyl chloride and adipoyl chloride was performed in *N,N*-dimethylacetamide, chloroform and dimethylsulphoxide in the absence and presence of pyridine or triethylamine and lead to the formation of novel polymers. Some structural characterization and physical properties of these novel polymers are reported.

**Key Words:** viscometry, 1-methyl-2,5-bis[1-(4-phenylurazoly)] pyrrole, polyamidation reaction  
suberoyl chloride, adipoyl chloride

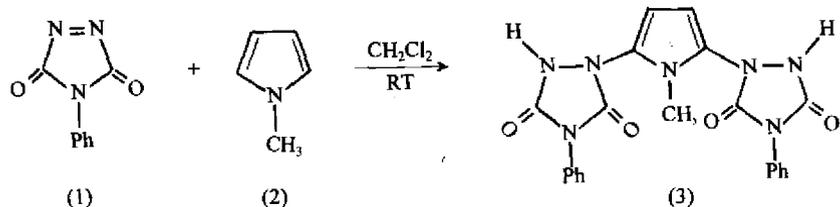
## INTRODUCTION

The reaction of 4-phenyl-1,2,4-triazoline-3,5-dione, PhTD, (**1**) with *N*-methylpyrrole, NMP, (**2**) has been reported [1, 2] to give a 2:1 adduct of 1-methyl-2,5-bis[1-(4-phenylurazoly)] pyrrole (**3**), in high yield (Scheme I).

The urazole derived from the ene reaction of triazolinediones with alkenes and polydienes has one N-H proton, which seems to be very acidic. The acidity of this proton has been measured and is quite acidic with pKa of 4.71 which is almost the same as that of acetic acid [3]. The urazoly group from compound

**3** has also two N-H protons which are acidic. The compound **3** has potential to undergo *N*-acylation. 4-Substituted-urazole was converted to 1-acyl derivatives by acylation reaction with a series of carboxylic acid anhydrides [4]. A simplified procedure for the *N*-acylation of oxazolidin-2-one chiral auxiliaries has also been reported [5]. As it has been reported in previous paper [6] compound **3** was converted to its dianion salt and its reaction with methyl iodide and polymerization reaction with alkyl-dihalide were investigated. These reactions give *N*-alkylation almost exclusively and led to the formation of novel polymers containing urazole-pyrrole linkages.

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Scheme 1

The purpose of this investigation was to synthesize compound 3 and use it as a monomer for the synthesis of novel polymers by polyamidation reactions.

## EXPERIMENTAL

### Materials and Equipment

Reagents were purchased from Fluka Chemical Co., Aldrich Chemical Co. and Riedel-dehaen AG. 4-Phenyl-1,2,4-triazoline-3,5-dione was synthesized according to published procedures [7–10].

All melting points were taken with a Gallenham melting point apparatus and are uncorrected. Inherent viscosities were measured by standard procedure using a Cannon Fensk Routine viscometer. Thermal Gravimetric Analysis (TGA) for polymers were taken on a Stanton-650 TGA and differential scanning calorimetric (DSC) data for polymers were taken on DSC-PL by Iran Polymer Institute (IPI). Elemental analyses were performed by Research Institute of Petroleum Industry, Tehran, I.R.Iran.

IR Spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br).

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument. Multiplicities of proton resonances are designated as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). Tetramethylsilane (TMS) was used as internal reference.

