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POLYMERIZATION OF ACRYLATES AND METHACRYLATES TO MAKE HOMOPOLMERS AND BLOCK COPOLYMERS INITIATED BY *N*-ALKOXYPHTHALIMIDES AND SUCCINIMIDES

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Various *N*-alkoxyphthalimides were prepared and tested as initiators for polymerization of a variety of monomers. Acrylates and methacrylates polymerized at 40–50 °C. Vinyl acetate and styrene were moderately reactive at 60–65 °C. Rates of reaction were sensitive to the choice of solvent. THF generally gave the highest conversions, with much reduced reactivities in solvents of higher polarity, such as acetonitrile, acetone, DMSO or DMF. In aliphatic hydrocarbon solvents or di-*n*-butyl ether no polymers were obtained. Bulk polymerizations proceeded well, depending on the monomer. Rates of polymerization were sensitive to the structure of the group attached to nitrogen. OR groups, where R contained α-electron-withdrawing esters, benzylic or allylic groups, were more reactive than when R was an aliphatic group. A–B block copolymers were readily prepared, starting with PMA, PBA or PMMA. However, because the rates of initiation were slow, relative to rates of propagation, *N*-alkoxyphthalimide initiators survived mostly intact. Consequently, final A–B block copolymers were invariably contaminated with indeterminate amounts of homopolymer from polymerization of the second monomer.

INTRODUCTION

It has been reported that living radical polymerization of acrylates and methacrylates can be achieved using combinations of donor and acceptor compounds as initiators.[1] Some combinations included *N*-hydroxysuccinimides or -phthalimides as donors in combination with α-halo esters, nitriles or perfluoroalkyls as acceptors. It was subsequently shown that *N*-hydroxysuccinimides [N(OH)S] or -phthalimides [N(OH)Ph] alone initiated the polymerizations. Sato *et al.*[2] also reported studies of N(OH)S- and N(OH)Ph-initiated polymerization of acrylates. Finally, we found that *N*-alkoxyphthalimides [N(OR)Ph] efficiently initiate the polymerization of acyrlates and methacrylates. A–B block copolymers can be prepared by polymerization of monomer A, followed by removal of unreacted monomer A under vacuum, followed by addition and polymerization of monomer B. Almost all of monomer A, in several cases, must have been capped by an end group derived from the *N*-alkoxyphthalimide initiator because almost no homopolymer derived from A remains in the final A–B block copolymer. However, because the rates of initiation were slow, relative to rates of propagation, *N*-alkoxyphthalimide initiators survived the polymerization of monomer A mostly in tact. Consequently, final A–B block copolymers were invariably contaminated with indeterminate amounts of homopolymer from polymerization of monomer B. Various approaches have been tried to counteract the fact that first-formed A homopolymers contained undercomposed initiators, before carrying out polymerizations of B monomers. The scope of monomers, solvents and [N(OR)Ph] initiators, and mechanistic possibilities are discussed.

RESULTS AND DISCUSSION

N(OR)Ph initiation: comparison of R groups

Table 1 gives comparative conversions, M_w, M_n and polydispersity (P/D) results for a variety of *N*-substituted phthalimides [(N(X)Ph] for the polymerization of MA or MMA in THF at 50 °C. All N(OR)Ph initiators gave significant conversions. When X = H, R, OCOR or NCO, little if any conversion took place. All initiators were stable to the reaction conditions, except when X = NCO. In this case, IR evidence indicated that linkage isomerization could be occurring, involving

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Table 1. Effects of nitrogen substitutent of N(X)-phthalimide initiators in the polymerization of MA or MMA

