IR and ^{1}H-NMR Investigations for Molecular Interactions between Methyl Methacrylate and Methylcyanoacetate

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Summary: The molecular interactions between methyl methacrylate (MMA) and methyl Cyanoacetate (MCA) has been studied. The IR results show a lower electron density for vinyl as well as for the carbonyl double bond of methyl methacrylate as the concentration of methylcyanoacetate increases in the solution. The ^{1}H-NMR data also coinside with the results of IR investigations. These results lead to the conclusions that a cyclic structure of MMA-MCA complex is formed by the interaction of the oxygen of the carbonyl group and active hydrogen atom of MCA with methylene group of the vinyl double bond and oxygen of the carbonyl group of the MMA respectively. This cyclic structure facilitate the abstraction of H α atom in MCA by MMA and formation of transition radical which after rearrangement can start the polymerization reaction.

Introduction

It has been reported that some organic compounds containing active hydrogen atom can initiate the radical polymerization of some polar vinyl monomers [1-8]. The mechanism of the reaction involving transfer of the hydrogen radical abstracted from these compounds to the monomer originally proposed by Ouchi *et al.*, for methyl methacrylate (MMA) initiated with aldehydes and later discussed for (MMA) polymerization started by cyclohexanone [3] is based on the strong interactions between MMA and organic compounds containing active hydrogen atom. The radical character of the polymerization seems to be well established [2-3,9] the proof of the discussed mechanism by means of electron paramagnetic resonance (e.p.r.) failed, however [10]. Moreover, the spectral studies (IR, UV, ^{1}H-NMR) of the mixed solution of benzaldehyde and methyl methacrylate have not shown any substantial shift in the absorption frequencies of carbonyl and vinyl double bonds [11].

In the present paper we report the IR and ^{1}H-NMR data obtained for the solutions of the MMA-methyl cyanoacetate (MCA) mixtures. The results are discussed in the scope of the potential evidence for the interactions between MMA and organic compound (MCA) containing active hydrogen atom.

Results and Discussion

The IR results for the various solutions of different concentrations of MMA and MCA are listed in Table-1.

For the MMA+MCA mixture benzene was used as a solvent instead of cyclohexane because the later was immissble with methyl cyanoacetate.

It is noted from the data given in Table-1 that as the concentration of MCA in the solution containing MMA increases the stretching frequency of carbonyl as well as that of the vinyl double bond

Table-1: IR results of MMA and MCA solutions in cm^{-1}

Methyl methacrylate						Methylcyanoacetate		
C=O			C=C			C=O		
Without solvent	20% solution in MCA	1% solution in MCA	without solvent	20% solution in MCA	1% solution in MCA	without solvent	20% solution in benzene	1% solution in benzene
1725.7	1718	1718	1638.9	1635.4	1633.7	1750	1757.5	1758.7
20% solution in benzene	1% solution in benzene		20% solution in benzene	1% solution in benzene				
1717.3	1724		1637.9	1638.7				

Table-2: ^{1}H-NMR results of MMA and MCA solutions in δ ppm.

No	Description of sample	H_a	H_b	H_c	H_d	H_α	H_β
1.	MMA (conc:) in C_6D_6	5.967	5.282	1.765	3.456	-	-
2.	MCA (conc:) in C_6D_6	-	-	-	-	3.409	3.601
3.	90% MCA in MMA + C_6D_6	6.080	5.559	1.887	3.418	3.486	3.718
4.	95% MCA in MMA + C_6D_6	6.082	5.568	1.916	4.423	3.491	3.704
5.	1% MCA in MMA + C_6D_6	6.053	5.338	1.845	3.512	No peak was observed	
6.	1% MCA in C_6D_6	-	-	-	-	2.197	3.056
7.	1% MMA in C_6D_6	6.202	5.019	1.793	3.357	-	-
8.	5% MMA in C_6D_6	6.085	5.169	1.803	3.362	-	-
9.	20% MMA in C_6D_6	6.071	5.179	1.808	3.376	-	-

of MMA decreases what is in conformity with the well known Hook's formula [12] which indicates a lower electron density of both the double bonds. Decreasing stretching frequencies of carbonyl and vinyl double bonds of MMA by increasing the concentration of MCA is well observed when the data for pure MMA are compared with 20% MMA and 1% MMA in MCA. However dilution of MMA in benzene (1% MMA in benzene) almost does not affect its frequencies which is in contradiction to its dilution in cyclohexane [8]. This is probably due to the effect of π-electrons of benzene. Similarly, the carbonyl double bond stretching frequencies of MCA on dilution in benzene increases which indicate a stronger double bond.

