SHORT COMMUNICATION

Effect of azoinitiators on nitroxide-mediated photo-living radical polymerization of methyl methacrylate

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Abstract In order to clarify the initiator factor dominating the molecular weight distribution of the resulting polymer, the nitroxide-mediated photo-living radical polymerization of methyl methacrylate was performed using eight different kinds of azoinitiators: i.e., 2,2′-azobisisobutyronitrile, 2,2′-azobis(2-methylbutyronitrile), 2,2′-azobis(2,4-dimethylvaleronitrile), 1,1′-azobis(cyclohexane-1-carbonitrile), racemic-(2RS,2′RS)-azobis(4-methoxy-2,4-dimethylvaleronitrile), meso-(2RS,2′SR)-azobis(4-methoxy-2,4-dimethylvaleronitrile), dimethyl 2,2′-azobis(2-methylpropionate), and 2,2′-azobis(N-butyl-2-methylpropionamide). The bulk polymerization was carried out at room temperature for 3 h using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as the mediator in the presence of bis (alkylphenyl)iodonium hexafluorophosphate as the photo-acid generator. All the initiators provided a molecular weight distribution below 1.7 for the MTEMPO/initiator ratio of 2, although at the ratio of unity, about half of the initiators produced the molecular weight distribution around 2.3–3.4. The UV analysis revealed that the initiators having a higher ε value tended to more strictly control the molecular weight and provide a higher initiator efficiency. The half-lives of the initiators had little effect on the molecular weight control and initiator efficiency.

Introduction

Aliphatic azo compounds are convenient initiators and have been widely used for radical polymerization as well as peroxides. This is based on the fact that the azoinitiators have half-lives over a wide range of temperature, dependent on the substituents attached to the azo group [1]. Their nonexplosive safety and less ability to abstract hydrogen from monomers [2] are also important reasons for the wide application of the azoinitiators. Furthermore, the azoinitiators have a significant advantage over the peroxides in serving not only as thermal initiators, but also as photoinitiators [3–6]. While the azoinitiators have such a superiority over the peroxides, they have higher chain transfer constants [7–9] and lower initiator efficiencies than the peroxides [10–13]. In particular, the production of ketenimine by the decomposition of the azoinitiator [14, 15] can be responsible for broadening of the molecular weight distribution of a polymer obtained by the living radical polymerization where no other compounds participate in the decomposition of the azoinitiator. The ketenimine is formed due to the cage effect during the azoinitiator decomposition and has a different initiation rate constant from the parent azoinitiator [16–18].

Recently, the nitroxide-mediated photo-living radical polymerization of methyl methacrylate (MMA) has been determined using the azoinitiators, such as 2,2′-azobisisobutyronitrile (AIBN) and 2,2′-azobis(4-methoxy-2,4-dime-

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thylvaleronitrile), in the presence of diaryliodonium salts [19–22]. There was a difference in the molecular weight distribution of the resulting poly(methyl methacrylate) (PMMA) between these azoinitiators even for identical molar ratios of the nitroxide to the initiator and of the diaryliodonium salt to the nitroxide. In order to clarify which characteristic of the azoinitiator dominates the molecular weight distribution of the PMMA, the polymerization was performed using eight different kinds of azoinitiators. This short communication describes the effect of the azoinitiators on the photo-living radical polymerization

of MMA using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as the mediator and bis(alkylphenyl) iodonium hexafluorophosphate (BAI) as the photo-acid generator.

Experimental

Instrumentation The photopolymerization was carried out using a Wacom HX-500 illuminator with a 500 W high-pressure mercury lamp. Gel permeation chromatography

