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Synthesis of poly(mesogenic methacrylate)s with narrow molecular-weight distributions and their thermal properties

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The photopolymerization of various mesogenic methacrylates (MEMs) by using an aluminium porphyrin complex (MTPP) as a photocatalyst has been investigated to show that the resulting polymers are 'living' in nature. The polymerization of 6-[4-(4-cyanophenylazo)phenoxy]hexyl methacrylate (MAC) was exceptionally slow when compared to other mesogenic methacrylates, such as those containing ester and/or cyano groups in their mesogens. Interference of the light absorption of MTPP and/or the active propagating chain end by the MAC itself has been considered as being one possible reason for its slow polymerization, as a result of electron spectroscopy studies. Addition of methylaluminium bis(2,4-di-t-butylphenolate) greatly accelerated the polymerization of MEMs initiated with MTPP, as was also observed in the case of methyl methacrylate (MMA), with the exception of MAC, to yield polymers with very narrow molecular-weight distributions. Copolymerization of various MEMs with MMA revealed that both types of monomer are similar in their copolymerization reactivities. Poly(MEM)s formed with MTPP were found to have a higher content of syndiotactic triads than those obtained with a radical initiator. The phase transition behaviour of the polymers that were obtained was studied by focusing on polymers derived from 6{4-[4-(methoxyphenoxy)carbonyl]phenoxy}hexyl methacrylate (MPM). This was because anionically obtained poly(MPM)s with higher contents of syndiotactic triads were reported to show different thermal behaviour from those poly(MPM)s formed via a radical mechanism. It appeared that poly(MPM)s obtained with MTPP have identical thermal properties to the latter but not to the former. The reason for such a discrepancy is not clear at the present time.

(Keywords: living polymerization; aluminium porphyrin complex; mesogenic methacrylate)

INTRODUCTION

The achievement of living polymerization is one of the most important targets for polymer chemists, since it allows them to obtain polymers with narrow molecular-weight distributions (*MWD*s) and controlled molecular weights. Furthermore, it opens up new synthetic routes for producing polymers with unique structures, such as block copolymers and end-functionalized polymers. For this reason, the living processes which have been developed so far have been applied to the polymerization of various mesogenic monomers to prove that some of these can be polymerized via a living mechanism[1–7]. Cases where the molecular weight and its distribution, together with tacticity, influence the liquid crystalline (LC) properties of the polymers obtained have also been found[1,7]. Our studies on the polymerization of mesogenic methacrylates such as 6-{4-[4-(butoxyphenoxy)carbonyl]phenoxy}hexyl methacrylate (MOB) and 6-{4-[4-(cyanophenoxy)carbonyl]phenoxy}hexyl methacrylate (MCB), using (5,10,15,20-tetraphenylporphinato) aluminium methyl (MTPP) have been undertaken as investigations along this line[5,6], since MTPP has been reported as being an effective photocatalyst for the living polymerization of methyl methacrylate (MMA)[8]. The synthesis of block copolymers with a LC polymeric chain as one component was also successfully achieved[9]. Anionic polymerizations initiated with 3-methyl-1,1-diphenylpentyllithium (DPPL) have also been proved to proceed in a living manner[7] and to be applicable to the synthesis of block copolymers with a LC polymeric chain forming one of the components[10]. These block copolymers showed mesogenic behaviour and were suggested as having structures with microphase separation[9,10]. However, the number and variety of the mesogenic methacrylates which can be polymerized via a living mechanism are still limited. In addition, the living nature of the group-transfer polymerization of mesogenic methacrylates has been shown to be influenced by the functional groups present in their mesogens[4]. Considering the fact that many side-chain LC polymers have been synthesized from mesogenic methacrylates[11], it is important to enlarge the range and variety of the monomers which can be polymerized through a living mechanism process.