### Reaction of Compound 3 with Excess Acetyl Chloride

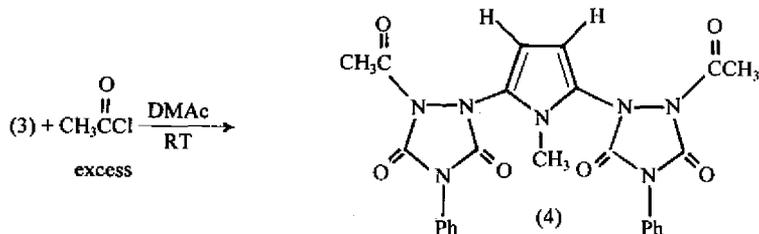
Into a 25 mL one-necked round-bottomed flask, which was equipped with a magnetic stirrer, 0.50 g ( $1.16 \times 10^{-3}$  mol) of compound 3 and 10 mL of acetyl chloride were added. The stirrer was started and after 15 min a clear solution was formed. A white solid was precipitated after 45 min and the mixture was stirred overnight. The excess acetyl chloride was removed and the resulted solid was added into 55 mL of distilled water, filtered and dried under vacuum for 16 h at  $60^\circ\text{C}$  to give 0.55 g (92%) of white solid (4). Recrystallization from ethyl acetate/n-hexane (4:1) gave white crystals, mp  $148\text{--}150^\circ\text{C}$ ; IR(KBr): 3140 (w), 3080 (w), 2900 (s), 2850 (m), 1800 (s), 1740 (s, br), 1600 (m), 1490 (s), 1460 (m), 1400 (s), 1340 (m), 1250 (s), 1140 (s), 1080 (w), 1040 (w), 1010 (m), 990 (m), 840 (m), 820 (m), 760 (s), 690 (m), 640 (m), 620 (m), 580 (m), 500 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta$  2.60 (s, 6H), 3.85 (s, 3H), 6.25 (s, 2H), 7.55 (s, 10H).

The elemental analysis results obtained as follows:

$\text{C}_{25}\text{H}_{21}\text{N}_7\text{O}_6$	C (%)	H (%)	N (%)
Calculated	58.25	4.00	18.51
Found	58.20	4.20	18.50

### Polymerization of Compound 3 with Suberoyl Chloride (5)

Method A: Compound 3 (1.00 g,  $2.32 \times 10^{-3}$  mol) and 6 mL of DMAc were placed into a one-necked round-bottomed flask. The stirrer was started and a clear solution was formed. Suberoyl chloride (0.417 mL,



Scheme 11

$2.32 \times 10^{-3}$  mol) was added dropwise. A red colour solution was formed, then turned to a brown colour solution. The mixture was stirred for 12 h. This mixture was poured into a beaker containing 80 mL of water/methanol mixture (1:1). The solid was filtered and dried under vacuum to give 1.31 g (99.2 %) of pale-pink polyamide (7A), mp 105–107 °C; IR(KBr): 3050 (w), 2920 (m), 2850 (w), 1790 (s), 1740 (s, br), 1600 (w), 1500 (s), 1460 (m), 1400 (s), 1300 (m), 1240 (s), 1180 (m), 1120 (m), 1060 (m), 760 (s), 690 (m), 640 (w)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS):  $\delta$  1.35–1.90 (m, br, 8H), 2.45 (DMAc), 2.75–3.25 (m, 4H, DMAc), 3.85 (s, 3H), 6.35 (s, 2H), 7.70 (s, 10H).

The elemental analysis results obtained as follows:

$\text{C}_{25}\text{H}_{27}\text{N}_7\text{O}_6$	C (%)	H (%)	N (%)
Calculated	61.14	4.78	17.22
Found	59.30	5.50	13.10

**Method B:** The above polyamidation reaction was repeated in methylene chloride solution and pyridine was used as scavenger. The solvent was removed to give 99.2% of yield of polyamide (7B), mp 105 °C.

#### Polymerization of Compound 3 with Adipoyl Chloride (6)

**Method A:** Into a 25 mL of one-necked round bottomed flask was placed 0.20 g ( $4.64 \times 10^{-3}$  mol) of compound 3, 2 mL of DMAc and 0.10 mL of trimethyl amine. The mixture was cooled to 7 °C and 0.066 mL of adipoyl chloride was added dropwise. The reaction mixture was stirred for 12 h and was

precipitated in water, to give 0.251 g (100%) of white solid polyamide (8A), mp 100–110 °C; IR(KBr): 3100 (w, br), 2900 (w), 1795 (m), 1740 (s), 1600 (w), 1560 (w), 1500 (m), 1460 (w), 1400 (s), 1240 (m, br), 1180 (m, br), 1060 (m, br), 760 (m), 690 (m), 640 (w)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS):  $\delta$  1.50–1.90 (m, br, 2 $\text{CH}_2$  and DMAc), 2.25–2.60 (m, br, 2 $\text{CH}_2$ ), 2.80–3.15 (m, br, DMAc), 3.80 (s, 3H), 6.25 (s, 2H), 7.55 (s, 10H). C: 55.60; H: 5.00; N: 13.70.

