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Publisher *Taylor & Francis*

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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Deshpande, Dinkar D. and Aravindakshan, Perincheery(1984) 'Effect of Cholesteric Liquid Crystalline Compounds on the Radical Polymerization of Methyl Methacrylate', Journal of Macromolecular Science, Part A, 21: 4, 509 – 517

**To link to this Article:** DOI: 10.1080/00222338408056565

**URL:** <http://dx.doi.org/10.1080/00222338408056565>

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## Effect of Cholesteric Liquid Crystalline Compounds on the Radical Polymerization of Methyl Methacrylate

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### ABSTRACT

Polymerization of methyl methacrylate was carried out at 55 and 65°C using benzoyl peroxide as initiator in the presence of the following additives: (a) cholesteric compounds like cholesterol, cholesteryl acetate, cholesteryl caprylate, cholesteryl stearate, cholesteryl chloride, cholesteryl laurate, cholesteryl oleyl carbonate, and cholesteryl 2-ethylhexyl carbonate, (b) a nematic liquid crystal, N-(p-methoxy benzylidene)-p-butyl aniline, and (c) rodlike molecules like 2-butynediol and diacetylene diol. The rates of polymerization, activation energies, molecular weights, and tacticities of the polymer are discussed in the light of monomer + additive interactions. It is found that monomer-additive complexes affect the polymerization rates.

### INTRODUCTION

The use of thermotropic liquid crystals as solvents in polymerization studies has been reported by several authors [1-3] with the expect-

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tation that these ordered solvents would yield polymers with better stereoregularity. One of us has shown [4, 5] that tacticities are not much affected by variations in the concentration of a liquid crystalline solvent. It was also reported from our laboratory [5] that a cholesteryl liquid crystal, cholesteryl 2-(ethoxy ethoxy) ethyl carbonate, can initiate the polymerization of methyl methacrylate (MMA).

In this work we report the details of investigations carried out on the effects of cholesteryl compounds such as cholesterol (Ch), cholesteryl acetate (ChAc), cholesteryl caprylate (ChCp), cholesteryl stearate (ChSt), cholesteryl chloride (ChCl), cholesteryl laurate (ChLau), cholesteryl oleyl carbonate (ChOC), cholesteryl 2-ethylhexyl carbonate (ChEHC), a nematic liquid crystal N-(p-methoxy benzylidene)-p-butyl aniline (MBBA), and other rodlike molecules, 2-butynediol (2BD) and diacetylene diol (DAD), when used as additives in small amounts in the polymerization of MMA initiated with benzoyl peroxide (BPO).

## EXPERIMENTAL

### Materials

(a) Reagent grade MMA (Aldrich Chemical Co.) was purified by standard procedures. (b) Ch, ChCp, ChSt, ChCl, ChLau, ChOC, ChEHC, and MBBA supplied by Aldrich Chemical Co. were used as delivered. ChAc was prepared by esterification of Ch with acetic acid in the presence of concentrated sulfuric acid, and purified by washing the organic layer with water and by precipitating into methanol. (c) 2BD (Fluka A.G.) was purified by crystallization from methanol and DAD was prepared from propargyl alcohol. (d) Reagent grade solvents, chloroform, methanol, and toluene, were purified and dried by standard procedures. (e) Carbon tetrachloride (Spectroscopic grade) was used as such.

### Polymerization Procedure

The required amounts of the monomer, liquid crystal/additive, and initiator were placed in glass ampules which were sealed under vacuum. The ampules were allowed to tumble in a thermostatic bath. After the required period the ampules were broken and the reaction mixture was poured into methanol. The precipitate was filtered and the liquid crystal/additive was removed by extraction in ether. The polymer was purified by repeatedly dissolving it in  $\text{CHCl}_3$  and precipitating it in methanol. Percent conversions were estimated gravimetrically after drying the polymer at  $50^\circ\text{C}$  in vacuum for several days.

### Characterization

Number-average molecular weights ( $\bar{M}_n$ ) were determined in  $\text{CHCl}_3$  solutions, using a Knauer Membrane Osmometer. Tacticities, copolymer compositions, and reactivity ratios were determined from  $^1\text{H-NMR}$  spectra obtained in  $\text{CDCl}_3$  at room temperature using a Varian XL-100 Spectrometer.

### Viscometry

A fixed amount (0.5 g) containing different ratios of the vinyl monomer and the other component was dissolved in 5 mL of toluene, and the time of flow of the solutions was measured at  $30.0^\circ\text{C}$  using an Ubbelohde viscometer.

### Spectrophotometry

Optical absorption spectra were recorded on a Perkin-Elmer 402 UV-VIS Spectrophotometer in the normal mode. The additive concentration was kept constant and the monomer concentration was varied from  $10^{-3}$  to 1 mol/L.