Based on these considerations, the polymerization

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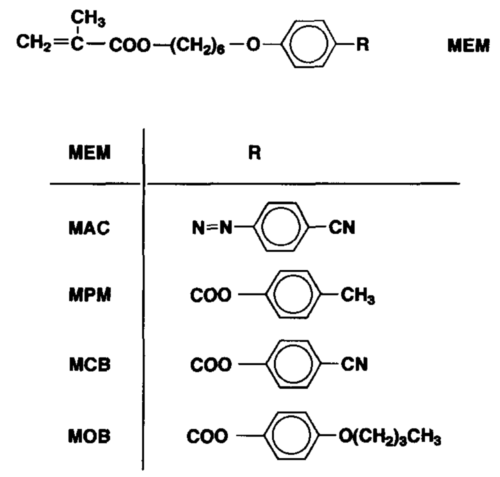

Scheme 1

behaviour of the mesogenic methacrylates (MEMs) shown in *Scheme 1*, and the thermal properties of the corresponding polymers that were obtained, have been investigated by focusing on the following three points. First, the applicability of MTPP to the living polymerization of 6-[4-(4-cyanophenylazo)phenoxy]hexyl methacrylate (MAC), i.e. the synthesis of poly(MAC) with a narrow *MWD*, has been investigated. Secondly, in order to get a comprehensive understanding of the reactivities of MEMs, their copolymerization tendencies and the effect of methylaluminium bis(2,4-di-t-butylphenolate) (ALC) on their polymerization with MTPP were investigated. Various polymerization reactions in the presence of ALC were undertaken, since addition of the latter to the polymerization system of MMA initiated with MTPP greatly accelerates the rate of polymerization[12]. Finally, the thermal properties of the LC polymers that were obtained have been studied. The phase transition behaviour of polymers derived from 6-{4-[4-(methoxyphenoxy)carbonyl]phenoxy}hexyl methacrylate (MPM) has been the centre of our interest. This is because the molecular weight and its distribution, plus the tacticity of the polymer, have been reported to strongly influence the thermal properties of poly(MPM)s[10,13].

EXPERIMENTAL

Materials

The mesogenic methacrylates, MAC[14], MPM[15,16], MCB[17], and MOB[18] were synthesized according to previously reported procedures. Methyl methacrylate and solvents were purified by the usual methods. Trimethyl aluminium solution in hexane (Tokyo Kasei Co., Ltd), 5,10,14,20-tetraphenyl-21*H*,23*H*-porphyrin (TPP, containing <0.1% corresponding chlorin, Aldrich Chemical Co., Ltd), and 2,4-di-t-butylphenol (Tokyo Kasei Co., Ltd) were used as received. ALC was prepared by the reaction of TPP and 2 equivalents of 2,4-di-t-butylphenol in CH_2Cl_2 under dry nitrogen and was then used without any further purification[19]. Commercial azobisisobutyronitrile (AIBN) was recrystallized from ethyl alcohol.

Polymerization

The preparations of MTPP and the various polymerization mixtures are essentially the same as those reported for MMA[8]. In the cases where polymerization was carried out for a longer period of time, the polymerization ampoules which contained given amounts of reagents and a solvent were sealed off after several freeze–pump–thaw cycles. Photoirradiation was carried out throughout the polymerization process by using a 2 kW Xenon arc lamp from a distance of 25 cm through a Toshiba V-Y 46 colour glass filter at room temperature. After photoirradiation for a given amount of time, an excess of methyl alcohol was added, and the volatile materials were removed under reduced pressure. The solid residue that was obtained was dissolved in methylene chloride and then precipitated into methyl alcohol. In order to observe the effect of ALC on the polymerization with MTPP, the polymerization mixture was photoirradiated for 1 h and an ALC solution, prepared as described above, which contained 3 equivalents of ALC with respect to MTPP, was added at room temperature to the polymerization mixture under diffused light conditions. Radical polymerization was carried out in benzene solution. Given amounts of monomer, solvent, and AIBN were placed in glass ampoules, which were subjected to several

Table 1 Polymerization of MEMs in the presence of MTPP[a]

