Radiation polymerization of methyl methacrylate in the presence of liquid crystals

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Radiation polymerization of methyl methacrylate (MMA) was studied in the presence of two liquid crystals: *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA, nematic) and cholesteryl 2-(ethoxy–ethoxy) ethyl carbonate (CHEECO, cholesteric). For comparison, polymerization was also carried out in the presence of benzene and cholesterol. Tacticities of the resultant poly(methyl methacrylate) were determined from nuclear magnetic resonance spectroscopy. Enhancement of syndiotacticity of the polymer obtained in the presence of cholesteric liquid crystal was observed. The rates of polymerization of pure MMA and MMA with different additives at various concentrations were studied. The viscosity-average molecular weights at one dose were also determined. Replica polymerization in the presence of preformed isotactic poly(methyl methacrylate) [i-PMMA] or syndiotactic poly(methyl methacrylate) [s-PMMA] with and without CHEECO was studied. Enhancement of syndiotacticity was observed in the presence of i-PMMA with and without CHEECO.

INTRODUCTION

Thermal polymerization of non-mesomorphic monomers in liquid crystalline solvents has been reported; these solvents influence the rates of polymerization, molecular weight and tacticity of the polymers formed[1–4]. Polymerization of systems wherein the monomer itself is a liquid crystal such as cholesteryl methacrylate[5], 4-(2-vinyloxyethoxy) benzoic acid[5] and *N*-(*p*-cyanobenzylidene)-*p*-aminostyrene[7] have also been investigated.

So far as the methacrylate systems are concerned, thermal polymerization of different methacrylates has been carried out by Tanaka *et al.*[8]. The initiator 2,2′-azobisisobutyronitrile in *N*-(4-ethoxy phenyl methylene)-4-butyl phenyl amine and cholesteryl octadeconate as nematic and cholesteric liquid crystalline solvents, respectively, and in benzene as an isotropic solvent was used. According to these authors, the polymers obtained in the cholesteric phase are more stereoregular than those prepared in the nematic phase. Moreover, the rate of polymerization (as may be seen from the percentage of conversion) is greater in the cholesteric than in the nematic phase.

In the present work, we have studied the polymerization of MMA in the presence of liquid crystals using γ-radiation as the source of initiation. The liquid crystals chosen were *N*-(*p*-methoxybenzylidene)-*p*-butyl aniline (MBBA) and cholesteryl 2-(ethoxy–ethoxy) ethyl carbonate (CHEECO) as typical nematic and cholesteric liquid crystals respectively. Their effect on tacticity, rate and molecular weight in the polymerization of MMA have been examined. For reference purposes, polymerization was also carried out in the presence of benzene and of cholesterol. In addition the effect of CHEECO in the polymerization (replica type) of MMA in the presence of iso-PMMA (i-PMMA) or syndio-PMMA (s-PMMA) has been investigated.

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EXPERIMENTAL

Materials

MMA reagent grade (Fluka), containing stabilizer, was purified by washing with 10% sodium hydroxide; it was dried over anhydrous sodium sulphate after repeated washings with distilled water. Further purification was carried out by fractional distillation retaining middle fractions for use.

Cholesterol obtained from J. T. Baker and Co. was recrystallized in methanol and dried *in vacuo*. Liquid crystals MBBA and CHEECO supplied by the Aldrich Chemical Company were used as received. Samples of i-PMMA and s-PMMA obtained from Dr E. Roerdink, The Netherlands were used. Reagent grade benzene, chloroform, petroleum ether and methanol were purified and dried by standard methods[9].

Radiation source

A 1970 Ci ^{60}Co gamma chamber-900 supplied by Bhabha Atomic Research Centre, Trombay was used. The dose rate as measured by Fricke Dosimeter[10] was found to be 0.29 ± 0.02 Mrads/h.