	N(X)Ph							
Run no.	X	Concentration (M)	Monomer (M)	Solvent	Conversion (%)	M_w	M_n	P/D
1	H	0·075	MMA, 3·4	THF	4[a]			
2	OH	0·075	MA, 3·7	THF	84[b]	51800	14900	3·5
3	$CH(CH_3)CO_2Me$	0·043	MA, 1·7	THF-d_8	0[b]			
4	$CH(CO_2Et)_2$	0·09	MA, 3·6	THF	0[b]			
5	CH_2CH_2OH	0·09	MA, 3·6	THF	0[b]			
6	$OCH(CH_3)_2$	0·078	MA, 3·7	THF	19[b]			
7	$OCH(CH_3)CO_2Me$	0·033	MA, 3·7	THF	41[c]	47500	21100	2·3
8	$OCH(CO_3)CO_2Me$	0·033	MA, 3·7	THF-d_8	72[b]	170000	31700	5·4
9	$OCH_2CH{=}CH_2$	0·081	MA, 4·0	THF	21[b]	295000	154000	2·5
10	$OCH{=}CHCH_3$	0·09	MA, 3·8	THF-d_8	30[b]	794000	171000	4·6
11	$OCH{=}CH\phi$	0·088	MA, 3·6	THF-d_8	36[b]	64500	18300	3·5
12	OC_8F_{17}	0·089	MA, 3·7	THF-d_8	95[b]	779000	154000	5·1
13	$OCH_2\phi$	0·067	MMA, 3·4	THF	24[b]	570000	172000	3·3
14	$OCH_2\phi$-$p(OCH_3)$	0·13	MA, 20	THF-d_8	45[b]	796000	192000	4·1
15	$OCH_2\phi$-p(CN)	0·13	MA, 20	THF	53[b]	855000	246000	3·5
16	$OCH_2\phi$	0·08	MA, 3·7	THF	56[d]	43200	19000	2·3
17	OH	0·08	MA, 3·7	THF	49[d]	41900	20100	2·1
18	$OCH(CH_3)CO_2Me$	0·08	MA, 3·7	THF	36[d]	46900	21500	2·2
19	O-2-thiopheneyl	0·089	MA, 3·7	THF-d_8	26[b]	725000	22000	3·5
20	$OCOCH_3$	0·08	MMA, 3·4	THF	0[e]			
21	$OCOCH{=}CH_2$	0·075	MA, 3·7	THF	8[B]			
22	OCO_2Et	0·27	MA, 3·7	THF-d_8	0[b]			
23	NCO	0·072	MMA, 3·7	THF	7[a]			
24	OSO_2CF_3	0·09	MA, 3·7	THF	23[b]	1020000	279000	3·7
25	OSO_2CF_3	0·067	MMA, 3·4	THF	23[b]	382000	102000	3·7
26	OAg	0·86	MA, 3·7	THF-d_8	84[b]	132000	39400	3·4

[a] 65 °C, 3 h, 3·5 ml vial, stir bar.
[b] 50 °C, 4 h, 3·5 ml vial, stir bar.
[c] 50 °C, 4 h, 50 ml filter flask, stir bar.
[d] 50 °C, 4 h, 6 ml vial, stir bar.
[e] 65 °C, 3·5 h, 6 ml vial, stir bar.

perhaps N or O attachment to the phthalimide N, even at ambient temperatures. In all samples analyzed, the M_n numbers were at least ten times greater than would be expected had each equivalent of initiator started a polymer chain. ^1H NMR of polymers also showed no evidence for changes in starting initiator resonances. These two findings are consistent with a very slow initiation step in which only a small fraction of the initiators actually starts chain growth, followed by a relatively more rapid chain propagation rate. These conclusions are also consistent with broad P/D values. Narrower P/Ds appeared to have resulted, however, when using larger (6 ml) vials versus 3·5 ml vials, or when using a 50 ml filter flask versus 3·5 ml vials, both probably related to better mixing.

Scope of monomers

Within the limited range of monomers tested, (Table 2), acrylates and methacrylates were efficiently polymerized. Styrene gave only very low conversions at 65 °C and almost no polymer at lower temperatures. Vinyl acetate was unreactive at 50 °C, using $N(OCH(CH_3)CO_2CH_3)Ph$ as initiator. However, vinyl acetate did give differing extents of conversion to polymer at 60 °C, depending on the initiator. For example, using N(OR)Ph, with $R = OCH_2\phi$-p-OCH_3, in THF, 34% conversion to PVOAc took place after 15 h at 60 °C with $M_w = 6340$ and P/D = 2·44. An otherwise identical experiment, except that R = OH, gave 3·3% conversion to PVOAc with $M_w = 4990$ and P/D = 2.19 Acrylonitrile, methyl crotonate, dimethyl maleate, diethyl fumarate and cyclohexenone were all inactive at the temperatures tried.

Solvent effects

Tables 3 and 4 show several comparisons of solvent effects in the polymerization of MMA, MA and BA. In Table 3 it is seen that for N(X)Ph, and $X = OCH_2\phi$ or $OCH(CH_3)CO_2CH_3$, either bulk polymerization or use of THF solvent led to the greatest conversions. Interestingly, $(nBu)_2O$ was not effective. Likewise,