No.	Monomer	$[M]_0$ (mmol)	$[I]_0$ (mol%)	Time (h)	$M_n \times 10^{-3}$ Obsd	Calcd	M_w/M_n	Conversion (%)
1	MAC	2.6	3.3	48	7.5	8.3	1.12	70
2	MAC	2.6	3.3	70	8.6	10.8	1.20	91
3	MPM	2.4	3.6	5	4.6	6.3	1.25	55
4	MPM	2.4	3.6	10	8.5	8.7	1.31	76
5[b]	MOB	2.2	3.9	10	8.5	10.7	1.13	92
6[c]	MCB	2.2	3.9	10	8.5	9.1	1.14	86
7[d]	MAC	1.1	2.0	36	13.6	–	1.63	71
8[d]	MPM	1.1	2.0	36	33.5		3.65	91
9[b,d]	MOB	1.1	2.0	36	44.0		2.94	86
10[c,d]	MCB	1.1	2.0	36	14.2		1.65	95

[a] Carried out at room temperature using 6.5 ml of CH_2Cl_2 as solvent

[b] Results taken from ref. 5

[c] Results taken from ref. 6

[d] Radical polymerization at 60°C initiated with AIBN, using 6 ml of benzene as solvent

freeze–pump–thaw cycles and then sealed. After polymerization in a constant-temperature bath, the polymers were isolated by pouring into methyl alcohol. The copolymerization reactions were carried out using the same experimental procedures as those described for homopolymerizations.

Measurements

^{1}H (270 MHz) nuclear magnetic resonance (n.m.r.) spectra were obtained in $CDCl_3$, with tetramethylsilane as an internal standard, using a JEOL GX-270 FT NMR spectrometer. The differential scanning calorimetry (d.s.c.) measurements were performed with a Rigaku DSC-8230B instrument. In all cases the heating rate was $10^{\circ}C\,min^{-1}$. The d.s.c. curves were recorded during the second heating scan after first heating above the isotropization temperature and then cooling below $-20^{\circ}C$. Gel permeation chromatography (g.p.c.) was performed on a JASCO TRI ROTAR-II using THF as the eluent. The column set consisted of a Shodex KF-802.5 and two A-80M columns. A molecular-weight calibration curve was obtained by using polystyrene standards. Electronic spectra were recorded by a Hitachi U3200 spectrophotometer.

RESULTS AND DISCUSSION

Homopolymerization of mesogenic methacrylates

The results of the polymerization of a number of mesogenic monomers in the presence of MTPP are given in *Table 1*, together with those of the equivalent radical polymerizations. The results previously reported for MOB[5] and MCB[6] are given for comparison. The g.p.c. profiles of poly(MAC) and poly(MPM) obtained with MTPP are illustrated in *Figure 1*. A narrow *MWD* can be recognized (ratio of weight-average to number-average molecular weight (M_w/M_n) $\leqslant 1.31$). Furthermore, the M_n values of the polymer are in good agreement with the calculated values, assuming that at the beginning all MTPP molecules form active species. Molecular weights and their corresponding distributions which have been determined from g.p.c. profiles calibrated against polystyrene standards do not represent true values. However, the M_n values of poly(MPM)s[7] and the polymers derived from 4-[4-(4-methoxyphenylazo)phenoxy]butyl methacrylate[10] determined by membrane osmosis have been reported to be in fairly good agreement with those obtained from g.p.c. measurements (calibrated against polystyrene standards). This allows us to assume that the M_n values of poly(MEM)s which have been obtained from g.p.c. measurements are not that much different from their true values, since the polymers derived from these mesogenic methacrylates all have similar structures. Accordingly, it can be said that those methacrylates with azo and cyano groups in the mesogen, in addition to those with ester groups, can be polymerized via a living mechanism by using MTPP.

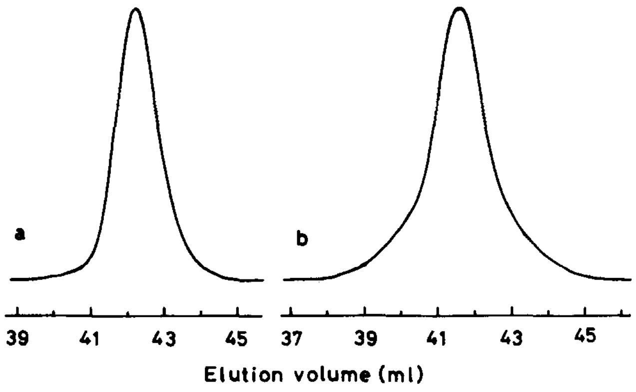

Figure 1 G.p.c. traces of: (a) poly(MAC) (No. 1 in *Table 1*); (b) poly(MPM) (No. 4 in *Table 1*)

