

Initiation of Polymerization of Vinyl Monomers by Charge Transfer Mechanism

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ABSTRACT: The charge transfer initiated polymerization of acrylonitrile by 2,4-dinitrophenylhydrazine (DNPH) and Cu^{2+} in the presence of carbon tetrachloride was studied in dimethyl sulphoxide at 60°C. The rate of polymerization became maximum when the mol ratio of [DNPH] to $[\text{Cu}^{2+}]$ was 4:1. The polymerization was inhibited after a very short period when the above ratio was 2:1, mainly due to the liberated bromine. A suitable mechanism for the experimental observation is proposed.

KEY WORDS Charge Transfer Polymerization / Acrylonitrile / 2,4-Dinitrophenylhydrazine / Dimethyl Sulphoxide / Carbon Tetrachloride / Tetrakis Dimethyl Sulphoxide Copper(II) Perchlorate / Association of Bromine with Polyacrylonitrile /

Our previous works¹⁻⁷ reveal that compounds containing a donor nitrogen atom can play a significant role in initiation and propagation steps of charge transfer (CT) initiated polymerization. The CT initiated polymerization of vinyl monomers like methyl methacrylate (MMA),¹⁻⁷ 2-vinylpyridine,⁸ etc. has already been reported. It was found that metal ions have profound effect on the rate of CT initiated polymerization. It should be worthwhile to follow the rate of polymerization of acrylonitrile (AN) in the presence of metal ions and carbon tetrachloride for elucidating this complex but important problem. The present communication reports the polymerization of AN in the presence of 2,4-dinitrophenylhydrazine (DNPH) and tetrakis dimethyl sulphoxide copper(II) perchlorate, $[\text{Cu}(\text{DMSO})_4](\text{ClO}_4)_2$, **A** with carbon tetrachlorides in dimethyl sulphoxide (DMSO) at 60°C.

EXPERIMENTAL

Materials

AN,⁹ DMSO⁵ and carbon tetrachloride⁵ were purified as reported in the literature. Carbon tetrachloride and DNPH were used without further purification.

The complex, **A**, was prepared as before.⁵

Polymerization

Experiments were done in a three limbed vessel and the rates of polymerization were measured dilatometrically in the usual way.¹⁰

Molecular Weight Determination

Polymers were washed with methanol and dried after precipitation with water. The weight average molecular weights of AN polymers were determined viscometrically in *N,N*-dimethylformamide at 25°C. The following relation was used in the calculation.

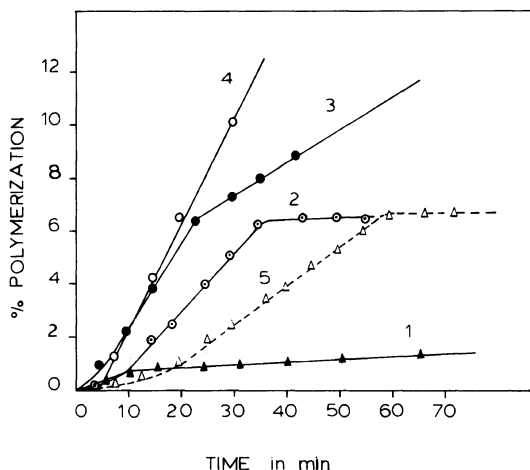


Figure 1. Polymerization of AN in DMSO initiated by DNPB and CBr₄ in the presence of A at 60°C. [AN]= 2.92 mol l⁻¹; [CBr₄]=1 × 10⁻² mol l⁻¹; [A]=2 × 10⁻³ mol l⁻¹; [DNPB]=2 × 10⁻³ mol l⁻¹ for curve 1, 4 × 10⁻³ mol l⁻¹ for curve 2, 6 × 10⁻³ mol l⁻¹ for curve 3, 8 × 10⁻³ mol l⁻¹ for curve 4 and [KBr]=1 × 10⁻² mol l⁻¹ for curve 5.

$$[\eta] = 3.46 \times 10^{-4} (\bar{M}_w)^{0.733}$$

Molecular weights of PMMA was determined with a Wescan 232A osmometer.

RESULTS AND DISCUSSION

A series of experiments were done by adding different amounts of DNPB to a constant composition of AN, A, and CBr₄ in DMSO at 60°C. A few experimental curves are shown in Figure 1. Similar experiments were done using CCl₄ in place of CBr₄ (Figure 2). Experimentally it was found that the CT initiated polymerization of AN with DNPB alone was too slow. However, in the presence of a Lewis acid, like Cu²⁺, accelerated rate was observed. In all the cases, a very short induction period was recorded indicating that during induction period Cu²⁺ should be reduced to Cu¹⁺ due to electron transfer¹²⁻¹⁴ from the primary radical to Cu²⁺. The rate of polymerization attained its maximum value when the mol ratio of DNPB to A was 4:1 in both the cases (Figures 1 and 2). Rate of