## RESULTS AND DISCUSSION

Polymerization of MMA initiated with BPO in the presence of various additives was carried out at  $55$  and  $65^\circ\text{C}$ . It was intended to use those additives which consist of molecules with high orientational order or molecular anisotropy so that the monomer molecules would be preferentially oriented. From this point of view, cholesteryl derivatives were selected. Many liquid crystalline compounds can meet the requirement of molecular anisotropy. They exhibit molecular ordering, however, only in a certain definite temperature range which may not be suitable for carrying out the polymerization. Further, the liquid crystalline nature, or mesophase, would invariably be destroyed upon being mixed with other substances such as monomers. Hence, the liquid crystalline compounds used here may be looked upon simply as additives having molecular anisotropy. In this respect then, a variety of other substances consisting of molecules having rigid rod structures can also be utilized. Hence, in addition to cholesteryl derivatives, we have used N-(p-methoxy benzylidene)-p-butyl aniline and acetylene diols. In the presence of these additives, polymerization of MMA, initiated with BPO, has been studied in detail to find the

TABLE 1. Polymerization of MMA at 65°C for 1 h in the Presence of Various Additives

System	% Concentration, 60 min	Concentration of additive (mol%)	% I	% H	% S
MMA <sup>a</sup>	9.0	Nil	6.3	42.6	51.1
MMA + BPO	9.8	Nil	3.8	34.3	61.4
MMA + BPO + Ch	8.9	0.4	3.8	36.3	59.9
+ ChAc	8.6	0.4	4.4	39.2	56.4
+ ChCp	9.3	0.4	12.9	36.3	50.8
	4.4	4.0	7.5	33.0	59.4
+ ChSt	9.4	0.4	5.7	35.7	58.6
	7.7	4.0	11.7	33.0	55.3
+ ChCl	8.8	0.4	3.9	37.8	58.3
+ ChLau	9.3	0.4	3.4	35.6	61.0
+ ChOC	9.8	0.4	8.8	33.6	57.5
	8.2	4.0	6.5	34.8	58.7
+ ChEHC	11.5	0.4	4.5	33.7	61.8
	11.3	4.0	7.3	32.3	60.1
+ MBBA	2.9	0.4	3.3	35.3	61.4
+ 2BD	8.9	4.0	5.1	33.6	61.3
+ DAD	10.7	4.0	6.7	30.0	63.3

<sup>a</sup>Polymer obtained thermally after 3 h at 85°C without any initiator or additive.

effect of the additives on the polymerization rate, the tacticity of PMMA, and the molecular weights.

The effect of the additives on percent conversion at 65°C and the percent isotactic, heterotactic, and syndiotactic tacticities of PMMA determined from <sup>1</sup>H-NMR spectra by Bovey's [6] procedure are given in Table 1. Table 2 gives the percent conversion at 55 and 65°C, the activation energy ( $E_a$ ) for the overall polymerization reaction, and the number-average molecular weight  $\bar{M}_n$  of the polymer formed at 65°C.

At 55°C, the percent conversion is slightly higher in the presence of the additives Ch, ChAc, ChCp, ChOC, and ChEHC than that without any additive for the polymerization of MMA initiated with BPO. On the other hand, the percent conversions at 65°C in the presence of most of the additives are marginally lower than that in the absence of any additive. Only in the cases of ChEHC and DAD are the conversions slightly increased. In the case of the additive MBBA, the conversion is much reduced at 55°C and 65°C.

A maximum increase of isotactic triads is observed with the additives ChCp and ChSt—an increase from 3.8% I to 12.9% I and 11.7% I, respectively, while ChOC gives a rise of isotacticity to 8.8%. Increasing the concentrations of ChCp and ChOC reduces the percent isotacticity. On the other hand, increasing the concentrations of ChSt and

TABLE 2. Polymerization of MMA in the Presence of Various Additives (0.4 mol% with respect to monomer)

System	% Conversion		$E_a$ (kJ/mol)	$\bar{M}_n \times 10^{-5}$ for sample at 65°C
	55°C, 60 min	55°C, 90 min		
MMA + BPO	9.8	5.7	87.1	0.90
MMA + BPO + Ch	8.9	6.5	66.8	1.68
MMA + BPO + ChAc	8.6	7.3	52.2	1.58
MMA + BPO + ChCp	9.3	7.1	61.9	1.62
MMA + BPO + ChSt	9.4	5.4	88.7	1.34
MMA + BPO + ChCl	8.8	5.4	82.0	1.65
MMA + BPO + ChLau	9.3	5.7	81.9	3.20
MMA + BPO + ChOC	9.8	6.4	76.5	1.37
MMA + BPO + ChEHC	11.5	6.6	87.7	1.90
MMA + BPO + MBBA	2.9	0.9	144.4	1.11

ChEHC increases the percent isotacticity. The results do give an indication that some of these additives have an influence on the orientation of MMA monomer, though to a small extent.

A maximum decrease of activation energy ( $E_a$ ) to 52.2 kJ/mol is shown by the additive cholesteryl acetate. Only MBBA causes an increase of  $E_a$  to 144 kJ/mol due to its radical scavenging action [7]. There is, however, no correlation between the extent of decrease in activation energy and the ability of the additive to increase the percent isotacticity of the polymer.

Molecular weights of polymers formed in the presence of all these cholesteric liquid crystals are higher, and the effect is significant in the presence of ChLau.