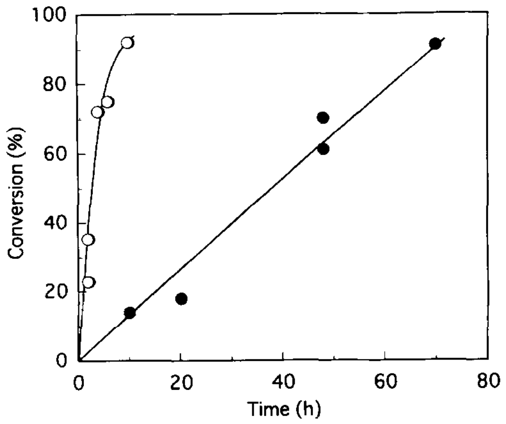

Figure 2 Time–conversion diagrams for the polymerization of MAC (●) and MOB (○) with MTPP (see *Table 1* for polymerization conditions); the results obtained for MOB reported in ref. 5 were utilized for the plot

Polymerization of MAC with MTPP

Since the results given in *Table 1* suggest that the polymerization of MAC initiated with MTPP proceeds much more slowly when compared to the other mesogenic methacrylates investigated so far, its polymerization behaviour was studied in detail. A time–conversion curve obtained for the polymerization of MAC is illustrated in *Figure 2*. The previously reported results obtained for the polymerization of MOB[5] are also shown for comparison purposes. The lower polymerizability of MAC can be clearly noticed. However, polymer yield increases with time, eventually attaining a conversion of more than 90%. The relationship between M_n and conversion obtained from the polymerization of MAC is illustrated in *Figure 3*. The M_n of the polymer is directly proportional to the monomer conversion, with the value being in reasonably good agreement with that calculated. Furthermore, the *MWD* of the polymer remains narrow throughout the polymerization. Therefore, the polymerization of MAC with MTPP is considered to proceed via a living mechanism process.

Electronic spectra of MAC, MOB and ETPP

The electronic spectra of MAC, MOB and (5,10,15,20-tetraphenylporphinato)aluminium ethyl (ETPP) are compared in *Figure 4*. The spectrum of MAC (curve b) was measured for the same concentration as that of the polymerization mixture. The spectra of MAC and ETPP show clearly that light absorption by MAC interferes with that of the aluminium porphyrin complex. ETPP was adopted for comparison instead of MTPP, although the latter was used in this polymerization system. This is

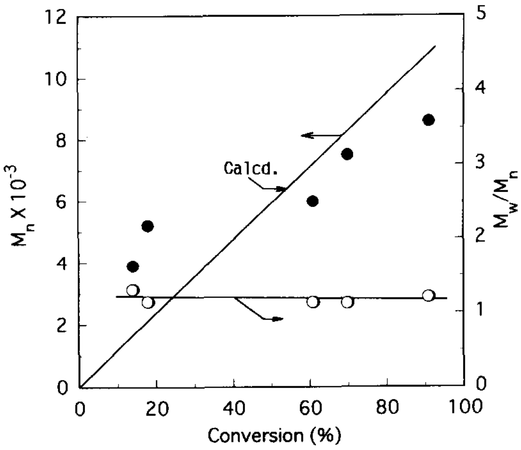

Figure 3 Dependence of number-average molecular weight M_n and ratio of weight- to number-average molecular weights M_w/M_n of poly(MAC) on conversion (see *Table 1* for polymerization conditions)

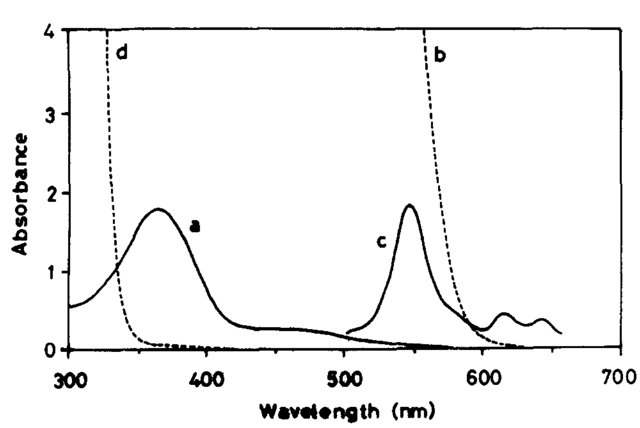

Figure 4 Electronic spectra measured in CH_2Cl_2: (a) MAC, 6.4×10^{-5} M; (b) MAC, 0.4 M; (c) ETPP (taken from ref. 20, with the ordinate of this spectrum presented in arbitrary units); (d) MOB, 0.4 M