The ^{1}H-NMR results for the solution of different concentrations of MMA - MCA mixtures are placed in Table 2 and Fig. 1-3 respectively. As shown in Table 2 and Fig. 1-3 by increasing the concentration of MCA in the solution containing MMA the peak of proton H_a and H_b shifts towards the lower field. Although chemical shift data do not show a big difference even then this phenomenon is clearly indicated when the chemical shift data of 1%, 90% and 95% of MCA in solution containing MMA are compared with the chemical shift data of concentrated MMA in C_6D_6. Therefore, it can be deduced that the shielding effect of electron density around these protons decreases by increasing the concentration of methyl cyanoacetate. In other words it can be said that the vinyl double bond becomes weaker. Similarly, alpha proton of MCA show a tendency to shift in the lower field.

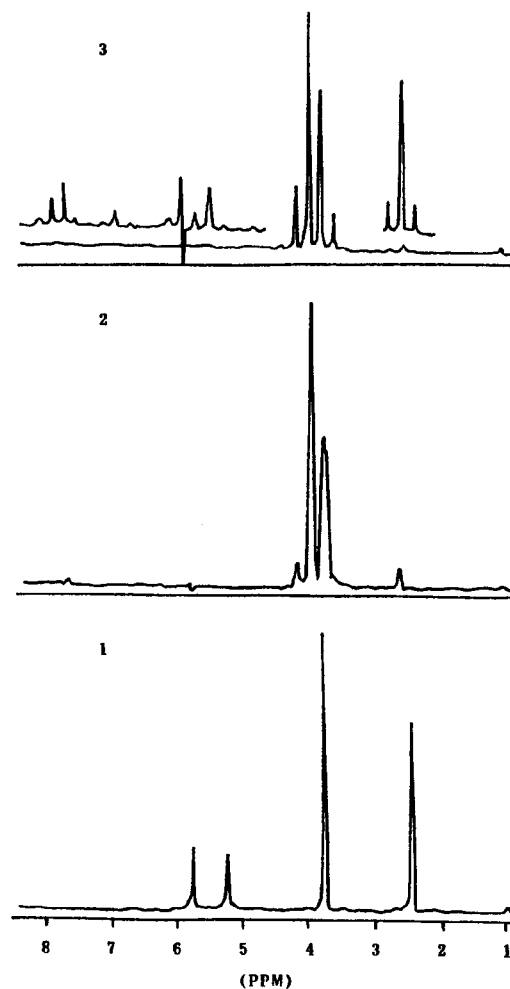On the other hand on dilution in deuterated benzene the MMA, and MCA indicate a chemical

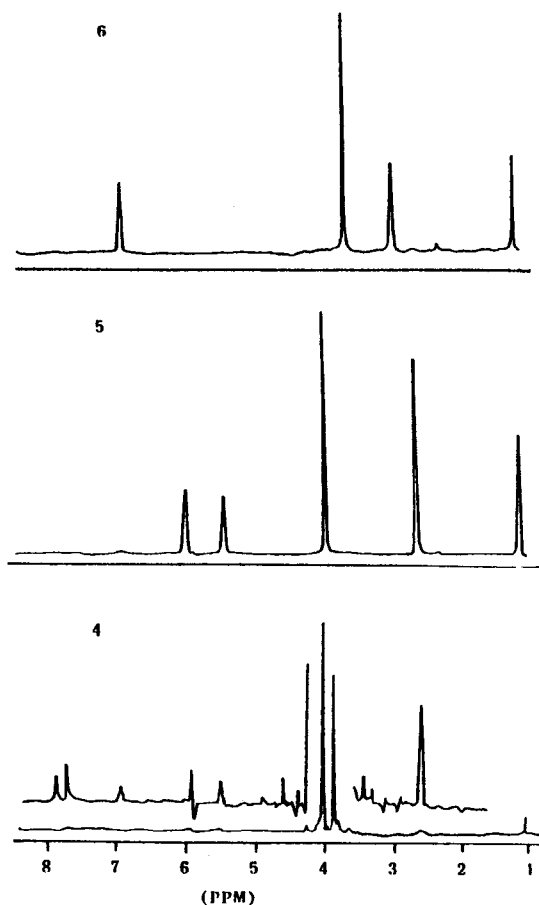Fig. 1: I) Conc MMA in C_6D_6, 2. Conc: MCA in C_6D_6, 3). 90% MCA in MMA and + C_6D_6.

Fig. 2:   4) .95% MCA + C₆D₆, 5). 1% MCA in
MMA + C₆D₆ 6). 1% MCA in C₆D₆.

Fig. 3:   7). 1% MMA in C₆D₆. 8), 5% MMA in
C₆D₆. 9) .20% MMA in C₆D₆.

shift towards the higher field particularly for H_b and H_α respectively; which shows a strong shielding effect of electron density around these protons. This is well noticeable from the data of 1% MMA and 1% MCA in deuterated benzene (Table-2). These results indicate that vinyl double bond (of MMA) becomes stronger on dilution probably because of MMA-MMA interactions due to the destruction of MMA structure on dilution. However, it is interesting that by increasing the concentration of MMA in the solution i-e 5% and 20% MMA in deuterated benzene shows the chemical shift towards the lower field for H_b proton in comparison to the data of 1% MMA in deuterated benzene.