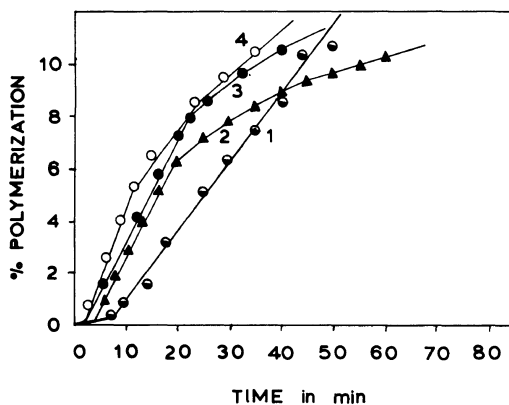
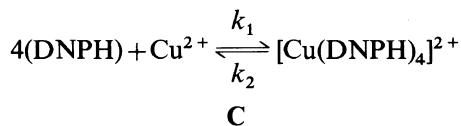
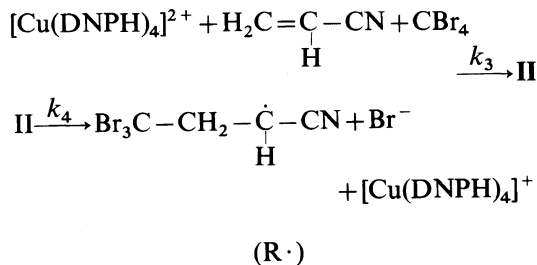


Figure 2. Polymerization of AN in DMSO initiated by DNPB and CCl₄ in the presence of A at 60°C. [AN]= 2.92 mol l⁻¹; [CCl₄]=1.04 mol l⁻¹; [A]=2 × 10⁻³ mol l⁻¹; [DNPB]=1.2 × 10⁻² mol l⁻¹ for curve 1, 4 × 10⁻³ mol l⁻¹ for curve 2, 6 × 10⁻³ mol l⁻¹ for curve 3, 8 × 10⁻³ mol l⁻¹ for curve 4.

polymerization decreased above this ratio due to the excess DNPB. Therefore, [Cu(DNPB)₄]²⁺ is an accelerator. The following reaction scheme may explain the accelerated rate of polymerization of AN in presence of DNPB, A and CBr₄.



The complex C, formed in situ will have unfavorable charge distribution around the metal ion. Therefore, a CT complex (II) will be formed in between C and AN in presence of CBr₄ which readily decomposes to form the primary radical R.



The weak charge-transfer complex formed between AN and DNPB in presence of CBr₄

Table I. Molecular weight of PAN, determined viscometrically

[DNPH] mol ⁻¹	Ratio [DNPH] to [A]	Molecular weight
4×10^{-3}	2:1	1.7×10^3
8×10^{-3}	4:1	6.2×10^3
1.2×10^{-2}	6:1	2.6×10^3

Time of reaction, 1.5 h

could not initiate the polymerization of AN. The nitrogen atom in the unsubstituted hydrazine group of DNPH acts as the donor atom.³ Due to the electron withdrawing inductive effect of the benzene ring, the free electrons in the nitrogen atom of the amine group of DNPH are less available than those of an aliphatic amine which alone can initiate the polymerization.¹ Lewis acids are good electron acceptors and so Cu^{2+} increased the electron donating capacity of DNPH resulting in the rapid formation of free radicals.

The rate of polymerization with [DNPH] : $[\text{Cu}^{2+}]$ greater than 4 : 1 was found to fall with the increase of added DNPH. The retarding effect of free DNPH is obvious since it is an aromatic nitro compound.

The molecular weight of the polymer formed was highest when the ratio of [DNPH] to [A] was 4 : 1. Some of the data for molecular weight of the polymer formed with different ratios of [DNPH] to [A] are quoted in Table I.

An interesting phenomenon occurred when the mol ratio of [DNPH] to [A] was 2 : 1. Here, the reaction was inhibited after a certain period. The reaction time decreased with the increase in the amount of DNPH with a fixed ratio of 2 : 1 of [DNPH] to [A]. It may be due to CBr_4 , liberated DNPH and consumption of primary radical for reduction of Cu^{2+} . Since inhibition was more significant in the system with CBr_4 , we added KBr to it (Figure 1). The addition of KBr reduced the rate and increased the reaction time for polymerization as well as the induction period.

