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Spontaneous Polymerization Studies on Methyl Methacrylate and Vinyl Acetate in the Presence of a Cholesteric Liquid Crystal, Cholesteryl 2-(Ethoxy Ethoxy) Ethyl Carbonate

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Summary

Spontaneous polymerization of methyl methacrylate (MMA) takes place in the presence of cholesteryl 2-(ethoxy ethoxy) ethyl carbonate (CHEEC) in liquid crystalline phase at 12.5°C and in isotropic phase at 30.0°C. Percentage of conversion increases, whereas molecular weight decreases, with increase in the concentration of CHEEC. Tacticities of the polymers (as analysed by NMR) are independent of the concentration of CHEEC. The interaction between CHEEC and MMA in various solvents are investigated by viscometry and U.V. spectrophotometry.

Similar experiments with a mixture of vinyl acetate (VAc) gave no evidence of spontaneous polymerization.

A plausible mechanism of the spontaneous polymerization of MMA, involving formation of a complex between MMA and CHEEC, is discussed.

Introduction

In polymerization studies, use of thermotropic liquid crystals as solvents is reported by several authors (AMERIK et al.1968 ; BLUMSTEIN et al.1974 ; TANAKA et al. 1978). In our laboratory, the radiation polymerization of methyl methacrylate (MMA) in presence of some liquid crystals is under investigation. We have found in these studies (BISWAS et al.) an enhancement of tacticity with 35% of cholesteryl 2-(ethoxy ethoxy)ethyl carbonate (CHEEC). In contrast, TANAKA et al.(1978) reported no change in tacticity with 90% cholesteryl octadeconate liquid crystal for the same monomer by thermal polymerization using 2,2'-azobisisobutyronitrile as an initiator. In view of these differnces, further work is being done to study the thermal polymerization of MMA in the presence of CHEEC. The preliminary experiments carried out for this purpose showed the formation of poly (methyl methacrylate) [PMMA] in the mixture

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of MMA and CHEEC when left over night. A detailed study of this spontaneous polymerization is described in this paper.

Experimental

Materials :(a) Reagent grade MMA was purified as described in the earlier paper (BISWAS et al.). (b) Vinyl acetate (Vac) was purified by fractional distillation after washing with an aqueous sodium bisulphite solution and drying over calcium chloride. (c) CHEEC supplied by Aldrich Chemical Company was used as such. (d) All reagent grade solvents were purified and dried by standard methods (RIDDICK and BUNGER, 1970).

Polymerization procedure : Polymerization was carried out in sealed glass ampoules for 10 hrs at 12.5° and at 30.0°C. After polymerization, polymer was separated by extracting CHEEC and the unreacted monomer in ether. The polymers were further purified by dissolving in benzene and precipitating in excess of methanol. Finally the polymers were separated, dried at 50°C under vacuum and the percentage of conversions were estimated gravimetrically.

Characterization of polymers: Viscosity average molecular weights ($\bar{M}v$) were determined from the intrinsic viscosity measured in benzene at 30.0 ± 0.05 °C. ^{1}H NMR spectra in $CDCl_3$ were obtained on XL - 100 spectrometer and the tacticities were evaluated therefrom as discribed elsewhere (BOVEY, 1972).

Viscometry and Spectrophotometry of solutions : A fixed amount of 0.5 g containing different amounts of CHEEC and monomer, was made up in 5 ml of tetrachloromethane or benzene or cyclohexane and the viscosity of the solutions in tetrachloromethane was measured at 30.0°C and 12.5°C, whereas for the other solutions it was measured at only one temperature 30.0°C. The optical absorption spectra of the solutions in tetrachloromethane and benzene were also measured at room temperature (28°C) on Perkin Elmer 402 Ultraviolet-visible spectrophotometer.