Table 2. Choice of monomer in N(X)-phthalimide-initiated polymerizations in THF

Run no.	N(X)Ph X	N(X)Ph Concentration (M)	Monomer (M)	Temperature (°C)	Time (h)	(%) Conversion	Glass RXT (ml)
1	$OCH(CH_3)CO_2Me$	0·076	MA, 3·4	50	4	57	3·5
2	$OCH_2\phi$	0·035	MMA, 3·5	65	3	17	3·5
3	OH	0·035	MMA, 3·5	65	3	19	3·5
4	OH	0·1	HEMA, 7·9	37–60[a]	0·5	Bulk, jelled	15
5	$OCH_2\phi$	0·13	Methyl crotonate[b]	65	65	N.R.	NMR tube
6	OH	0·13	Methyl crotonate[b]	65	21	N.R.	3·5
7	$OCH_2\phi$	0·13	*tert*-Butyl-MA[b]	50	2	N.R.	3·5
8	$OCH_2\phi$	0·13	*tert*-Butyl-MA[b]	65	65	83	3·5
9	OH	0·44	Dimethyl maleate	50	17	N.R.	3·5
10	OH	0·38	Diethyl fumarate	50	17	N.R.	3·5
11	$OCH(CH_3)CO_2Me$	0·44	Dimethyl maleate	50	17	N.R.	3·5
12	$OCH(CH_3)CO_2Me$	0·38	Diethyl fumarate	50	17	N.R.	3·5
13	$OCH(CH_3)CO_2Me$	0·094	Vinyl acetate	50	4	N.R.	3·5
14	$OCH(CH_3)CO_2Me$	0·094	Acrylonitrile	50	4	N.R.	3·5
15	OH	0·26	2-Cyclohexenon[b]	65	71	N.R.	NMR tube
16	OH	0·037	Styrene	65	7	4·8	3·5
17	$OCH_2\phi$	0·034	Styrene	65	7	4·6	3·5
18	$OCH(CH_3)CO_2Me$	0·024	Styrene[b]	60	5	N.R.	3·5
19	$OCH(CH_3)CO_2Me$	0·21	Styrene[c]	95	5	N.R.	3·5

[a] Bulk polymerization. Sample jelled within 0·5 h when heated and stirred from 37 to 60 °C.
[b] THF-d_8
[c] Bulk polymerization.

Table 3. Effects of solvents and nitrogen substitutent of N(X)-phthalimide initiators in the polymerization of MA or MMA

Run no.	N[OCH(CH$_3$)CO$_2$Me]Ph (M)	Monomer (M)	Solvent	Conversion (%)
1	0·085	3·7	Pyridine	0[a]
2	0·085	3·7	CD_3CN	3
3	0·084	3·7	DMF	0
4	0·086	3·7	DMSO-d_6	0
5	0·088	3·7	Acetone	11
6	0·087	3·7	Acetone	0
7	0·089	3·7	$CDCl_3$	0
8	0·085	3·7	$CDCl_3$	17
9	0·09	3·7	EtOAc	0
10	0·084	3·7	MeOH	0
11	0·086	3·7	$Et(CH_3)_2COH$	0
12	0·088	3·7	2,2,6,6-$(Me)_4$-piperidine	0
13	0·076	3·7	THF	57
14	0·089	3·7	$(nB)_2O$[b]	0
15	0·088	3·7	CyC_6H1_2	0
16	0·088	11·2	Bulk; no solvent	68
17	0·087	3·7	Toluene-d_8	
18	0·023	BA, 0·4	Toluene	0[c]
19	0·066	MMA, 3·4	Toluene	1[d]
20	0·067[e]	MMA, 3·4	THF[f]	24
21	0·067[e]	MMA, 3·4	MeOH	0
22	0·069[e]	MMA, 3·4	Acetone	0

[a] Reactions run at 50 °C for 4 h using stir bars and solvents dried over 4A molecular sieves in 3·5 ml vials.
[b] Passed over neutral Al_2O_3 to remove peroxides.
[c] 40 °C, 1 h.
[d] 65 °C, 3 h.
[e] N($OCH_2\phi$)Ph used as initiator.
[f] Distilled from $Na\phi CO\phi$.

Table 4. Effect of solvents in the N(OH)-phthalimide-initiated polymerization of MA or MMA

Run no.	N(OH)Ph(M)	Monomer (M)	Solvent	Conversion (%)[a]
1	0·075	MA, 3·7	THF[b]	56·47
2	0·075	MA, 3·7	THF[b]	83
3	0·077	MA, 3·7	CH_3CN[c]	<1
4	0·077	MA, 3·7	EtOAc	<1
5	0·079	MA, 3·5	Toluene	13
6	0·075	MMA, 3·4	THF	3
7	0·074	MMA, 3·4	THF	51
8	0·076	MMA, 3·4	CH_3CN[c]	9
9	0·072	MMA, 3·4	EtOAc	13
10	0·079	MMA, 3·7	Toluene	1
11	0·072	MMA, MeOH	0	
12	0·072	MMA, 3·4	Acetone	34

[a] Reactions run at 50 °C, 4 h, stir bars, 3·5 ml vials.
[b] Distilled from $Na\phi CO\phi$.
[c] Solvent dried over 4A molecular sieves.

hydrocarbons (CyC_6H_{12}, toluene), acetone and ethyl acetate were not effective. Alcoholic, basic or polar solvents were inferior. Table 4 shows the results of N(OH)Ph-initiated polymerizations of MA and MMA in a variety of solvents. THF was the preferred solvent for both MMA and MA. However, toluene was moderately good for both MA and for MMA. Acetone was fairly active for MMA. Sato *et al.*[2] also reported results for the polymerization of MMA, using N(OH)S, in a variety of solvents. Sato *et al.* rationalized the trends by saying, 'Such a considerably large solvent effect is reasonably expected, because N(OH)S shows a fairly small pK_a value (9.40) and so it can form a strong hydrogen bond with solvents or the monomer. Ethers, alcohols and sulfoxides are considered to form stronger hydrogen bonds with N(OH)S than ketones or esters.' The data in Tables 3 and 4 allow for only limited comparisons, but agree qualitatively, with the possible exception of the ordering of THF.