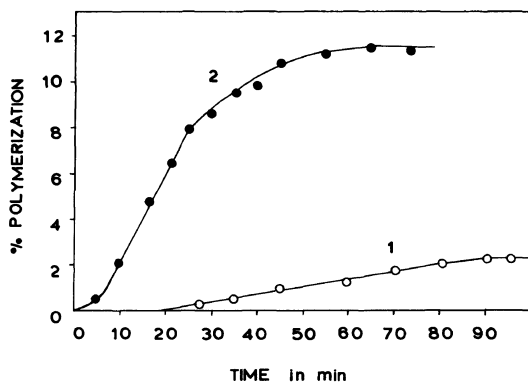


Figure 3. Polymerization of MMA in DMSO initiated by DNPH and CBr_4 in the presence of A at 60°C. $[\text{MMA}] = 1.73 \text{ mol l}^{-1}$; $[\text{CBr}_4] = 1 \times 10^{-2} \text{ mol l}^{-1}$; $[\text{A}] = 2 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{DNPH}] = 4 \times 10^{-3} \text{ mol l}^{-1}$ for curve 1 and $8 \times 10^{-3} \text{ mol l}^{-1}$ for curve 2.

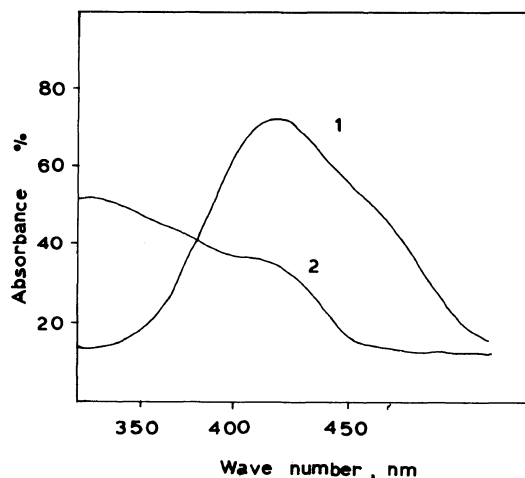


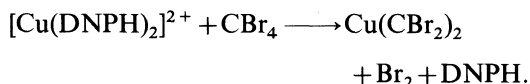
Figure 4. UV spectra of poly(MMA) in CCl_4 . (1) Br_2 in CCl_4 ; (2) poly(MMA) in CCl_4 .

But addition of KBr alone did not effect the rate of polymerization in the absence of Cu^{2+} , suggesting CuBr_2 acted as a retarder. But if CuBr_2 is the only inhibiting species, the reaction time would have decreased drastically which was not experimentally observed.

The presence of DNPH in polyacrylonitrile (PAN) was difficult to establish by microanalysis, since the monomer itself contains nitrogen and IR analysis is not very sensitive to the end group present in the long chain.

Though the quantitative isolation of pure PAN is possible, the quantitative estimation of DNPH was not possible since it complexed with Cu^{2+} in solution. The estimation of uncomplexed DNPH was also alluding since it involved a number of repeated steps to get the pure solid DNPH from the reaction mixture. So, some of the experiments were repeated replacing AN by MMA (Figure 3). The polymerization was inhibited after a short period even when MMA was used in place on AN and colored polymers of MMA with low molecular weight (3.6×10^3) were obtained, soluble even in alcohol and carbon tetrachloride. However, the polymer can be recovered from alcohol solution indicating its low solubility in alcohol. The presence of any end group containing nitrogen or halogen could not be established by IR analysis of the polymer. But the UV spectra of the polymer in CCl_4 showed the presence of bromine. The appearance of a peak at 417 nm in the UV region for the polymer solution in carbon tetrachloride indicated the association of bromine in the polymer. The polymer obtained by this system was brownish in color and gave the test for bromine when the sample was dissolved in dil. HNO_3 and tested with AgNO_3 solution. The spot test¹⁵ with the polymer recovered from alcohol solution supported the inference. Estimation of bromine in PAN indicated that the termination was by molecular bromine in the experiment where $[\text{Cu}^{2+}] : [\text{DNPH}]$ was 1 : 2 (found 21.6%, calculated 23.51%), but the termination was due to combination when the ratio was 1 : 4 (found 7.69%, calculated 7.73%). Since some associated bromine are likely to escape during fusion, the amount of bromine was found always lower than the theoretical value. Therefore, bromine should be the inhibiting species¹⁶ for 2 : 1 experiment. It was found that the added bromine inhibits the polymerization. The following scheme may explain the reaction. Initiation must be due to tribromomethyl radical but an additional re-

action takes place when the molar ratio of $[\text{DNPH}] : [\text{Cu}^{2+}]$ is 2 : 1.



The presence of bromine in the polymer was further confirmed from the far IR spectra of the poly(MMA) sample. A weak peak¹⁷ at 225 cm^{-1} indicated the formation of a CT complex between poly(MMA) radical and molecular bromine. The appearance of the strong peaks at $\sim 1730 \text{ cm}^{-1}$ in IR and at $\sim 362 \text{ cm}^{-1}$ in the far IR region indicated the incorporation of MMA in the polymer.

Since, bromine could be detected by UV spectroscopy, far IR and spot test, the inhibiting species should be bromine produced *in situ*. Estimation of bromine in the polymer indicates the presence of five bromine atoms, three due to end group CBr_3 and two for the associated molecular bromine.

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