Polymerization procedure

Polymerization was carried out under a nitrogen atmosphere in a double-walled glass reaction vessel, with circulating water in the outer jacket from a thermostat. After polymerization, the polymer was precipitated in excess methanol and separated. The percentage conversion of monomer was estimated gravimetrically after reprecipitation and drying to constant weight under vacuum. Since replica polymerization led to a rigid mass, the latter was first dissolved in chloro-

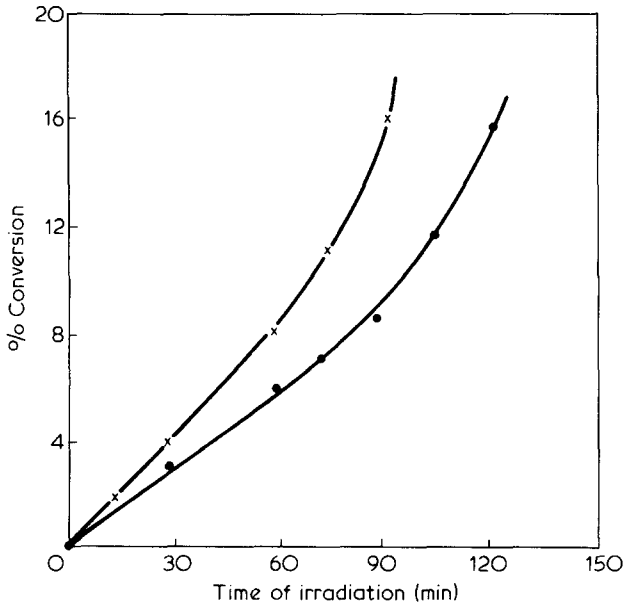

Figure 1 Percentage conversions of monomer vs. time of irradiation at 30°C: ●, MMA; and x, in the presence of 0.025 M cholesterol

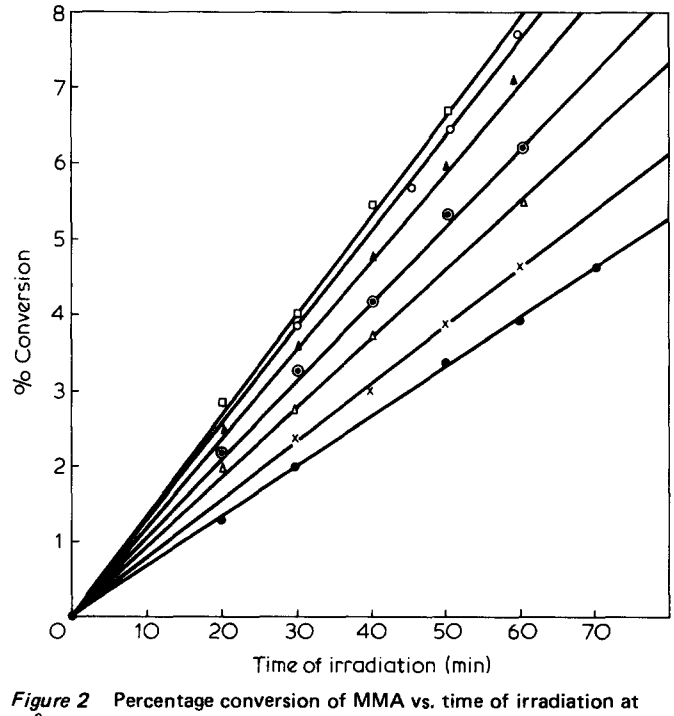

Figure 2 Percentage conversion of MMA vs. time of irradiation at 30°C in the presence of benzene concentrations of ●, 4M; x, 3 M; △, 1 M; ⊙, 0 M and with cholesterol concentrations ▲, 0.139 M; ○, 0.085 M and □, 0.025 M

form and the polymer was precipitated in petroleum ether, and finally separated and weighed after drying.

As the quantities of the liquid crystals available were limited, the maximum concentration used was 1 M in MMA. In the case of cholesterol, its low solubility in MMA was another limiting factor. It was observed that the mixture of liquid crystal and monomer, and also the mixture containing the polymer after irradiation, were homogeneous. However, in the case of replica polymerization the contents were homogeneous before irradiation, but became a rigid mass after irradiation.