Table 2 Effect of MTPP concentration on the polymerization of MOB[a]

No.	$[I]_0$ (mol%)	Time (h)	Conversion (%)	$M_n \times 10^{-3}$ Obsd	$M_n \times 10^{-3}$ Calcd	M_w/M_n
1	3.9	10	92	8.5	10.7	1.14
2	2.0	20	41	9.2	9.3	1.14
3	2.0	40	74	13.3	16.7	1.18

[a] Polymerization conditions are the same as those described in *Table 1*

because the spectrum of ETPP has already been reported[20] and no essential differences between the spectra of MTPP and ETPP are considered to exist. The spectrum of MOB measured at the same concentration as that of the polymerization mixture shows that MOB does not interfere with light absorption by the aluminium porphyrin complex. In accordance with this fact, the polymerization of MOB proceeds much more rapidly than that of MAC (see *Figure 2*). Photoirradiation was carried out throughout the polymerization processes of the various MEMs, since visible light is effective not only for the initiation step but also for the propagation stage in the polymerization of MMA, although photoexcitation is essential for the former, but not for the latter[8]. Thus, these spectroscopic studies suggest that interference of the light absorption of the MTPP and/or the active propagating chain end by the MAC itself is one possible reason for its lower polymerizability. The polymerization behaviour of MAC and other MEMs suggests that the role of visible light in the propagation step of mesogenic methacrylates might be much more significant than in MMA. However, the influence of the azo group on MTPP and/or the active propagating chain end, which decreases their activities through some interaction which is unknown at present, cannot be ruled out. Further details of the mechanism for this slow polymerization remain for future studies.

Effect of ALC on the polymerization with MTPP

The effect of the concentration of MTPP on the polymerization of MOB in the presence of the former is given in *Table 2*. The results obtained using lower concentrations of MTPP suggest the difficulty in obtaining poly(MOB) with a higher molecular weight and a narrow *MWD*. For this reason, polymerization of MEM using the MTPP–ALC system was carried out. This initiator system has been reported to give an extremely rapid polymerization of MMA, leading to the formation of poly(MMA) with a higher molecular weight and a narrow *MWD*[12]. The results obtained (*Table 3*) indicate that this initiator system also allows us to control the molecular weights and their distributions in the polymerization of the various MEMs, with the exception of MAC.

In the case of MAC, the presence of ALC accelerates the polymerization process, but it stops without attaining a higher conversion. Furthermore, the M_n of the polymer that is obtained is different from the calculated value and its *MWD* is broad.

Copolymerization of MMA with MEM

The copolymerization behaviours of MMA with MAC and MOB, in the presence of MTPP, are summarized in *Table 4*. The formation of tapered block copolymers was expected from these copolymerizations, particularly in the case of MAC, since the latter has an extremely different polymerization tendency to that of MMA. However, it can be reasonably concluded that random copolymers are formed and that the copolymerizability of both of the mesogenic methacrylates is comparable to that of MMA, since the copolymer compositions obtained are almost the same as those of the monomer mixtures in the feed, even for those copolymers formed with lower conversions (Nos 1 and 3 in *Table 4*). This copolymerization behaviour of MAC is not contradictory to the above mentioned suggestion that its slower polymerization is due to interference of the light absorption of MTPP and/or the active propagating chain end by the MAC itself.

