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Polymerization and chelating behavior of *N*-acryloyl, *N*-phenylthiourea

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SUMMARY

The title monomer has been prepared for the first time. It has been polymerized by a free radical mechanism in different solvents. Only oligomers were obtained so far. The dependence of the rate of polymerization on monomer and initiator concentrations has been measured and was found to follow the usual free radical scheme. The overall activation energy of polymerization has been measured in two solvents and was found to be 21.2 and 15.03 K.Cal/mol in tetrahydrofuran (THF) and N,N-dimethyl formamide (DMF) respectively. The prepared monomer has excellent chelating ability with different metal cations. The stability constant of the monomer with copper (II) ions has been measured in acetone as well as in dioxane. The complexes have no tendency for free radical polymerization.

INTRODUCTION

Recently polymer-metal complexes have been of great interest because they have been found to offer an excellent model for the metalloenzymes (KANEKO and TSUCHIDA 1981), and also lead to developments of highly efficient catalysis (TSUCHIDA and NISHIDE 1977). These polymer-metal complexes are synthesized by reaction of a polymer containing donating group such as amine , imine, heterocyclic nitrogen, carboxylic acid, ketone, phosphoric acid or thiol with metal ion (KANEKO & TSUCHIDA 1981 and COWIE 1985) . The synthesis of new polymer ligands is always of some interest , and here a new monomer with pendent thiourea derivative group is being reported. Thiourea is known to have numerous applications, it undergoes complexation with a variety of metal ions (VALIGURA 1985).

It is an efficient corrosion inhibitor (SAHA 1983, GUPTA 1983) and as an antioxidant agents since it acts as a free radical scavenger as well as antiradiation compound (FOYE 1984). The mechanism of protection against ionizing radiation by thioureas is probably due to hydrogen atom transfer. The newly synthesized monomer is capable of free radical polymerization and copolymerization.

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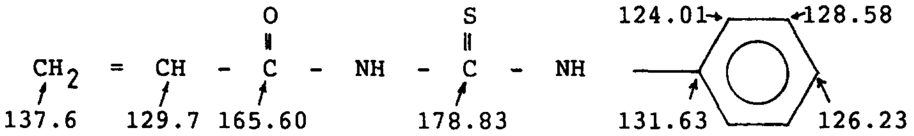
EXPERIMENTAL

Preparation of the monomer N-acryloyl, N′-phenylthiourea (APTU) . Dry ammonium thiocyanate is dissolved in dried acetone and cooled in an ice-salt bath to 0 - 5 °C. A cold solution of acryloyl chloride in acetone is then added dropwise keeping the temperature always below 5 °C . After the complete addition of the acryloyl chloride solution, the mixture is stirred with a magnetic stirrer for one hour till the complete precipitation of ammonium chloride, which is filtered quickly on a Buchner funnel fixed on a dry receiver. The filtrate is again stirred with a magnetic stirrer and a cold aniline solution in acetone is added dropwise. After complete addition, the solution was stirred for another one hour then poured over a large excess of ice-cold water. Yellow crystalline precipitate was filtered and dried in air (m.p.: 98 °C). The reaction product has been proved to be the title compound based on the following facts:

^{1}HNMR (DMSO,D_6 -Varian 90 MHz) revealed a pattern which can be interpreted only for the proposed structure; a doublet at δ 6.4 and a triplet at δ 6.0 ppm for two ($-CH_2$) and one proton (-CH) respectively, the phenyl proton multiplet at δ7.6 and the two NH signals at 10.2 and 12.4 ppm.

^{13}C NMR spectrum (was kindly measured by Prof. M.-W. Kulicke at the University of Hamburg) was found to be in agreement with the proposed structure as shown;



Elemental analysis : found C= 57.7, H= 4.4, N= 13.0 and S=15.1 %

Calculated C= 58.2, H= 4.84, N= 13.59, S= 15.5% .

Azobisisobutyronitrile (AIBN) (Merk) was recrystallized from methanol before use m.p. 104 °C.

All solvents were purified according to standard methods.

Measurement of the rate of polymerization. The rate of polymerization was measured dilatometrically. After the required time,the dilatometer was quickly cooled in an ice-salt mixture, the content was sucked by vacuum and precipitated in ethanol , filtered and dried to constant weight. The conversion was then calculated gravimetrically. Since in all cases the decrease in volume was a linear function of time, the rate curves were then easily converted into mol./l.S.