Characterization of polymers

Average molecular weights ($\bar{M}_v$) were determined from the intrinsic viscosities measured at 30° ± 0.05°C in benzene; chloroform was used for samples obtained by replica polymerization. Infra-red (i.r.) spectra of polymers were recorded in benzene on a Perkin–Elmer 237-B spectrophotometer. The tacticity of PMMA samples were measured from ^{1}H n.m.r. spectra[11] obtained in $CDCl_3$ using a XL-100 spectrometer.

RESULTS AND DISCUSSION

Radiation polymerization of MMA at a constant dose rate at 30°C with and without cholesterol was carried out and a plot of percentage of conversion *versus* time of irradiation (*Figure 1*) indicates that the percentage conversion is not linear with time of irradiation for conversions exceeding about 6–8%. Hence the rates of polymerization of MMA and the rate in the presence of benzene, cholesterol, MBBA and CHEECO at various concentrations were determined from the initial linear portions in *Figures 2* to *4*. The polymerization in the presence of MBBA was accompanied by an induction period; however, the rates with low concentrations of MBBA were evaluated from the slopes of the plots shown in *Figure 3*. For the other concentration (1 M) it was calculated from a single measurement. The rates of polymerization obtained with different additives and the molecular weights of the polymers are tabulated in *Table 1*. There is a remarkable decrease in the rates with an increase in the concentration of MBBA. This does not occur with benzene or with cholesterol. The exact effect of nematic liquid crystal MBBA is not known but it is likely to act as an inhibitor. On the other hand, with increasing concentration of CHEECO rates increase at both 12.5° and 30°C. With increasing concentrations of the additives, the viscosity-average molecular weights of the polymers obtained decrease in the case of benzene and MBBA and increase in case of CHEECO, while the observed decrease in the case of cholesterol is marginal. I.r. spectra of all the PMMA

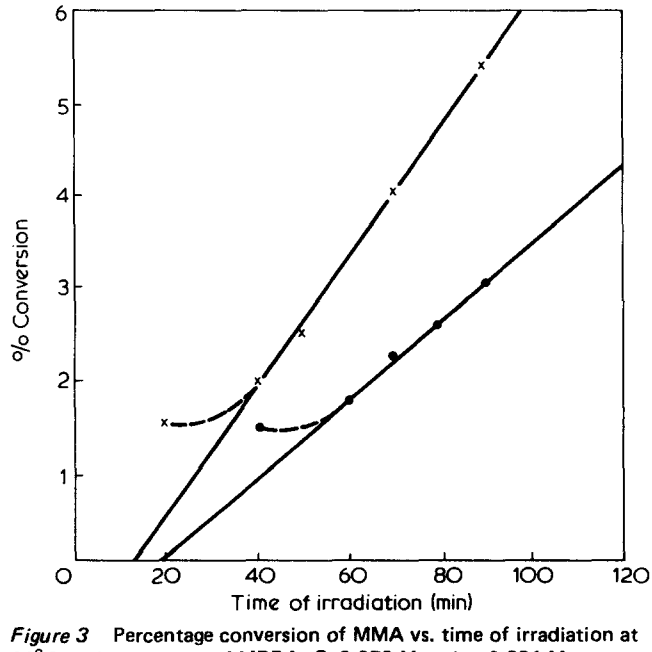

Figure 3 Percentage conversion of MMA vs. time of irradiation at 30°C in the presence of MBBA: ●, 0.059 M and x, 0.031 M

obtained with different additives are compared with standard spectra of iso- and syndiotactic PMMA. The characteristic[12] bands of syndiotactic PMMA in the region 1450 and 1275 cm^{-1} with splitting are observed, suggesting that all the samples of PMMA are syndiotactic in nature. N.m.r. results have been utilized for quantitative estimation of tacticities. *Figure 5* shows the integrated intensities of the peaks at 8.78, 8.98 and 9.08 ppm are used to calculate the population of (*mm*), (*mr*) and (*rr*) triads where *m* and *r* represent meso and racemic addition, respectively[11,13]. The stereoregularity of the polymers may be discussed in terms of probability, P_m, of producing a meso sequence when a new monomer is added at the end of the growing chain. The frequencies of isotactic, heterotactic and syndiotactic triads are related to P_m through:

$$(mm) = P_m^2 \quad (1)$$

$$(mr) = 2P_m(1 - P_m) \quad (2)$$

$$(rr) = (1 - P_m)^2 \quad (3)$$

The probabilities calculated from (*mm*), (*mr*) and (*rr*) are shown in *Table 2*. A unique value of P_m is not obtained for any of the samples, suggesting that the polymerization is not Bernoullian. The same conclusion is obtained from (*m*) and (*r*) calculated from the following equations:

$$(mm) = P_m^2 = (m)^2 \quad (4)$$

$$(rr) = (1 - P_m)^2 = (r)^2 \quad (5)$$

It was therefore necessary to use first order Markov equations in which the stereochemistry of the growing chain end is considered. The independent probabilities[14] $P_{m/r}$ and $P_{r/m}$ are calculated from equations (6) and (7), respectively:

$$P_{m/r} = (mr)/[2(mm) + (mr)] \quad (6)$$

$$P_{r/m} = (mr)/[2(rr) + (mr)] \quad (7)$$

Table 2 shows that for all the samples $P_{m/r}$ is greater than 0.5 and $P_{r/m}$ is less than 0.5 indicating predominant syndiotactic growth. However, the polymers obtained with CHEECO show a higher percentage of syndiotacticity than those with MBBA or benzene as additive. In this connection

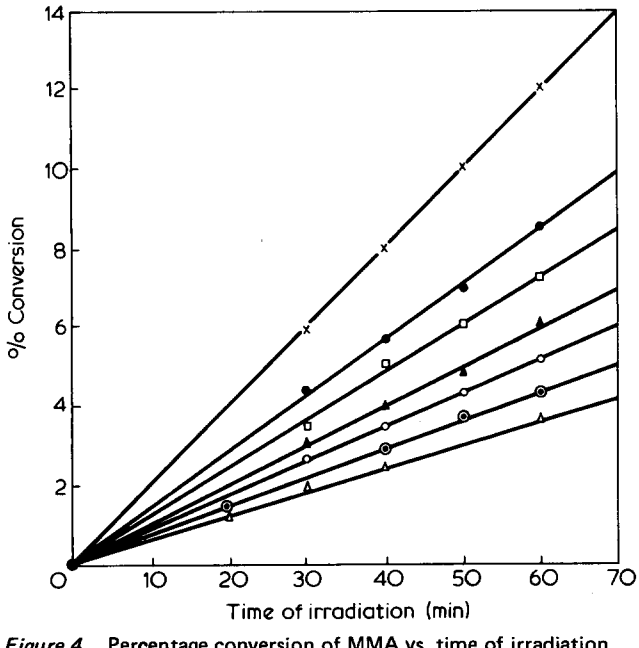

Figure 4 Percentage conversion of MMA vs. time of irradiation with various concentrations of CHEECO at (i) 12.5°C: △, 0.06 M; ⊙, pure MMA; ○, 0.48 M; ▲, 0.89 M; (ii) 30°C: □, 0.05 M; ●, 0.49 M and x, 1.01 M

Table 1 Effect of additives on rates and viscosity-average molecular weight ($\bar{M}_v$) in the radiation polymeization of MMA