Effects of O_2, H_2O and radical scavengers

In order to try to ascertain whether or not radical mechanisms were involved in the N(X)Ph-initiated polymerizations of MA or MMA, several reactions were carried out to test for the effects of added O_2, H_2O or radical scavengers (Table 5). The comparisons involving prior O_2 sparging versus the routine N_2 sparging tend to indicate that adventitious O_2 did not significantly affect the conversions. Likewise, the one example involving added water did not indicate any adverse affect. The presence of phenathiazine and of *p*-hydroquinone, however, did completely prevent moderate conversions of MA or MMA. 2,6-Di-*tert*-butylphenol was only slightly effective, if at all. These results do not prove that radical chain reactions were involved, since additional work would be needed to rule out inhibition by complexation of the radical scavenger with the N(X)Ph compound.

Preparation of block copolymers

Table 6 lists various examples of reactions carried out to prepare A–B block copolymers whereby MA or MMA was first polymerized, initiated by a given N(X)Ph compound, followed by removal of unreacted monomer under vacuum, followed by addition of a second monomer and heating and stirring to prepare the copolymer. The first four runs illustrate how at least 97% of the first monomer was completely grafted, as indicated by LC analysis. However, an indeterminate amount of homopolymer from the second monomer was also present in each case. The fifth and sixth runs were carried out starting with MA (in THF or in bulk, respectively), followed by polymerization with BA in toluene solvent. Toluene was chosen because BA was not polymerized by $N[OCH(CH_3)CO_2CH_3]Ph$ in toluene (Table 3). It was hoped that unreacted N(X)Ph from the first polymerization step would not initiate polymerization of BA, but the end-capped groups on the chains of PMA would graft on BA. As shown in Table 6, homopolymer of BA was obtained in run 5. The results for run 6 showed that although no homopolymer of MA remained after reaction with BA, an indeterminate amount of homopolymer of BA was also present. Perhaps the closest approach to achieving a clean A–B copolymer was that shown for run 7, starting with N(OAg)Ph and MA. The reason for the choice of N(OAg)Ph was that the silver salt of N(OH)Ph is completely insoluble in THF and thus unreacted initiator could be removed by filtration following the first polymerization reaction. When this was done, and a

Table 5. Effects of O_2, H_2O and radical scavengers in N(X)-phthalimide-initiated polymerizations in THF

Run no.	N(X)Ph X	N(X)Ph Concentration (M)	Monomer (M)	Temperature (°C)	Time (h)	(%) Conversion	Conditions[a]
1	$OCH_2\phi$	0·063	MMA, 3·4	50	4	19	Charged in air
2	$OCH_2\phi$	0·063	MMA, 3·4	50	4	24	N_2
3	OH	0·078	MA, 3·7	50	4	100	O_2 sparged 15 min[b]
4	OH	0·075	MA, 3·7	50	4	83	N_2
5	OH	0·078	MA, 3·7	50	4	84	N_2, 0·42 M H_2O
6	$OCH(CH_3)CO_2Me$	0·066	MMA, 3·4[b]	65	3	0·5	O_2, sparged 15 min
7	$OCH(CH_3)CO_2Me$	0·066	MMA, 3·4[b]	65	3	1	N_2
8	AIBN	0·041	MMA, 3·4[b]	80	2·33	100	O_2 sparged 15 min
9	AIBN	0·041	MMA, 3·4[b]	80	2·33	100	N_2
10	$OCH_2\phi$	0·035	MMA, 3·5	65	3	0	0·022 M PT[c]
11	$OCH_2\phi$	0·035	MMA, 3·5	65	3	17	
12	CH	0·035	MMA, 3·5	65	3	0	0·022 M PT[c]
13	CH	0·035	MMA, 3·5	65	3	19	
14	$OCH(CH_3)CO_2Me$	0·067	MMA, 3·4	60	3	7	0·017 M DTBP[d]
15	$OCH(CH_3)CO_2Me$	0·067	MMA, 3·4	60	3	12	
16	DCHN[e]	0·042	MMA, 3·4	60	3	100	0·017 M DTBP[d]
17	DCHN[e]	0·042	MMA, 3·4	6	3	100	
18	OCH2ϕ-*p*-OCH_3	0·33	MA, 10·7	50	0·42	0	0·1 M HQ[f]
19	$OCH_2\phi$-*p*-OCH_3	0·33	MA, 10·7	50	0·42	20	

[a] All reactions run in 3·5 ml vials, with stir bars, under N_2, unless noted otherwise.
[b] Toluene solvent.
[c] PT = phenathiazine.
[d] DTBP = 2,6-di-*tert*-butylphenol.
[e] DCHN = dicyclohexyl hyponitrite.
[f] HQ = *p*-hydroquinone.