Scheme 1 Azoinitiators used for the MTEMPO-mediated photopolymerization
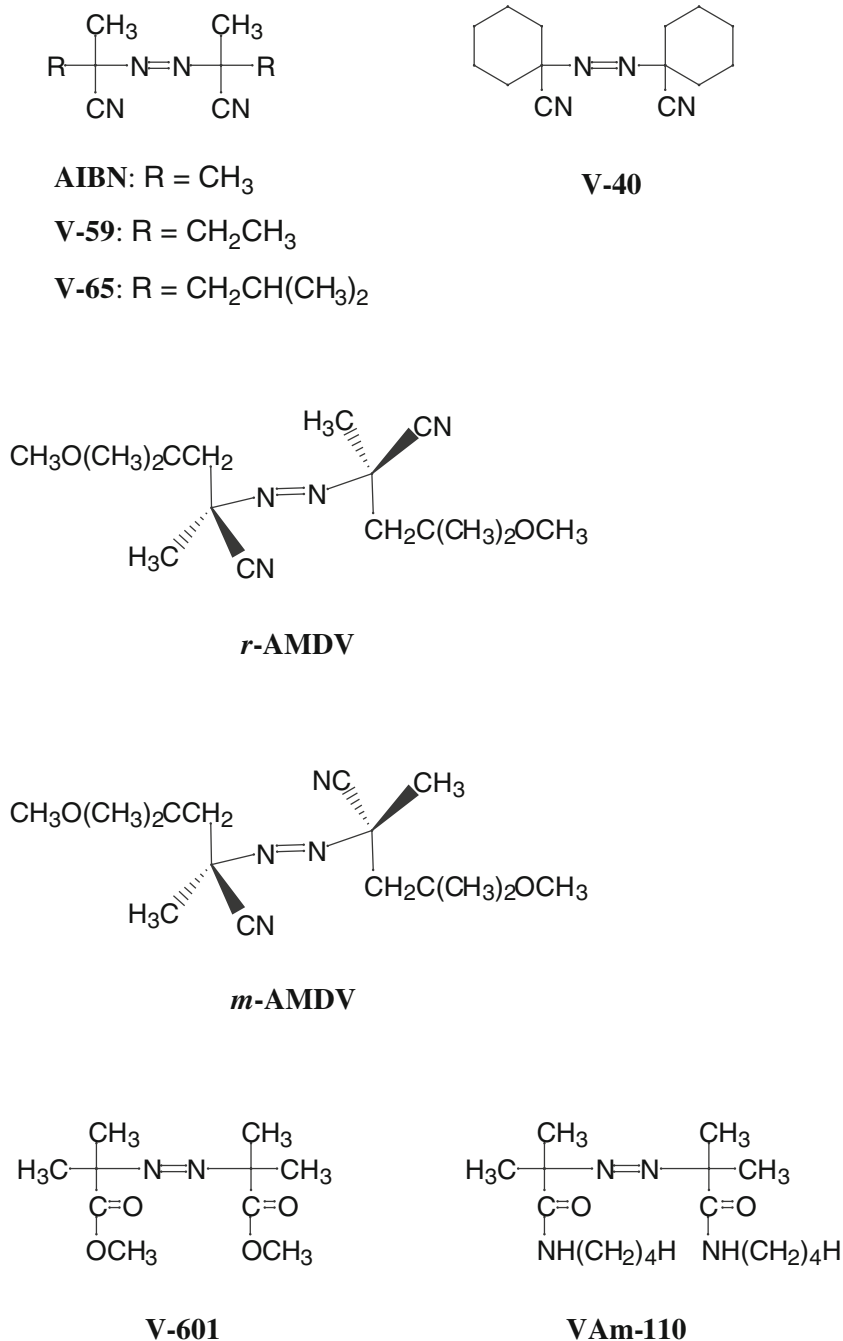
Table 1 The MTEMPO-mediated photoradical polymerization of MMA by the azoinitiators in the presence of BAI

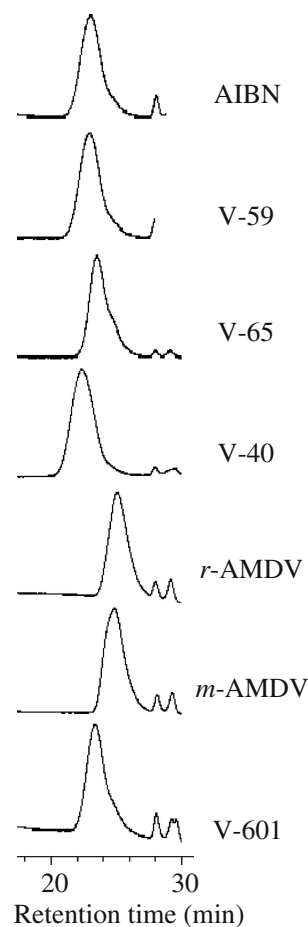| Initiators	MTEMPO/initiator	Conversion (%)	Mn[a]	Mw/Mn[a]	[P] (mM)	IE
AIBN	1	95	39,700	3.37	22.4	0.131
	2	36	15,300	1.68	22.0	0.129
V-59	1	97	31,600	3.37	28.8	0.173
	2	46	15,700	1.66	27.4	0.165
V-65	1	96	18,000	2.33	50.0	0.296
	2	62	9,410	1.53	61.7	0.365
V-40	1	98	38,200	3.24	24.0	0.140
	2	67	26,300	1.65	23.9	0.139
r-AMDV	1	60	7,640	1.52	73.5	0.436
	2	37	3,530	1.28	98.2	0.582
m-AMDV	1	68	10,100	1.50	63.3	0.375
	2	40	4,580	1.34	81.8	0.485
V-601	1	84	26,300	1.99	29.9	0.181
	2	35	10,700	1.68	30.6	0.185
VAm-110	1	25	16,600	1.53	14.1	0.0847

[Initiator]$_0$=84.3 mM, BAI/MTEMPO=0.52. Irradiated for 3 h

[a] Estimated by GPC based on the PMMA standard

(GPC) was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Three polystyrene gel columns, Tosoh TSKGEL G2000H$_{XL}$, G4000H$_{XL}$, and G6000H$_{XL}$ were used with tetrahydrofuran as the eluent at 40 °C. UV spectra were obtained using a Shimadzu UV-160A UV-Vis recording spectrophotometer.