The elemental analysis results obtained as follows:

$\text{C}_{27}\text{H}_{23}\text{N}_7\text{O}_6$	C (%)	H (%)	N (%)
Calculated	59.87	4.28	18.11
Found	55.60	5.00	13.70

**Method B:** The above polyamidation reaction was repeated using methylene chloride as a solvent and pyridine as a scavenger. The yield of the polymer is 100%.

**Method C:** The compound 3 was converted to its dianion salt [6]. This dianion salt was reacted with adipoyl chloride in DMSO under nitrogen atmosphere at 5 °C. A red colour solution was formed and after 12 h a white solid precipitated. The mixture was poured into water. The solid was collected, dried to give 0.21 g (84%) of white solid, mp 188–195 °C.

## RESULTS AND DISCUSSION

### Model Compound Studies

Compound 3 was reacted with excess acetyl chloride

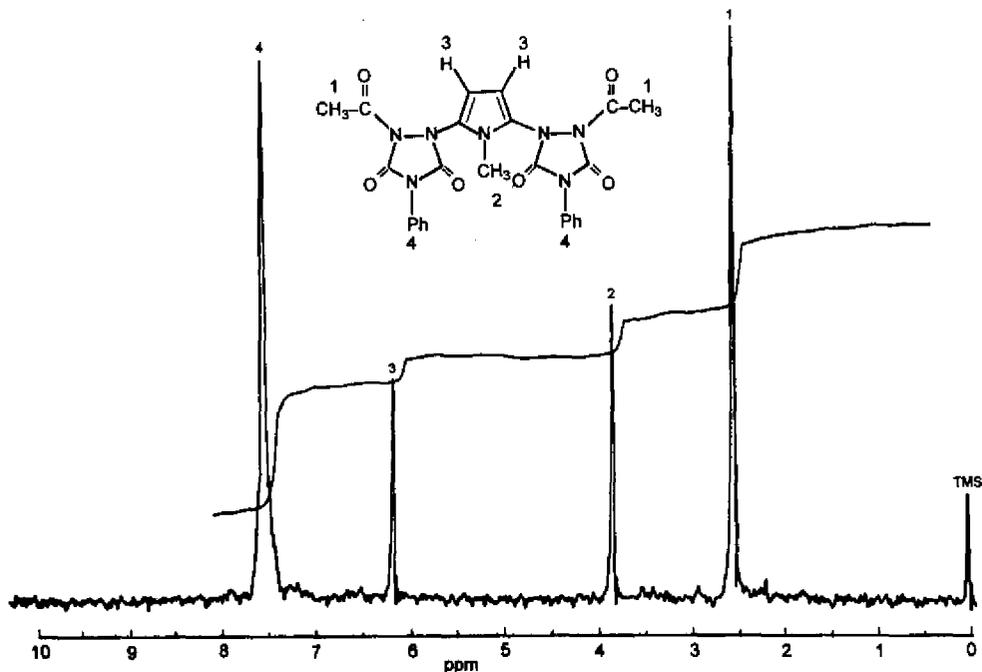


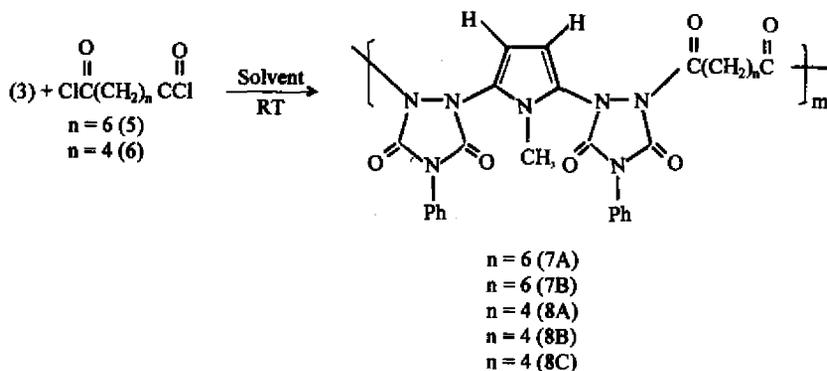
Figure 1. <sup>1</sup>H NMR (90 MHz) spectrum of compound (4) in CDCl<sub>3</sub> at room temp.