Table 6. Block copolymer experiments

Run no.	N(X)Ph X	N(X)Ph Concentration (M)	Polymer (M)	Monomer (M)	Solvent	Temperature (°C)	Time (h)	M_w	P/D	^{1}H NMR, LC
1	OH	0·077		MA, 3·7	THF	50	4	41900	2·1	[a]
			PMA, 0·45	BA, 2·2	THF	50	19	31300	9·2	[b,c]
2	$OCH(CH_3)CO_2Me$	0·077		MA, 3·7	THF	50	4	46900	2·2	[a]
			PMA, 0·40	BA, 2·2	THF	50	17	18500	5·5	[c,d]
3	$OCH_2\phi$	0·077		MA, 3·7	THF	50	4	43200	2·3	[a]
			PMA, 0·44	BA, 2·2	THF	50	17	20500	6·3	[c,e]
4	$OCH_2\phi$	0·063		MMA, 3·4	THF	50	2	387000	2·6	[f]
			PMMA, 0·28	BA, 3·6	THF	50	4	142000	3·7	[c,g]
5	$OCH(CH_3)CO_2Me$	0·12		MA, 3·7	THF	50	4	51000	2·2	[h]
			PMA, 1·6	BA, 2·4	Toluene	50	2·25	296000	8	[c,i]
6	$OCH(CH_3)CO_2Me$	0·11		MA, 11·2	None	50	1	3580000	9·6	[c]
			PMA, 0·67	BA, 2·4	Toluene	50	1·75	869000	4·3	[c,j]
7	OAg	0·11		MA, 7·8	THF	50	4	22100	6·1	[h]
			PMA, 0·23	BA, 2·4	THF	50	4	41900	2·4	[c,k]
8	$OCH(CH_3)CO_2Me$	0·035		MA, 3·7	THF	50	4	52100	2·2	[f]
			PMA, 2·6	Styrene, 8·8	None	95	5	336000	7·2	[c,l]

[a] 6 ml crimp-cap vial with stir bar.
[b] PBA/PMA = 7.5 (^{1}H NMR); 2·8% PMA in sample (LC).
[c] 3·5 ml glass vial with stir bar.
[d] PBA/PMA 4·2 (^{1}H NMR); 2·7% PMA in sample (LC).
[e] PBA/PMA 5·2 (^{1}H NMR); 2·1% PMA in smaple (LC).
[f] 50 ml filter flask with stir bar.
[g] PBA/PMMA = 7·5 (^{1}H NMR); 0·9% PMMA in sample (LC); PMMA precipitated twice from CH_2Cl_2 with pentane.
[h] 20 ml screw-cap vial with stir bar.
[i] PBA/PMA = 3·7 (^{1}H NMR); 57% PMA, 43% PBA in sample, not a block copolymer (LC).
[j] PBA/PMA 1 1·1 (^{1}H NMR); 0% PMA in sample (LC).
[k] PBA/PMA 8·9 (^{1}H NMR); 1·5% PMA in smaple (LC).
[l] PSty/PMA = 0·4 (^{1}H NMR); 42% PSty, 58% PMA in sample (LC), not a block copolymer.

second polymerization was carried out with BA, 98.5% of the PMA had been grafted with BA.

Figure 1 shows that the LC retention time of the PMA–PBA block copolymer (5·96 min) was longer than that of the PBA homopolymer (5·64 min). The GPC result for the PMA–PBA block copolymer from run 7 is also shown in Figure 1. It was noteworthy also that this was the first instance in which the P/D of the second polymer (2·4) was actually narrower than that of the first polymer (6·1). This broad P/D for the N(OAg)Ph-initiated polymerization of MA was perhaps due to the insolubility of the initiator in THF. Another distinction is that in run 7 M_w for the A–B copolymer was greater than M_w of the starting PMA. In all previous A–B copolymers the M_w values were smaller than the corresponding M_w values for the starting PMA polymers. This is probably due to competitive formation of PBA homopolymer, along with grafting of PBA on to PMA. The last run in Table 6 was from the reaction of MA, followed by a bulk polymerization of styrene, an abortive attempt to prepare a PMA–PSTY block copolymer.

MECHANISTIC CONSIDERATIONS

General considerations

It has been reported by Sato *et al.*[2] that N(OH)S and N(OH)Ph are capable of initiating the polymerization of acrylates and methacrylates. The mechanism proposed is shown in Scheme 1. Assuming that N(OH)S and N(OH)Ph function as proposed by Sato *et al.*, such a mechanism would not account for end-capping of chains which, in turn, form A–B copolymers unless the *N*-succinimidyloxyl radical (B) were reversibly associated with the growing chain end. Also, according to this mechanism, N(OR)S or N(OH)Ph compounds would have to undergo C—O bond cleavage, which seems unlikely. A different kind of dissociative mechanism, involving a six-center rearrangement, was also considered. Finally, an associative mechanism was considered, by default, to be most likely involved.