Results and Discussion

For a detailed study of the observed spontaneous polymerization, experiments were carried out with varying amount of CHEEC in MMA in liquid crystalline phase at 12.5°C and in isotropic phase at 30.0°C. Spontaneous polymerization was allowed to take place for a duration of 10 hrs. in which period a detectable amount of polymer could be obtained with the lowest concentration of CHEEC used in this series of experiments. The percentage of conversion increases with an acceleration whereas the molecular weight decreases linearly with increase in concentration of CHEEC at both the temperatures (Fig.1).

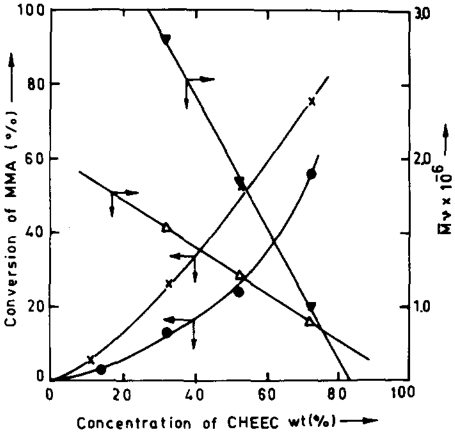

Fig.1 Percentage of conversion vs concentration of CHEEC at (●) 12.5°C and (×) 30.0°C ; Molecular weight vs concentration of CHEEC at (▼) 12.5°C and (△) 30.0°C.

From the ^{1}H NMR signals the percent population of isotactic (I), heterotactic (H) and syndiotactic (S) triads were estimated from the integrated intensities of the peaks at 8.78, 8.98 and 9.08 τ respectively (BOVEY, 1972). The results as given in the Table 1, show that the polymers obtained in both the phases are more syndiotactic than that obtained thermally at 80°C without any additive. Moreover, no significant change in tacticity is observed with increase in concentration of CHEEC.

An increase in the yield and a decrease in the molecular weight with increase in the concentration of CHEEC show that the number of initiating species or active sites depend on the concentration of the latter and therefore on the extent of interaction between CHEEC and MMA. This interaction leads to complex formation as will be discussed later.

Invoking the formation of complexes between monomers like MMA and certain additives is known in polymerization reactions. For example, GYLORD et al(1970) reported the formation of a complex between a metal halide and monomers like MMA, acrylonitrile etc., such complexes lead to homopolymerization or alternative co-polymerization in the presence of another monomer. MATSUDA et al. (1970) have also reported a charge transfer complex between poly 2-vinyl pyridine and liquid sulfur dioxide, the complex being responsible for the polymerization of MMA.

TABLE - 1

Spontaneous polymerization of MMA in the presence of CHEEC for 10 hrs.

Sample No.	CHEEC Conc. (%)	Temp. (°C)	MMA Conv. (%)	$\bar{M}v \times 10^{-6}$	(I)	(H) (%)	(S)
1	13.7	12.5	2.6	-	-	-	-
2	32.2	12.5	12.7	2.805	2	33	65
3	52.0	12.5	24.4	1.841	2	32	66
4	72.3	12.5	55.5	1.001	2	33	65
5	11.1	30.0	4.7	-	-	-	-
6	31.9	30.0	26.1	1.538	2	31	67
7	52.3	30.0	52.3	1.205	3	32	65
8	71.7	30.0	75.1	0.927	2	34	65
9	Nil	30.0	Nil	-	-	-	-
10 \$	Nil	80.0	9.2	-	6	35	59

\$ Polymers obtained thermally for 2 hrs. without any additive.

It is likely that the high electron density on the carbonate part in CHEEC on interaction with the electron deficient MMA as a whole would form a complex. The complex formation has a support from our viscosity measurements and the U.V. spectra of (MMA + CHEEC) mixture in different solvents (Figures 2 and 3). In Fig.2, change in reduced viscosity $(\Delta\eta / \eta_0)$ in the solvent tetrachloromethane are plotted against the weight-fraction of CHEEC at 12.5°C and 30.0°C. Similar plots are also shown in the same figure for two other solvents viz. benzene and cyclohexane at 30.0°C. A minimum in reduced viscosity in these plots indicate an association between CHEEC and MMA. [See for example CHALLA et al. (1976)] .