Spectral measurements. The UV spectra for the monomer and the metal cations in suitable solvents were recorded using Perkin Elmer Lambda 3 spectrophotometer, equipped with thermostated cells. Temperature was adjusted to ± 0.1 °C.

The stability constant K of the complex has been determined by the continuous variation method.

The corresponding values of the Gibb's free energy Δ G, the enthalpy Δ H and the entropy Δ S were calculated according to the following equations:-

$$\Delta G = - RT \cdot \ln K$$
$$\Delta G = \Delta H - T \Delta S$$
$$\ln K = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}$$

Plotting lnK against 1/T will give a straight line with a slope of $-\Delta H/R$ and an intercept of $\Delta S/R$.

RESULTS AND DISCUSSION

The prepared monomer (APTU) has been polymerized by the free radical mechanism using AIBN as initiator in different solvents. The rate of polymerization Rp was measured dilatometrically. The data are plotted in Fig. 1 .
It is observed that the rate decreases in the following order: DMF > Benzene > Tetrahydropyran > THF > Butan - 2- one > Acetonitrile > Dioxane .

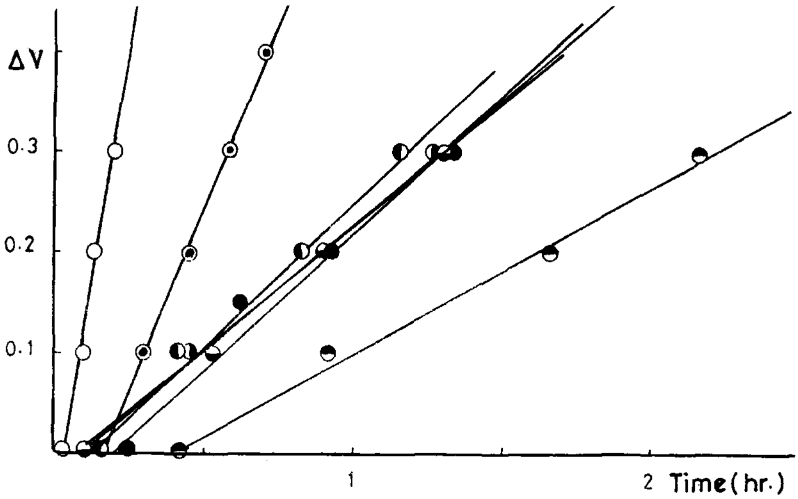


Fig 1 : Volume contraction versus time in different solvents at 60 °C, constant [M] = 1 mol/l, [I] = 1.1 x 10^{-2} mol/l
O DMF, ◎ Benzene, ◐ THP, ● THF, ◒ 2-butanone, ◑ Acetonitrile, ◓ Dioxane.

No correlation between the rate and the polarity, dielectric constant or the donor number of the solvents used could be found.
Dependence of the rate on the initiator and the monomer concentration. Figure 2 represents a log - log plot of the rate of the free radical polymerization of the APTU, in THF versus the initiator and the monomer concentration [I], and [M] respectively.
The variation of [I] was carried out at constant monomer concentration of 1 mol./l at 60 ° C (Fig. 2 a) while the second dependence of log Rp versus log [M] was conducted at a constant initiator concentration of 1.1 x 10^{-2} mol./l and constant temperature of 60 ° C (Fig. 2b). The rate equation follows the usual free radical mechanism :