N—O or O—C bond cleavage mechanisms

Mechanisms were considered which could involve N-O bond cleavage of N(OR)Ph compounds in the initiation

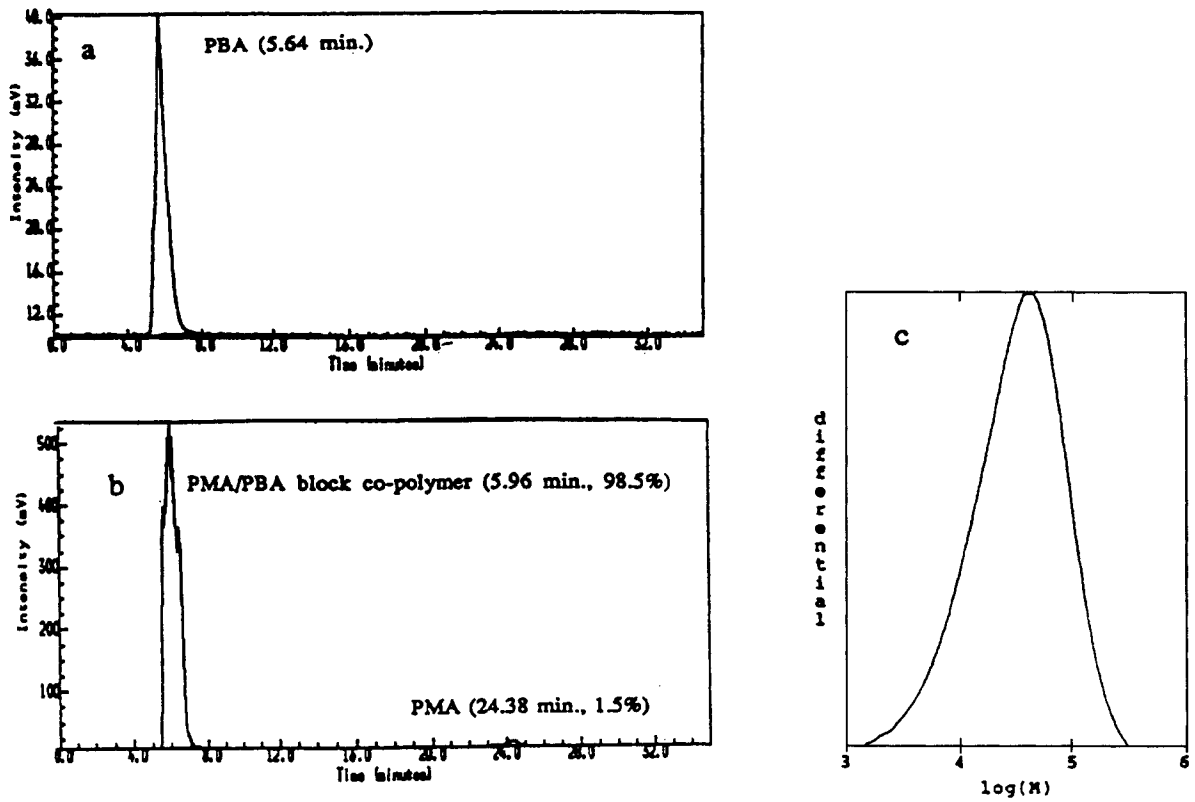
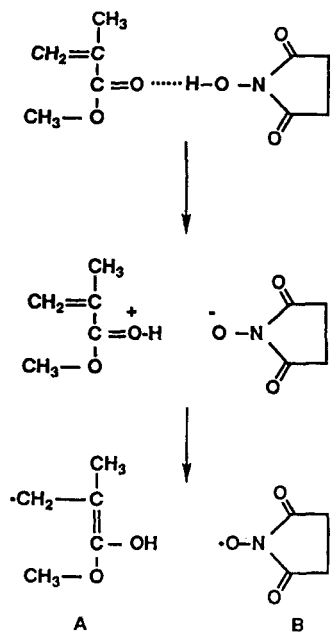
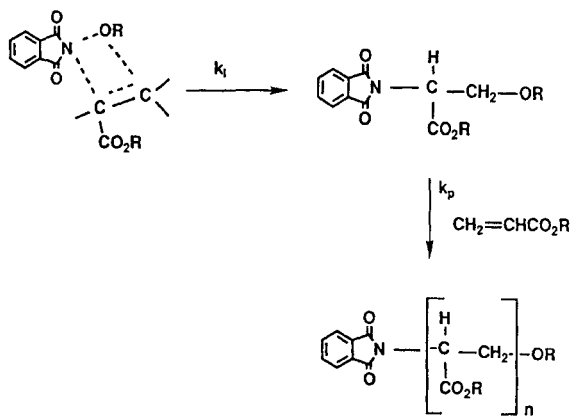