Phase transitions

Typical d.s.c profiles of poly(MPM)s are illustrated in *Figure 5*. The characteristic features of their phase transitions are summarized in *Table 5*, along with their fundamental properties. Tacticities were determined based on the ^1H n.m.r. signals of methyl groups attached to the backbone chains, as in the case of poly(MCB)[6], since they are well separated from other signals. The

Table 3 Polymerization of MEMs using the MTPP–ALC system

			Photopolymerization[a]		Dark[b]			
					$M_n \times 10^{-4}$			
No.	Monomer	$[\mathrm{MTPP}]_0$ (mol%)	M_n	M_w/M_n	Obsd	Calcd	M_w/M_n	Conversion (%)
1	MOB	3.9	3800	1.25	1.26	1.08	1.31	93
2	MOB	2.0	2400	1.36	2.88	2.09	1.17	92
3[c]	MOB	0.9	–	–	6.65	4.04	1.46	80
4[c]	MPM	3.5	–	–	1.20	1.11	1.43	95
5[c]	MCB	3.9	–	–	1.36	0.92	1.27	89
6[c]	MAC	3.3	–	–	2.43	0.47	1.71	39

[a] Polymerized for 1 h under the conditions described in *Table 1*

[b] After photopolymerization was carried out for 1 h, 3 equivalents of ALC in 1 ml of CH_2Cl_2 (with respect to MTPP) was added and the polymerization system was stood for 15 min under diffused light

[c] Molecular weights and distributions were not measured before the addition of ALC

Table 4 Copolymerization of MMA (M_1) with MEM (M_2), initiated with MTPP

				$M_n \times 10^{-4}$				
No.	M_2	$[\mathrm{I}]_0$ (mol%)	Time (h)	Obsd	Calcd	M_n/M_w	Conversion (%)	$[M_1]/[M_2]$
1[a]	MAC	3.6	1	0.46	0.13	1.18	10	4.1
2[a]	MAC	3.6	70	1.05	1.26	1.35	95	4.1
3[b]	MOB	3.6	1	0.58	0.37	1.21	25	4.9
4[b]	MOB	1.8	17	2.62	2.73	1.12	90	4.5

[a] $[M_1]_0/[M_2]_0 = 3.7$; initial amounts of MMA and MAC are 4.8 and 1.3 mmol, respectively

[b] $[M_1]_0/[M_2]_0 = 4.3$; initial amounts of MMA and MOB are 4.8 and 1.12 mmol, respectively

results reported so far are also listed in *Table 5*. It can be seen that the poly(MPM)s obtained by using MTPP and DPPL (Nos 1–5 in *Table 5*) have a common structural characteristic, i.e. a higher content of syndiotactic triads when compared to those obtained via a radical mechanism (Nos 6–9 in *Table 5*). However, they show substantial differences in their phase transition behaviour, despite the structural similarity. The poly(MPM)s obtained with MTPP have a rather similar thermal behaviour to those formed through a radical mechanism process. Poly(MPM)s with higher molecular weights and broader *MWD*s obtained by a radical initiator have only one endotherm at around 112°C (No. 9 in *Table 5*), which is due to the transition from a nematic to an isotropic phase[7,21]. The poly(MPM) obtained by us when using AIBN also showed essentially identical thermal behaviour (see *Figure 5* (curve c) and No. 6 in *Table 5*). Heterotactic poly(MPM)s with lower molecular weights have been reported to show two endotherms (Nos 7 and 8 in *Table 5*). Lower and higher endotherms were attributed to the transitions from a smectic A to a nematic phase and from a nematic to an isotropic phase, respectively. With increasing molecular weight, these endotherms moved to higher temperatures and the intensity of the lower endotherm decreased. Finally, the profile changed to one with a higher molecular weight and a broader *MWD* (No. 9 in *Table 5*). These characteristic features can also be seen in the polymers obtained when using MTPP and MTPP–ALC (see *Figure 5* (curves a and b) and Nos 1 and 3 in *Table 5*, respectively). However, in this case, the intensity of the lower endotherm of the poly(MPM) with the lower molecular weight (*Figure 5* (curve a) and No. 1 in *Table 5*) is not so strong as that observed for the polymer with a comparable molecular weight obtained when using AIBN (No. 7 in *Table 5*), while the LC phase below the endotherm has not yet been identified. For this reason, it is tentatively termed as an S_X phase.