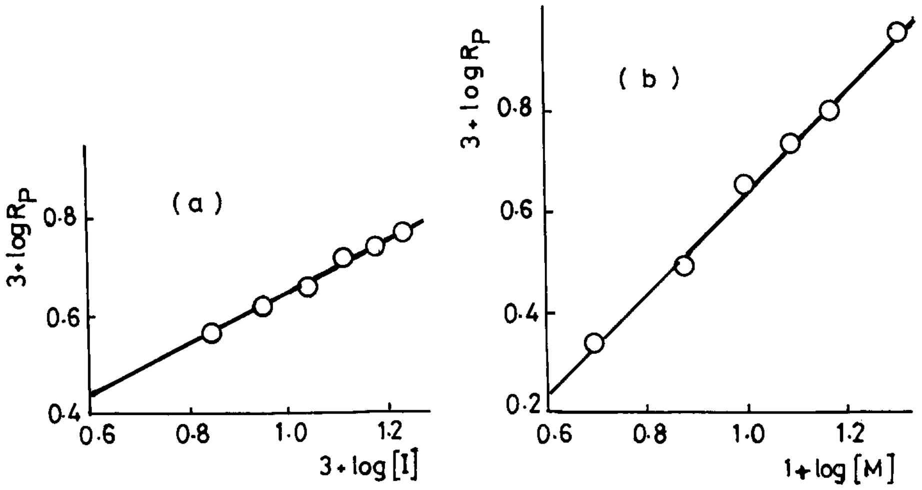


Fig 2: Dependence of the rate of polymerization on:

a) The initiator concentration [I] at constant [M] of 1 mol./l at 60 °C.

b) The monomer concentration [M] at constant [I]= 1.1 x 10^{-2} mol./l at 60 °C

$$Rp = K [M] [I]^{0.5}$$

where K is the overall polymerization rate constant:

$$K = Kp (Kd / Kt)^{0.5},$$

Kp is the rate constant of propagation, Kd is the rate constant of initiator decomposition and Kt is that of termination.

The 0.5 dependence on initiator concentration indicates that the termination occurs exclusively bimolecularly.

Activation energy of polymerization.

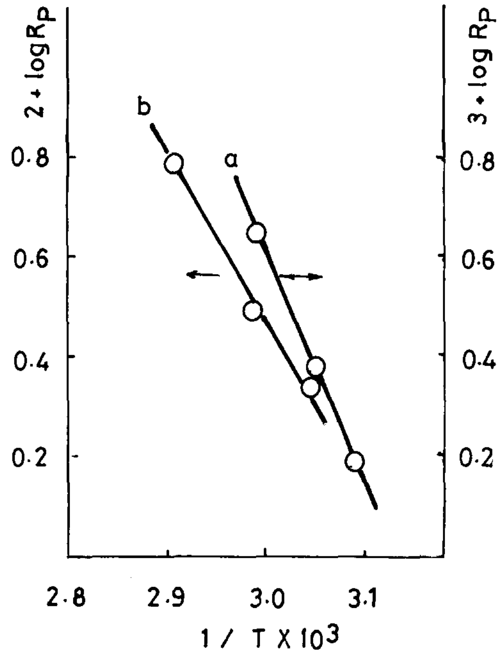
The overall activation energy of the free radical polymerization ΔE of APTU, which is a combination of terms ($Ep + \frac{1}{2}Ed - \frac{1}{2}Et$) where Ep refers to propagation, Ed to initiator decomposition and Et to termination, was calculated in two solvents DMF and THF.

ΔE is obtained from the slope of log Rp versus 1/T where Rp is the initial overall rate of polymerization as shown in Fig. 3. It has been found that ΔE equals to 21.2 and 15.03 K.Cal/mol. in THF and DMF respectively.

Effect of copper ion concentration on the rate of polymerization of APTU.

Our preliminary experiments have indicated that this new monomer is capable of forming complexes with many cations including copper (II).

Since one of our targets is to investigate the catalytic properties of these polymer-metal complexes, it was of interest to polymerize the monomer in the presence of different concentrations of cupric ions.



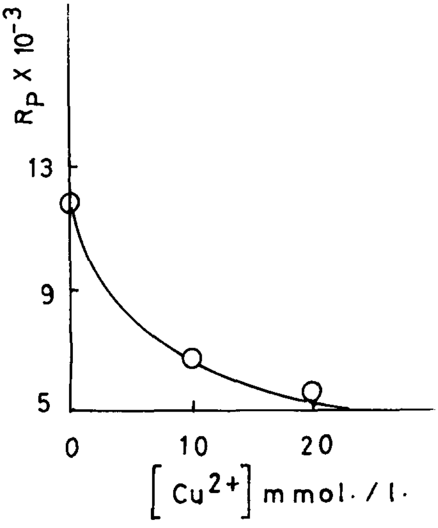


Fig 3: The logarithm of polymerization rate versus 1/T in: a) THF, b) DMF at $[M]=1$ mol/l & $[I]=1.1 \times 10^{-2}$ mol/l

Fig 4: Effect of [Cu II] on the rate of polymerization of APTU in dioxane at 60 °C, $[I]=1.1 \times 10^{-2}$ mol/l, $[M]=1$ mol/l

Figure 4 describes the effect of the cupric concentration on the overall rate of polymerization of APTU. The rate decreases and reaches zero with increasing the [Cu II] ions.
In the mean time the complexed monomer, after separation and dissolution in different solvents, shows no tendency for free radical polymerization.