The interaction of the oxygen of the carbonyl group of the MCA with the methylene group of the vinyl double bond of MMA and simultaneously
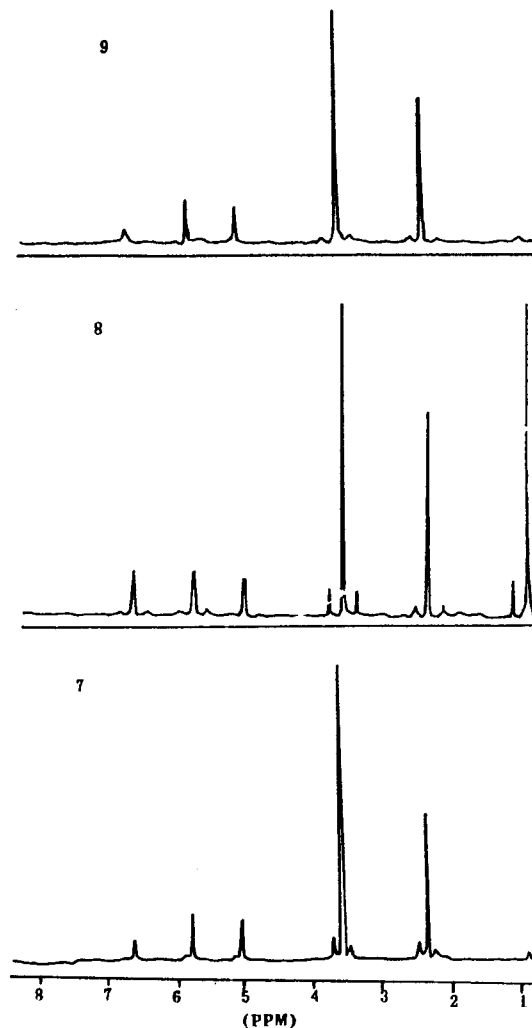
interaction of the active hydrogen atom of MCA with the oxygen of the carbonyl group of MMA would lead to the ¹H-NMR and IR results as obtained here by; the decreasing electron density of the vinyl double bond in MMA and of the single bond between carbon and H_α atom of MCA. On the other hand ¹H-NMR results show very high influence of MCA on the H_b of MMA. This would suggest (considering the cyclic structure of MMA-MCA complex Figure No. 4) that H_b and carbonyl of MMA should be in cis - position.

Experimental

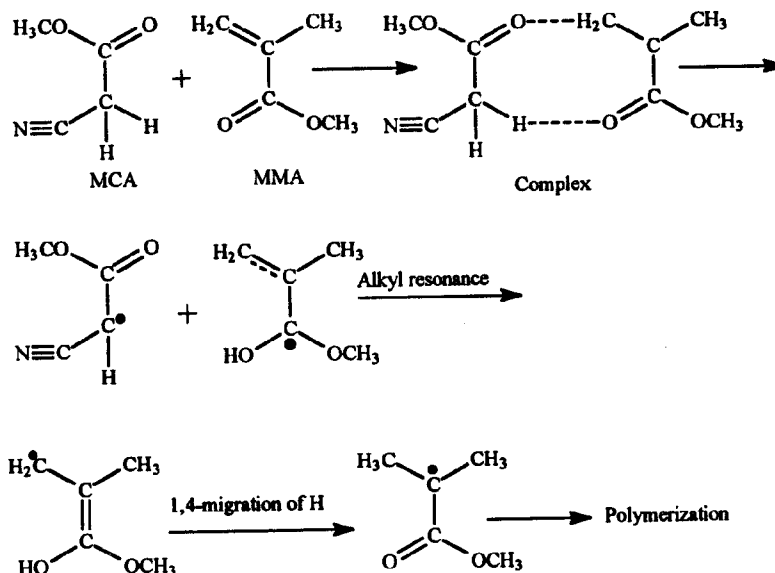Methyl methacrylate and methyl cyanoacetate were purified according to the methods reported

Fig. 4:   Scheme for the reaction of MMA and MCA.

previously [5,6]. The IR spectras for the solutions of different concentrations of MMA and MCA were obtained by using a Magna-IR spectrometer 550 (Nicolet England) and Ominic computer program to record and analyze the spectra, respectively.

^{1}H-NMR spectra were obtained by using Tesla BS-567 A spectrometer, operating at 100 MHz. Deuterated benzene (MMA-MCA mixture) was used as a solvent and tetramethylsilance as internal reference compound in all the experiments.

Conclusion

In conclusion it can be said that the IR and ^{1}H-NMR results support the idea of the cyclic structure of the MMA - MCA complex. This would facilitate the abstraction of Hα atom in MCA by MMA and formation of transition radical which after rearrangement can start the polymerization reaction as proposed by Ouchi *et al.,* [2]. We think that this assertion, even when the creation of the radical starting the copolymerization reaction could not be uptill now clearly and solely proved [10] makes the mechanism proposed by Ouchi more probable.

References

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