in DMAc solution and gave 1-methyl-2,5-bis[1-(2,2'-diacetyl-4-phenylurazoly)] pyrrole (4) in high yield (Scheme II). The compound 4 was characterized with IR, <sup>1</sup>H NMR, and elemental analysis techniques. The IR spectrum of 4 showed two strong peaks at 1800 and 1740 cm<sup>-1</sup> for the carbonyl groups. These are characteristic patterns for the urazole moiety. The <sup>1</sup>H NMR (Figure 1) spectrum of compound 4 showed a singlet at 2.60 ppm for the two methyl groups attached to the carbonyl groups. This peak shows that *N*-acylation reaction occurred. The other peaks are consistent with the assigned structure of compound 4.

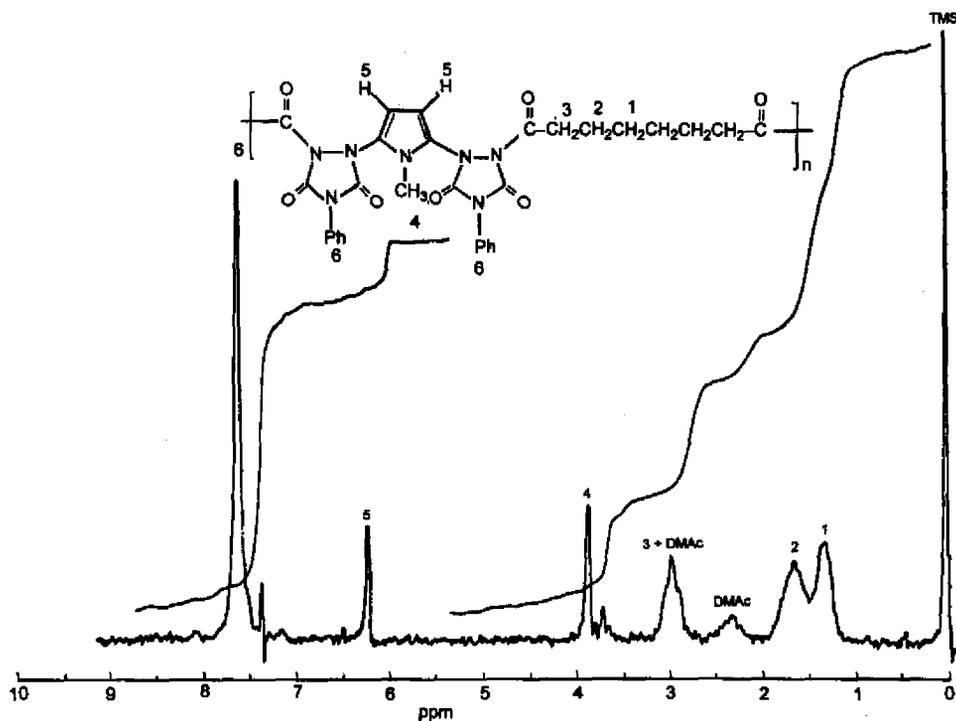
#### Polymerization Reactions

Since acetyl chloride reacted with monomer (3) with high yield and purity, we were encouraged to perform this type of reaction for formation of novel polyamides. Thus suberoyl chloride and adipoyl chloride