The decrease in conversion observed in the case of polymerization in the presence of MBBA is due to its radical scavenging ability. A similar effect of MBBA was reported by Rao [7] in the case of radiation polymerization of MMA wherein the induction period was increased with an increasing amount of MBBA.

For other additives, the observations that in the presence of these additives 1) percent conversion increases at 55°C, 2) percent conversion decreases at 65°C, and 3)  $\bar{M}_n$  increases require careful analysis.

An explanation may be offered on the basis of our earlier work [8, 9] that two of the additives, namely ChOC and ChEHC, are able to initiate the polymerization of MMA. It was further shown that monomer additive complex initiates polymerization by a radical mechanism [8].

For some of the additives used here, complex formation with monomer has been investigated through spectrophotometry and viscometry. Viscometric measurements were carried out for the monomer MMA and the additives Ch, ChCp, ChLau, ChOC, and ChCl. Figure 1 presents plots of reduced viscosity vs weight fraction of the additive for those cholesteric compounds. A minimum in these plots indicates that there is interaction between MMA and the additive.

The equilibrium constants ( $K$ ) and molar extinction coefficients ( $\epsilon_c$ ) for the complexes between MMA and the cholesteric liquid crystalline compounds Ch, ChCp, ChCl, and ChOC were determined from absorption spectra [10]. The results are given in Table 3. All the additives used form a donor-acceptor type 1:1 complex with MMA.

In the light of the complex formation of MMA with these compounds, the results may be explained as follows:



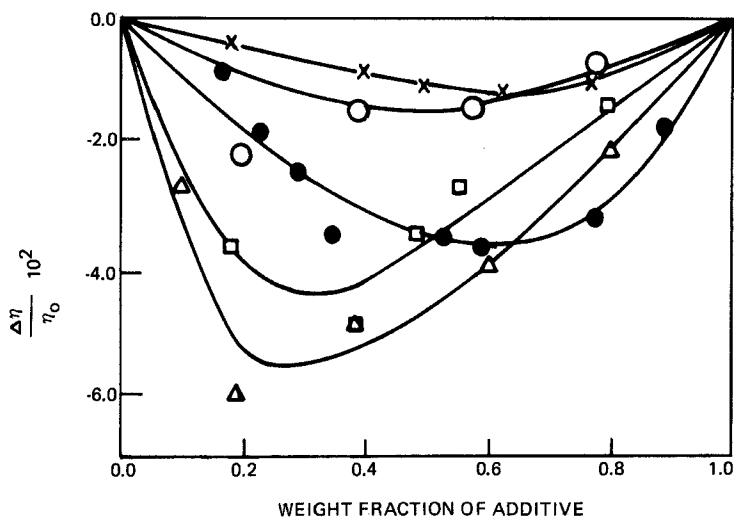


FIG. 1. Change in reduced viscosity ( $\Delta\eta/\eta_0$ ) vs weight fraction of additives at 30°C in toluene: (x) Ch, (o) ChCp, ( $\Delta$ ) ChLau, ( $\bullet$ ) ChOC, and ( $\square$ ) ChCl.

TABLE 3. Equilibrium Constants ( $K \text{ dm}^3 \text{ mol}^{-1}$  for 1:1 complex) and Molar Extinction Coefficients ( $\epsilon_c \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) for MMA with the Cholesteryl Additives

System	K	$\epsilon_c$
MMA + Ch	$15 \pm 1$	$1100 \pm 25$
+ ChCl	$6.3 \pm 0.5$	$368 \pm 10$
+ ChCp	$8.7 \pm 0.1$	$400 \pm 30$
+ ChOC	$5.3 \pm 0.5$	$445 \pm 30$





where A is additive, M is monomer, and C is the donor-acceptor complex formed. The complex C in the excited state, C\*, can combine with another monomer unit M to generate a radical CM\* for the initiation of polymerization. Simultaneously, the benzoyl peroxide initiator generates free radicals R\* for initiation.



and



It is clear that Reactions (3) and (6) are competing, and therefore the overall conversion in the presence of such an additive should increase. This is actually the case at 55°C. At higher temperatures, however, the courses of Reactions (1) and (5) are different. At higher temperatures there will be more decomposition of BPO, producing more free radicals and hence increasing the conversion. On the other hand, the equilibrium in Reaction (1) is shifted backward at high temperatures; the concentration of the complex species is diminished and consequently their effect on conversion is also diminished. Thus the increase in conversion at 55°C with a simultaneous decrease of conversions at 65°C is satisfactorily explained on the basis of complex equilibria between the monomer and the additives.

With the exception of MBBA, most of the additives cause a decrease of the energy of activation for polymerization and thus in general these additives enhance the rates of polymerization.

## CONCLUSIONS

For the radical polymerization of MMA initiated with BPO in the presence of the different additives investigated, it was observed that all of the additives affected the kinetics of polymerization, molecular weight, and/or tacticity of the resultant polymers. Donor-acceptor complexes formed between the monomer and the additives are responsible for radical initiation of the polymerization of MMA.

## ACKNOWLEDGMENT

One of us (P.A.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for a research fellowship.

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Accepted by editor August 17, 1983

Received for publication September 14, 1983