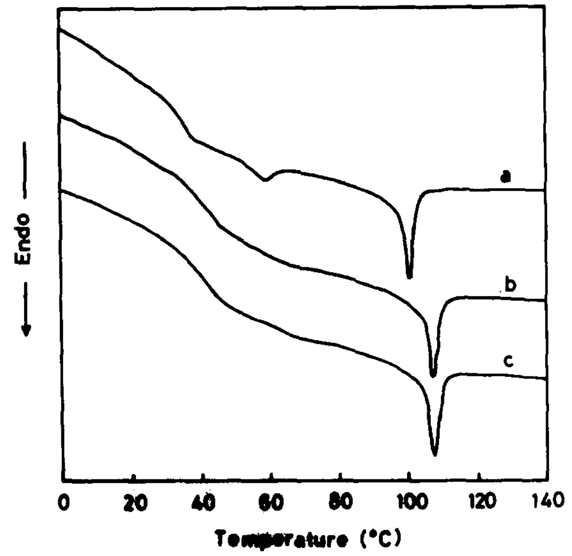

Figure 5 D.s.c. curves of poly(MPM)s: (a) No. 1 in *Table 5*; (b) No. 3 in *Table 5*; (c) No. 6 in *Table 5*

On the contrary, the anionically obtained poly(MPM)s showed one endotherm (Nos 4 and 5 in *Table 5*), which was ascribed to the transition from a nematic to an isotropic phase. This transition was observed at a considerably lower temperature than that of the poly(MPM) with a higher molecular weight and

Table 5 Characterization of poly(MPM) materials[a]

No.	Initiator	$M_n \times 10^{-3}$	M_n/M_w	Tacticity (%) mm	mr	rr	Phase transition temperature (°C) (enthalpy change ($J g^{-1}$))									Ref.
1	MTPP	4.6	1.25	–	25	75	g	35	S_x	59	(0.6)	N	101	(2.7)	I	This work
2	MTPP	8.5	1.31	–	28	72	g	38	S_x	64	(0.5)	N	105	(2.5)	I	This work
3	MTPP-ALC	12.0	1.43	–	22	78	g	40				N	107	(2.4)	I	This work
4	DPPL	8.7	1.29	–	30	70	g	30				N	58	(0.7)	I	7
5	DPPL	18.7	1.19	–	23	77	g	36				N	86	(2.1)	I	7
6	AIBN	33.5	3.65	1	34	65	g	40				N	107	(2.2)	I	This work
7	AIBN	5.2	1.18	–	60	40	g	26	S_A	65	(2.2)	N	90	(2.4)	I	7
8	AIBN	18.9	1.51	–	41	59	g	39	S_A	71	(0.8)	N	107	(2.3)	I	7
9	AIBN	115	3.10	–	34	66	g	38				N	112	(2.8)	I	7
10	AIBN	378	1.23	–	–	–	g	41	S_A	72	(0.2)	N	111	(2.8)	I	13

[a] Notations: mm, mr, and rr refer to contents of isotactic, heterotactic, and syndiotactic triads, respectively; g, glassy phase; S_x, unidentified phase; S_A, smectic A phase; N, nematic phase; I, isotropic phase

Table 6 Characterization of poly(MAC) materials[a]

No.	Initiator	$M_n \times 10^{-3}$	M_n/M_w	Tacticity (%) mm	mr	rr	Phase transition temperature (°C) (enthalpy change ($J g^{-1}$))					
1	MTPP	5.2	1.14	1	28	71	g	38	S_A	143	(4.7)	I
2	MTPP	8.6	1.20	1	25	74	g	47	S_A	154	(4.8)	I
3	AIBN	13.6	1.63	1	34	65	g	52	S_A	165	(3.5)	I