Additive	Molal conc. (M)	Temperature (°C)	Rate of polymerization mol l^{-1} s^{-1} x 10^4	$\bar{M}_v$ x 10^{-5} *
–	–	12.5	1.119	1.622
–	–	30.0	1.610	2.529
Benzene	1.0	30.0	1.438	2.239
	3.0	30.0	1.194	1.435
	4.0	30.0	1.043	1.324
Cholesterol	0.025	30.0	2.039	2.483
	0.085	30.0	1.992	2.366
	0.139	30.0	1.840	2.158
MBBA	0.031	30.0	1.075	2.239
	0.059	30.0	0.794	2.158
	1.010	30.0	0.194	1.914
CHEECO	0.063	12.5	0.966	0.859
	0.480	12.5	1.334	1.189
	0.890	12.5	1.856	1.422
CHEECO	0.05	30.0	1.521	1.845
	0.49	30.0	2.239	1.945
	1.01	30.0	3.065	2.080

* Molecular weights were determined for the polymers obtained by irradiation for 60 min in the presence of all the additives except MBBA; polymers obtained with MBBA by irradiation for 120 min were used for molecular weight determination

Table 2 Fraction of isotactic, heterotactic and syndiotactic triads obtained with different additives, and the corresponding probabilities

Sample No.	Additive	Temperature (°)	Molal conc. (M)	(*mm*)	(*mr*)	(*rr*)	(*m*)	(*r*)	P_m (*mm*)	P_m (*mr*)	P_m (*rr*)	$P_{m/r}$	$P_{r/m}$
1	–	12.5	–	0.03	0.39	0.58	0.17	0.76	0.17	0.26	0.24	0.870	0.252
2	–	30.0	–	0.02	0.40	0.58	0.14	0.76	0.14	0.26	0.24	0.909	0.256
3	Benzene	30.0	3.00	0.11	0.32	0.57	0.33	0.75	0.33	0.20	0.25	0.593	0.219
4	Cholesterol	30.0	0.139	0.02	0.39	0.59	0.14	0.77	0.14	0.26	0.23	0.907	0.248
5	MBBA	30.0	1.01	0.02	0.36	0.62	0.14	0.79	0.14	0.23	0.21	0.900	0.225
6	CHEECO	30.0	1.01	0.02	0.36	0.62	0.14	0.79	0.14	0.23	0.21	0.900	0.225
7	CHEECO	12.5	0.89	0.06	0.27	0.67	0.24	0.82	0.24	0.16	0.18	0.692	0.168

it may be noted that Tanaka *et al.*[8] with different liquid crystals as solvents (10% w/w of monomer) observed marginally small changes in tacticity in the thermal polymerization of MMA. In our irradiation experiments we have used MBBA and CHEECO as additives (i.e. the amount of monomer was always higher than that of liquid crystals) and found that the changes in tacticity are much higher than those observed by those authors. Moreover, it may be noted that enhanced syndiotacticity has been observed in spite of the fact that the systems are not likely to be mesomorphic.

The definite mechanism of increase in tacticity in the presence of small amounts of liquid crystals is yet to be established. One of the possible explanations might involve the formation of a complex between the monomer and the liquid crystal molecule leading to regular addition to the growing chain. It is also likely that the low temperatures used in this work help to minimize the random, thermal motion of the growing chain. Hence, small concentrations of liquid crystals are sufficient to cause increased tacticities.