Chelating behaviour of the APTU monomer.

The chelating behaviour of the monomer, and its homopolymer as well as some of its copolymers with conventional monomers is to be investigated. In the present work only data concerning the chelation of the monomer alone are reported.
The chelation experiments were carried out in non aqueous media as acetone and dioxane.
The solid complex can be prepared in methanol by the addition of the required amounts of copper salt in methanol to a methanol solution of the monomer, immediatly yellowish crystals precipitate which can be filtered and dried. The ^{1}H-NMR spectrum of this complex is given in Figure 5 together with the corresponding spectrum of the homopolymer.

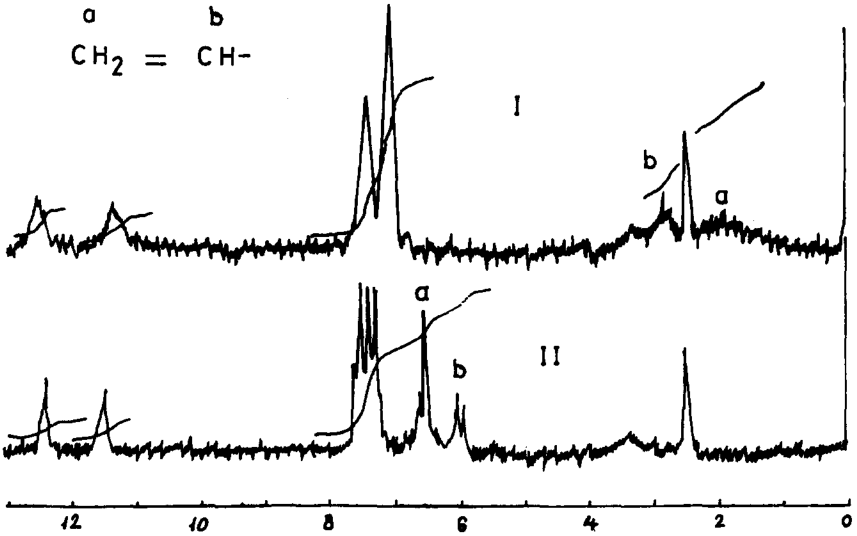
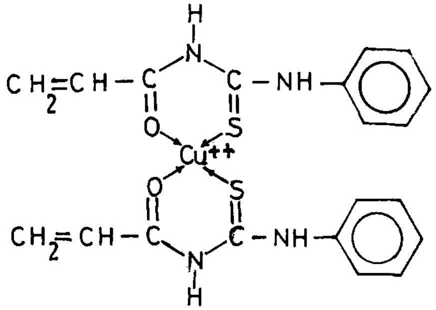


Fig 5 : The ^{1}H-NMR spectra in DMSO-d_6
I) Homopolymer of APTU
II) Complex of APTU with CuII ions

It can be observed that the chemical shift values of the methylene protons in the complex has been shifted to lower field and that the chemical shift values of methylene and methine protons have been reversed compared to the values in the free monomer state.

This deshielding effect on the CH_2 group could be explained by considering the structure of the complex which was found to be 1 : 2 [Cu II : Ligand] as follows :



The stability constant values of this complex have been determined by the continuous variation method in the two solvents dioxane and acetone at 20 °C and were found to be 1.05×10^{10} and 2.608×10^{8} respectively. The stability constant values were also measured in dioxane at different temperatures 20, 25, 30 and 35 °C in order to calculate the thermodynamical parameters ΔG, ΔH and ΔS and are given in the following table ;

Temperature °C	20	25	30	35
K(dioxane)	$1.05x10^{10}$	$3.75x10^{9}$	$3.018x10^{9}$	$1.507x10^{9}$
ΔG	-13.73	-13.35	-13.22	-13.00
ΔS	-42.54			
ΔH	26.13			

The analogous values of the complexes of the homo-and copolymers with different cations are to be the subject of a following report. The high stability constant values of the complexes could justify the applications of the prepared monomer and its homo - and copolymers as selective ion exchange resins. The same system may be also an effective catalyst.

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