Figure 1. Liquid chromatograms of (a) reference PBA and (b) PMA–PBA block copolymer (run 7, Table 7) and (c) gel permeation chromatofram of the same PMA–PBA block copolymer



Scheme 1

step (Scheme 2). This proposal seems unlikely because the thermal stability of *N*-alkyl phthalimides would seen to preclude them as propagating intermediates. Note that the propagating polymeric structure in Scheme 2 contains an alkyl phthalimide. For example, as shown in Table 1, $N(CH(CH_3)CO_2CH_3)Ph$ gave no PMA from the reaction of MA in THF at 50 °C after 4 h. Another possible mechanism might involve O-C bond cleavage of N(OR)Ph compounds (Scheme 3). The detraction of the propagating intermediate shown in Scheme 3 is that it is simply an N(OR)Ph compound. Even though



Scheme 2

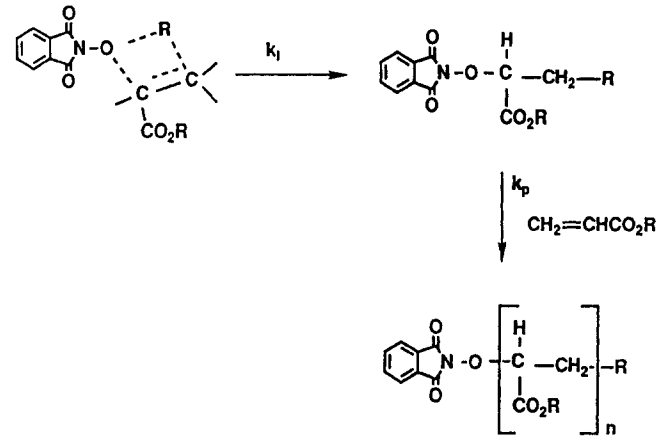
numerous N(OR)Ph compounds do initiate polymerization of acrylates and methacrylates (Table 1) at 50 °C, ^1H NMR and ^{13}C NMR spectroscopy have given no evidence for conversion of starting N(OR)Ph initiators into end-capping groups attached to polymeric chains. In the case of $N(OC_8F_{17})Ph$, MA and MMA were each polymerized to 50 and 14%, respectively, in THF-d_8 after 2 h. Comparison of PMA and PMMA by ^{19}F NMR spectroscopy with starting $N(OC_8F_{17})Ph$ showed no changes in the F resonances. Also, $N(OCH_2\phi)Ph$ and $N(OCH(CH_3)CO_2CH_3)Ph$ were found to be unchanged after heating in toluene at 60 °C for 1 h. Also, a facile cleavage of the O-C bond in $N(OCH{=}CH\phi)Ph$ or in $N(OCH{=}CHCH_3)Ph$ at 50 °C (Table 1) would seem unlikely.

Cyclic azaketene acetal mechanism

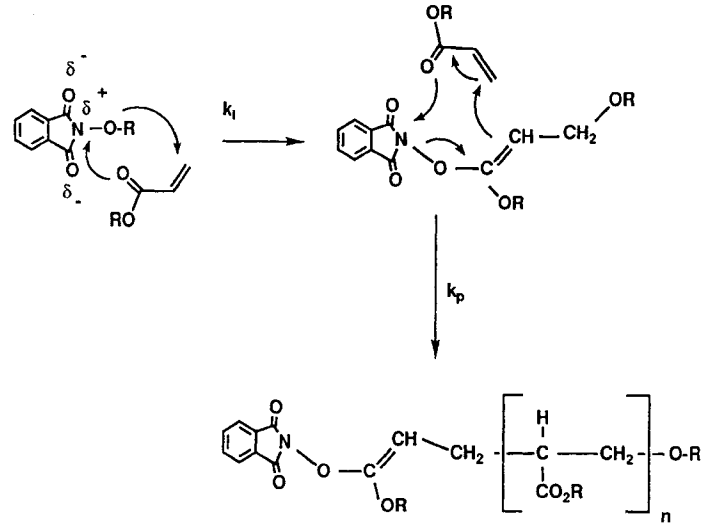
A mechanism which would also involve N—O bond cleavage is one in which a six-center transition state takes place in the initiation step (Scheme 4). The propagating intermediate, an aza keteneacetal (or aza keteneketal), might be expected to undergo rapid propagation of acrylates or methacrylates in analogy with silyl keteneacetals, proposed as intermediates in group-transfer polymerization.[3] Note that, if the N atom shown in the propagating intermediate in Scheme 4 were replaced by a Si atom, the resultant intermediate would be a silylketeneacetal. Numerous attempts were made to prepare an azaketeneacetal in order to be able to test directly the efficiency of such an intermediate (Table 7). However, none of the synthetic approaches succeeded. Hence the question of azaketeneacetal intermediates as propagating intermediates remains open. In order for such intermediates to be involved, however, the objections raised for N—O bond cleavage would have to be addressed.