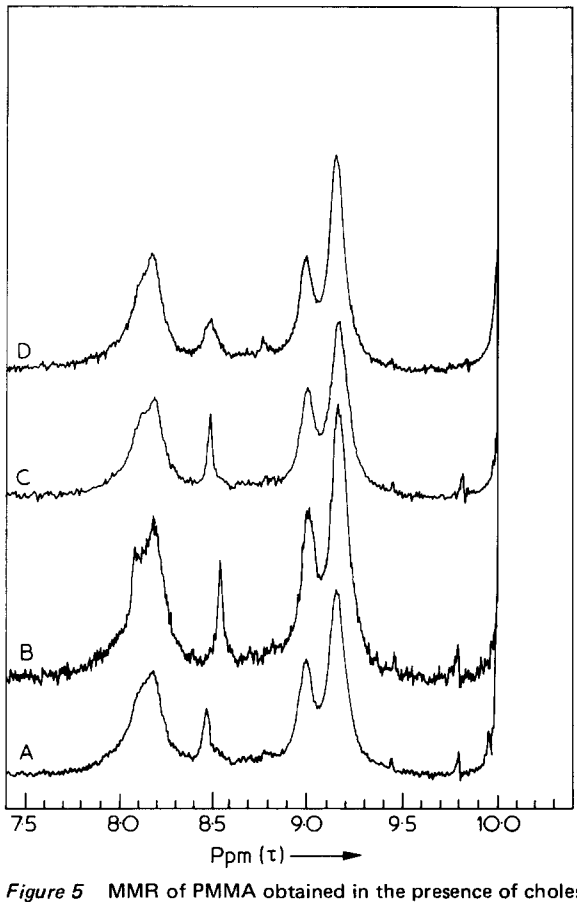

Figure 5 MMR of PMMA obtained in the presence of cholesterol: A, 0 M; B, 0.118 M; C, 1.01 M MBBA; D, 0.89 M CHEECO

The effect of CHEECO on the replica polymerization of MMA in the presence of preformed i-PMMA or s-PMMA at 12.5°C was studied at two doses. *Table 3* shows the influence of replica polymerization conditions on the yields, viscosity-average molecular weights and tacticities, with and without CHEECO. An increase in yield and molecular weight is observed in this replica polymerization with the cholesteric liquid crystal. In the presence of i-PMMA the polymerization proceeds as a replica polymerization[15] yielding s-PMMA at both doses, whereas no significant effect of s-PMMA is observed during irradiation for 30 min. This effect has been explained by Challa *et al.*[16] on the basis of weak interactions between s-PMMA and i-PMMA. But at higher doses (irradiation for 60 min) the formation of s-PMMA is increased. Introducing s-PMMA might produce small amounts of i-PMMA initially and this would further interact to produce s-PMMA. *Table 3* also shows that polymerizations carried out with cholesteric liquid crystal in the presence of i-PMMA at both doses yield marginally higher percentages of s-PMMA. In the presence of s-PMMA for a dose of 30 min duration, the syndiotacticity of PMMA formed is only 49% and increases to 60% in the presence of CHEECO. At higher doses, CHEECO again causes only a slight improvement in syndiotacticity. As the percentage of s-PMMA produced either in the presence of CHEECO or i-PMMA or both is almost the same, the effect of CHEECO may be parallel to that of i-PMMA.

In summary, the polymers obtained at low conversions in the presence of cholesteric liquid crystal are more syndiotactic than those prepared in the presence of nematic liquid crystal, the latter being more syndiotactic than those obtained with benzene or cholesterol. The same percentage of syndiotacticity may be achieved either by addition of CHEECO or preformed i-PMMA. Finally, the rates of polymerization and the molecular weights increase with increasing cholesteric liquid crystal concentration, while the rates and molecular weights decrease with increasing concentration MBBA, benzene or cholesterol concentrations.

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Table 3 Polymerizations with and without CHEECO at 12.5°C in the presence of 1% preformed i-PMMA ($\bar{M}_v$ = 1.1 x 10^6) or s-PMMA ($\bar{M}_v$ = 5.0 x 10^5)

Sample No.	Added polymer	Molal conc. CHEECO (M)	Time of irradiation (min)	Monomer conversion (%)	$\bar{M}_v \times 10^{-5}$	(*mm*)*	(*mr*)*	(*rr*)*
1	i-PMMA	–	30	1.8	–	0.02	0.33	0.65
2	i-PMMA	0.95	30	3.6	–	0.09	0.24	0.67
3	i-PMMA	–	60	4.5	3.631	0.05	0.29	0.66
4	i-PMMA	0.95	60	8.7	9.247	0.02	0.26	0.72
5	s-PMMA	–	30	0.8	–	0.06	0.45	0.49
6	s-PMMA	0.97	30	3.0	–	0.06	0.34	0.60
7	s-PMMA	–	60	4.1	2.904	0.02	0.33	0.65
8	s-PMMA	0.97	60	9.1	10.470	0.02	0.29	0.69

* Corrected values for polymers formed from n.m.r. spectra

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