Materials AIBN, 2,2′-azobis(2-methylbutyronitrile) (V-59), 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65), 1,1′-azobis(cy-

Fig. 1 GPC profiles of the PMMAs obtained by the MTEMPO-mediated photopolymerization in the presence of BAI. MTEMPO/initiator=1
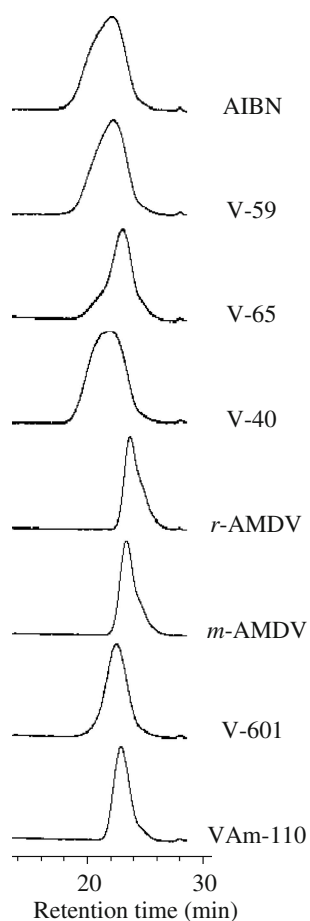
Fig. 2 GPC profiles of the PMMAs obtained by the MTEMPO-mediated photopolymerization in the presence of BAI. MTEMPO/initiator=2
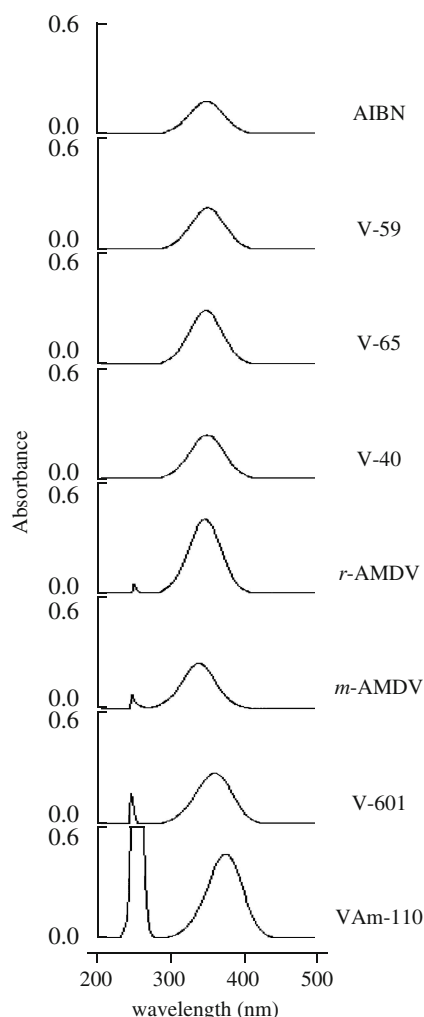
Fig. 3 UV spectra of the initiators. Solvent: methyl isobutyrate

Photopolymerization of MMA: general procedure MMA (936 mg, 9.35 mmol), V-65 (21 mg, 0.0846 mmol), MTEMPO (32 mg, 0.172 mmol), and BAI in 50 wt.% propylene carbonate solution (135 mg, 0.0885 mmol) were placed in an ampoule. After degassing the contents, the ampoule was sealed under vacuum. The bulk polymerization was carried out at room temperature for 3 h with irradiation by reflective light using a mirror with a 500 W high-pressure mercury lamp at 7.0 A. The resulting mass was dissolved in dichloromethane (10 mL). The solution was concentrated by an evaporator to remove the dichloromethane and the monomer unreacted and was freeze-dried with benzene (30 mL) at 40 °C to obtain the product as white powder (695 mg). The conversion was estimated with the weight. The product was dissolved in dichloromethane (3 mL) and poured into hexane (500 mL). The precipitate was collected by filtration and dried in vacuo for several hours to be subjected to GPC analysis.