were selected as alkyl diacid chlorides. The reaction of monomer 3 with suberoyl chloride was performed by two methods. In method A, the reaction was performed in DMAc solution without pyridine as a scavenger and the resulted polymer was obtained in quantitative yield (7A) (Scheme III). This polymer has a pale-pink colour. The polymer 7A was characterized by IR and <sup>1</sup>H NMR spectra (Figure 2), which are in agreement with structure (7A). From the <sup>1</sup>H NMR data it is clear that the proton ratio on the pyrrole linkage compared to phenyl groups on the urazole linkages is 2:10 (1:5). The polymer 7A is soluble in most of organic solvents such as DMSO, DMF, acetic acid, pyridine, acetone, chloroform, methylene chloride and THF, and is insoluble in solvents such as water, toluene and n-hexane. In method B the reaction was performed in methylene chloride solution and pyridine was used as scavenger.



Scheme III

Figure 2.  $^1\text{H}$  NMR (90 MHz) spectrum of compound (7A) in  $\text{CDCl}_3$  at room temp.

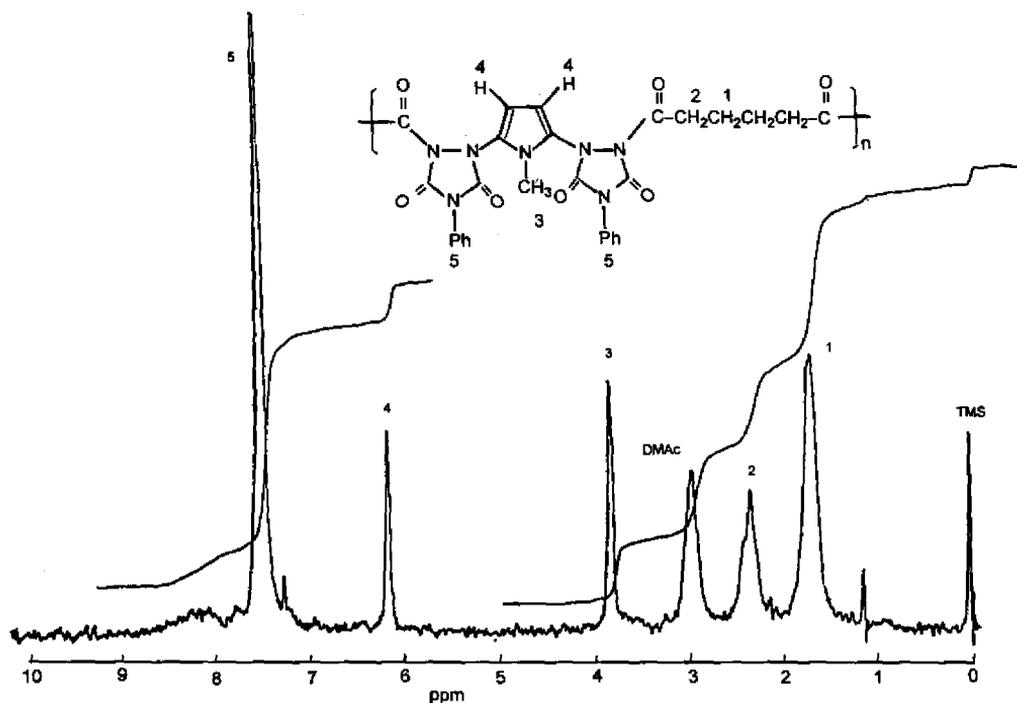


Figure 3.  $^1\text{H}$  NMR (90 MHz) spectrum of compound (8A) in  $\text{CDCl}_3$  at room temp.

Although the yield of polymerization reaction is very high, but lower inherent viscosity was obtained. Other results are the same as polymer 7A.

The reaction of monomer 3 with adipoyl chloride was performed by three methods. In method A, the reaction was performed in DMAc solution with triethylamine being as a scavenger and the resulted polymer was obtained in quantitative yield (8A) (Scheme III). This polymer has a pale-pink colour. The polymer 8A was characterized by IR and  $^1\text{H}$  NMR spectra (Figure 3), which are in agreement with structure 8A. In method B the polymerization reaction was performed in methylene chloride solution and pyridine was used as a scavenger.