Formation of a complex between (MMA + CHEEC) mixture results in the delocalization of the electrons on the π-bond of MMA and will therefore be readily available for initiating polymerization. Thus,

$$\text{MMA} + \text{CHEEC} \rightleftharpoons \text{COMPLEX}$$

$$\text{COMPLEX} + \text{MMA} \longrightarrow \sim\!\sim\!\sim\!\sim\text{M}^{\cdot}$$

Evidence of existance of free radicals in this mixture is obtained from ESR spectra. The details will be given elsewhere. A higher concentration of CHEEC which can increase the concentration of the complex species could cause a higher yield and a lowering in molecular weight. Further the increase in tacticity of the polymers obtained with CHEEC may be due to the stereo-specificity of the complex formed ; reason for tacticities remaining unaltered with varying amounts of CHEEC, is not understood.

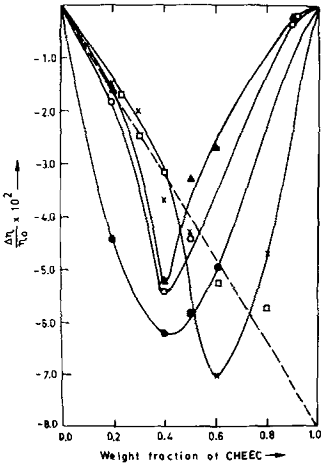

Fig. 2 : Change in reduced viscosity ($\Delta\eta/\eta_0$) vs. weight-fraction of CHEEC (a) CHEEC + MMA mixtures at 30°C in tetrachloromethane(○), cyclohexane (×), benzene (●); and at 12.5°C in tetrachloromethane (▲). (b) (CHEEC + VAc) mixtures at 30°C in tetrachloromethane (□).

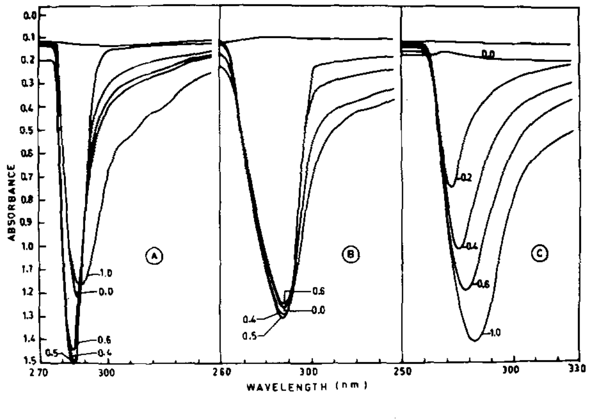

Fig.3 : U.V. spectra of mixtures containing CHEEC and (A) MMA in Benzene (B) MMA in CCl_4 (C) VAc in CCl_4. The figures along each curve indicate weight fraction of CHEEC.

In order to check whether the hypothesis of complex formation with CHEEC as envisaged above is applicable in the case of another monomer, experiments were carried out with vinyl acetate (VAc) in the presence of varying concentration of CHEEC at two temperatures 12.5°C and 30°C for 10 and 24 hrs.

At the end of the reaction period the contents were poured in excess of hexane. No polymer is precipitated even after 24 hrs. of reaction indicating VAc does not polymerize in the presence of CHEEC. This is not surprising, as VAc is not as efficient as MMA in acepting electrons from CHEEC and hence may not be able to form a complex with the latter. Moreover, viscometry and U.V. spectrophotometry results (Figs. 2 and 3) in tetrachloromethane show that VAc does not appear to interact with CHEEC.

Conclusions

MMA spontaneously polymerizes in the presence of CHEEC due to the formation of an intermediate complex which acts as an initiator. VAc on the other hand does not polymerize in the presence of CHEEC.

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