Results and discussion

The MTEMPO-mediated photoradical polymerization of MMA was performed using eight different kinds of azoinitiators in the presence of BAI. The bulk polymerization was carried out at the BAI/MTEMPO molar ratio of 0.52 at room temperature for 3 h by irradiation using a high-pressure mercury lamp. The azoinitiators used for the polymerization are shown in Scheme 1. The results are summarized in Table 1. When AIBN, V-59, V-65, and V-40 were used as the initiator, the MMA conversions were very

clohexane-1-carbonitrile) (V-40), dimethyl 2,2′-azobis(2-meth-ylpropionate) (V-601), and 2,2′-azobis(*N*-butyl-2-methylpro-pionamide) (VAm-110) were purchased from Wako Pure Chemical Industries and were purified by recrystallization from methanol at –25 °C. Racemic-(2RS,2′RS)-azobis(4-methoxy-2,4-dimethylvaleronitrile) (*r*-AMDV) and meso-(2RS,2′SR)-azobis(4-methoxy-2,4-dimethylvaleronitrile) (*m*-AMDV) were obtained by separation from their mixture by recrystallization from ether [23]. MTEMPO was prepared as reported previously [24]. BAI in 50 wt.% propylene carbonate solution was supplied from Wako Pure Chemical Industries and was used without further purification. MMA was washed with 5 wt.% sodium hydroxide solution and water and then distilled over calcium hydride. Methyl isobutyrate to be used as the solvent for the UV measurements was washed with saturated NaCl aqueous solution and dried with sodium carbonate, then distilled over phosphorous oxide.

Table 2 The UV absorption and 10-h half-life temperature of the azoinitiators

Initiators	λ_{max} (nm)	Absorbance	ε	$T_{1/2}$ (10 h)[a]
AIBN	345	0.176	12.3	65
V-59	348	0.226	15.8	67
V-65	348	0.291	20.4	51
V-40	350	0.236	16.5	88
r-AMDV	348	0.404	28.3	30
	253	0.050	3.50	
m-AMDV	341	0.245	17.2	30
	253	0.078	5.47	
V-601	363	0.273	19.1	66
	253	0.164	11.5	
VAm-110	376	0.455	31.9	110[b]
	258	2.392	167.7	

[a] Reference [23]

[b] Reference [26].

high at a molar ratio of unity for the MTEMPO/the initiator. However, the molecular weights of the resulting PMMA were not controlled at this ratio, and the broad molecular weight distributions were observed in the GPC (Fig. 1). Among these azoinitiators, only V-65 provided a slightly narrower molecular weight distribution. The concentration of the growing polymer chain ([P]) was estimated on the basis of the conversion and the molecular weight of the resulting PMMA. Based on the [P], the initiator efficiency (IE) was also determined. It was found that V-65 had a higher [P] and IE than AIBN, V-59, and V-40. r-AMDV, m-AMDV, V-601, and VAm-110 provided much narrower molecular weight distributions with moderate conversions, although VAm-110 produced only a 25% conversion. In particular, r-AMDV and m-AMDV produced the PMMA with the narrowest molecular weight distribution. r-AMDV had a higher [P] and IE than m-AMDV, being in good agreement with the fact that r-AMDV has a higher reactivity than m-AMDV [25].

As a result of doubling MTEMPO to the initiator, all the initiators produced the PMMA with a molecular weight distribution below 1.7. As can be seen in Fig. 2, the resulting PMMAs displayed sharp GPC curves, although the polymers had different molecular weights. There were negligible differences in the [P] and IE values between the MTEMPO/initiator ratios of unity and 2.

The UV spectra of the initiators are shown in Fig. 3. The UV measurements were performed using methyl isobuty-rate as the solvent. The azoinitiators containing the nitriles had a λ_{max} in the 340–350-nm range, while V-601 and VAm-110 showed it at a much higher wavelength. These absorptions were based on the $n \rightarrow \pi^*$ transition. r-AMDV, m-AMDV, V-601, and VAm-110 also displayed the $n \rightarrow \sigma^*$ transition around 250 nm. The characteristics of the UV absorption spectra of the initiators, coupled with their 10-h half-life temperatures are listed in Table 2. The initiators having higher ε values tended to more strictly control the molecular weight and provide a higher IE. The reason that r-AMDV, m-AMDV, V-601, and VAm-110 provided much narrower molecular weight distributions than the other initiators may include the fact that these initiators exhibit the $n \rightarrow \sigma^*$ transition in addition to the high ε. It is likely that the half-lives of the initiators have little effect on the molecular weight control. The [P] and IE were also independent of the half-life temperature.

Conclusion

The MTEMPO-mediated photoradical polymerization of MMA was performed using eight different kinds of azoinitiators in the presence of BAI. The molecular weight of the PMMA was controlled for all the initiators at the MTEMPO/initiator ratio of 2, although only r-AMDV, m-AMDV, V-601, and VAm-110 controlled the molecular weight at the ratio of unity. The UV analysis revealed that the initiators having higher ε values tended to more strictly control the molecular weight and provide a higher IE. It was found that the half-lives of the initiators had little effect on the molecular weight control and IE during the photopolymerization.

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