In method C monomer 3 was converted to its dianion salt [6] and the polymerization reaction was done in DMSO solution. In this case the resulted

polymer 8C has higher inherent viscosity and higher melting point. This increase in mp could be due to the increase in viscosity and ionic character of the polymer end groups. The solubility of these polymers are similar to those of polymers 7A and 7B. The reaction conditions, some physical properties for these novel polyamides are summarized in Tables 1 and 2.

Although the elemental analysis of the model compound is in agreement with the theoretical values, but in the case of the resulted polymers the elemental analyses have some differences with the theoretical values. These differences are due to the presence of DMAc in the polymer which under moderate heating and high vacuum was not removed. The presence of DMAc in the polymer has been proved by  $^1\text{H}$  NMR spectra (Figures 2 and 3).

**Table 1.** Reaction conditions and some physical properties for polymers (7A), (7B), (8A), (8B) and (8C).

Polymer	(7A)	(7B)	(8A)	(8B)	(8C)
Reaction time (h)	12	12	12	12	12
Scavenger	none	Py <sup>a</sup>	TEA <sup>b</sup>	Py	none
Solvent	DMAc	CH <sub>2</sub> Cl <sub>2</sub>	DMAc	CH <sub>2</sub> Cl <sub>2</sub>	DMSO
Nonsolvent	MeOH:water	water	water	water	water
Yield (%)	99.2	99.2	100	100	84
$\eta_{inh}^c$ , DMF, 25 °C	0.085 <sup>d</sup>	0.058	0.065	0.054	0.094
mp (°C)	105–107	105	100–110	100–110	188–195

(a) py = pyridine; (b) TEA = triethylamine; (c) measured at a concentration of 0.5 g dL<sup>-1</sup>; (d) measured at a concentration of 1.0 g dL<sup>-1</sup>.

### Thermal Properties

The thermal stability of polymers 7A, and 8A were measured by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min in nitrogen atmosphere. An examination of the data reveals that all of the above polymers are thermally stable up to 180 °C in nitrogen atmosphere. The polymers 7A, and 8A show 5% weight loss at 175 and 180 °C, respectively. The residual weight for these polymers at 600 °C are 16 and 12%, and the DSC analysis shows melting temperatures at 150 and 160 °C in nitrogen atmosphere,

respectively.

### CONCLUSION

1-Methyl-2,5-bis[1-(4-phenylurazoly)] pyrrole (3) has two acidic N-H groups and it can be readily acylated. This acylation reaction with acetyl chloride gives *N*-acylation adduct in quantitative yield. Thus compound 3 can act as bifunctional monomer and its polymerization reaction with alkyldiacid chlorides gave novel polyamides with pyrrole and urazole linkages which have very good solubility in most of the organic solvents. Although in this case the resulted novel polyamides have low inherent viscosity, but the 4-phenylurazole which has two N-H groups reacted with diacid chlorides at room temperature and gave higher inherent viscosities.

Polymerization of this monomer with diacid chlorides are under investigation and will be reported later.

### ACKNOWLEDGEMENTS

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**Table 2.** Solubilities of polymers (7A), (7B), (8A), (8B) and (8C) in different solvents.

Solvents	(7A) or (7B)	(8A) or (8B) or (8C)
DMSO	+	+
DMF	+	+
H <sub>2</sub> SO <sub>4</sub>	+	+
THF	+	+
Ethyl acetate	+	+
CH <sub>3</sub> COOH	+	+
Pyridine	+	+
CH <sub>2</sub> Cl <sub>2</sub>	+	+
CHCl <sub>3</sub>	+	+
Acetone	+	+
Toluene	-	-
n-Hexane	-	-
Ether	-	-
CCl <sub>4</sub>	-	-
Water	-	-

Concentration: 5 mg mL<sup>-1</sup>; (+) soluble within 1 h at room temperature; (-) insoluble even heated up to 100 °C.

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