[a] For notations, see *Table 5*

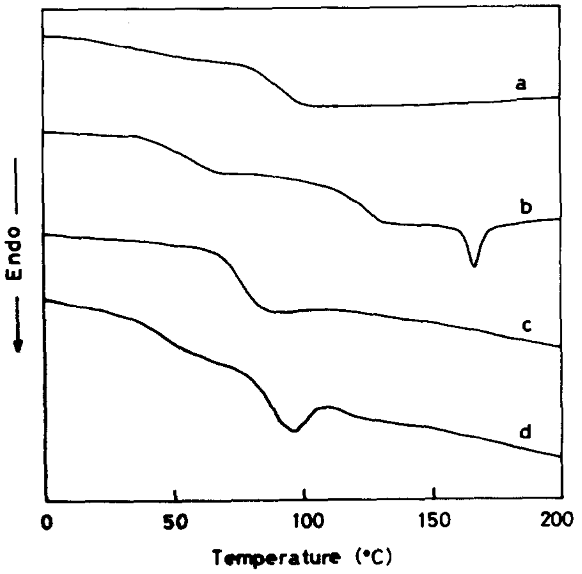

Figure 6 D.s.c. curves: (a) poly(MMA-*co*-MAC) (No. 2 in *Table 4*); (b) a mixture of poly(MMA) and poly(MAC); (c) poly(MMA-*co*-MOB) (No. 4 in *Table 4*); (d) poly(MMA)-*b*-poly(MOB) (results taken from ref. 9)

a broader *MWD* which was obtained when using AIBN. Any structural difference between the poly(MPM)s obtained with MTPP and DPPL does not exist, except for a bulky initiator fragment of DPPL in the anionically obtained polymers and a bulky porphyrin ring at the chain end in the polymers obtained with MTPP. However, it should be pointed out that any residual content of porphyrin ring left in the polymers is almost negligible, since any trace of signal due to this species is not detected in the ^1H n.m.r. spectra of the poly(MPM)s after repeated extraction with methanol, although they are slightly green in colour. The reason why such a difference exists is not clear at present.

It has been reported that poly(MPM)s obtained with a radical initiator show two endothermic peaks (No. 10 in *Table 5*), even if they have a higher molecular weight, although the enthalpy change of the transition at the lower temperature is small[13]. This is somewhat different from the situation described above. Observations of the phase transition behaviour of poly(MPM)s obtained by using MTPP have added another contradiction to the phase transition behaviour of poly(MPM)s in general.

Some of the phase transitions of poly(MAC) are given in *Table 6*, together with their fundamental properties. The structural characteristics of the poly(MAC)s obtained with MTPP and AIBN are essentially similar to those of the poly(MPM) materials. In this case too, the thermal behaviour of the poly(MAC) formed when using MTPP does not have any substantial difference from that of the polymer obtained by radical polymerization[14], except for the change in transition temperature, which depends on the molecular weight.

D.s.c. profiles of the copolymers obtained from the copolymerization of MMA with MAC and MOB are illustrated in *Figure 6*, along with those of poly(MMA)-*b*-poly(MOB) and a blend of poly(MMA) and poly(MAC). The block copolymer clearly shows endothermic peaks over almost the same temperature range as that of poly(MOB). In the d.s.c. profile of the mixture of poly(MMA) and poly(MAC), the glass transitions of the component homopolymers are observed, together with an endothermic peak which is due to the smectic A to isotropic transition of the latter. Poly(MMA-*co*-MAC) and poly(MMA-*co*-MOB) do not show any endotherms, and only glass transitions are observed over the temperature regions between the glass transition temperatures of poly(MMA) and poly(MAC) or poly(MOB). These results are additional evidence to support the aforementioned conclusion that the copolymer compositions are random in nature.

CONCLUSIONS

1. The polymerization of mesogenic methacrylates such as MAC and MPM has been shown to proceed via a living mechanism process when using MTPP as a photocatalyst to yield polymers with a narrow *MWD*, although the polymerization of MAC proceeds more slowly when compared with other MEMs. Interference of the light absorption of MTPP and/or the active propagating chain end by the MAC itself has been attributed as a possible reason for its slower polymerization.
2. The addition of ALC to the polymerization systems of MEMs initiated with MTPP accelerated the polymerizations (with the exception of MAC), to yield polymers with higher molecular weights and considerably narrower *MWD*s.
3. The copolymerizability of MAC and MOB was found to be almost comparable to that of MMA.
4. The influence of tacticities, and molecular weights, and their distributions, on the phase transition behaviour of the poly(MPM)s investigated in this study was somewhat different from that reported previously. The reason why such a discrepancy exists is not yet clear at the present time.

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