Association mechanisms

Because of lack of evidence for changes in starting N(OR)Ph compounds, an associative mechanism would seem, by default, to be reasonable to consider. The fact that PMA and PMMA, prepared using N(OR)Ph initiators, are fairly quantitatively converted into A–B block copolymers argues that the initially formed PMA or PMMA chains are somehow capped by the N(OR)Ph initiator [or something derived from it which yields unchanged N(OR)Ph]. Also, attempts to separate initially formed PMA or PMMA from unreacted N(OR)Ph, by precipitation from one solvent on addition of another, generally resulted in terminated chain ends. That is, such attempts to purify the initially formed PMA or PMMA led to a mixture of two homopolymers in the second polymerization step. However, run 4 in Table 6 was an exception to this generalization. Nevertheless, whatever the nature of the group associated



Scheme 3



Scheme 4

Table 7. Attempted routes to aza keteneacetals

N(OR)Ph[a], OR	Rectants	Reaction conditions	Desired product
$OCOCH{=}CH_2$	Et_3SiH, $Rh(P\phi_3)_3Cl$	16 h, 50 °C; 19 h 80 °C	$N[OC(OTMS){=}CHCH_3]Pha$
$OCOCH_3$	Et_3SiCl LDA	THF, −78 °C	$N[OC(OTMS){=}CH_2]Ph$
$OCOC_2H_5$	Cp_2Ti	THF, −25 to 25 °C	$N[OC(OC_2H_5){=}CH_2]Ph$
OTl	$CH_2{=}C(Br)OC_2H_5$	THF, 25 °C, 6 days	$N[OC(OC_2H_5){=}CH_2]Ph$
OTl	$CH_2{=}C(Br)OC_2H_5$	THF, 25 °C, 3 days	$N[OC(OC_2H_5){=}CH_2]Ph$
ONa	$CH_2{=}C(Br)OC_2H_5$	THF, 25 °C, 8 days	$N[OC(OC_2H_5){=}CH_2]Ph$
ONa	$CH_2{=}C(Br)OC_2H_5$	THF, 25 °C, days	$N[OC(OC_2H_5){=}CH_2]Ph$
OAg	$CH_2{=}C(Br)OC_2H_5$	THF, 25 °C, 5 days	$N[OC(OC_2H_5){=}CH_2]Ph$[b]
OAg	$CH_2{=}C(I)OC_2H_5$	THF, 25 °C, 3 days	$N[OC(OC_2H_5){=}CH_2]Ph$[c]
OAg	$CH_2{=}C(I)OC_2H_5$	THF, 25 °C, 3 days	$N[OC(OC_2H_5){=}CH_2]Ph$[d]

[a] Ph = phthalimide.
[b] Gray precipitate and unreacted $CH_2{=}C(Br)OC_2H_5$.
[c] Red–brown precipitate and unreacted $CH_2{=}C(I)OC_2H_5$.
[d] Gray precipitate and unreacted $CH_2{=}C(I)OC_2H_5$.

with the PMA or PMMA chain ends, the attachment appears to be fragile. Additional work is needed to substantiate the involvement of an associative mechanism.

CONCLUSION

The single most important impediment precluding the use of N(OR)Ph compounds for the preparation of clean A–B block copolymers is that unreacted N(OR)Ph initiators are left in the first formed polymer. This results in a mixture of the desired A–B block copolymer and undesired homopolymer of monomer B. One approach might to be to find a way to increase the slow initiation step, relative to the faster propagation step. The use of higher temperature, other monomers, other solvents or emulsions could be tried. Another approach would be to find a practical way to separate the first-formed polymer [stabilized by N(OR)Ph or N(OR)Ph-derived groups] from unreacted N(OR)Ph, prior to carrying out polymerization with the second B monomer. Run 7 in Table 6 shows one approach, using an insoluble N(OAg)Ph compound, which appears to be feasible. The final products are water-white and do not suffer from the color problems encountered previously using azo-based initiators of various kinds.[1] If ways were found to make the initiation step faster, then the resulting P/Ds would be expected to become more narrow.

EXPERIMENTAL

All monomers were purified by passing through neutral alumina, followed by N_2 purging. All solvents were dried over 4a molecular sieves or by distillation. Reactions were carried out in glass vials or flasks with Teflon-coated stir bars. Air was excluded by means of N_2 purging with syringe needles or by running reactions in an N_2-filled dry-box. All N(OR)Ph compounds were characterized by ^{1}H NMR spectroscopy.

Preparation of N[OCH(CH$_3$)CO$_2$CH$_3$]Ph. Into a 125 ml Erlenmeyer flask, equipped with a stir bar and thermometer, and placed in a wet ice-bath, were charged 20 ml of DMSO, 1·97 g (24 mmol) of fumed NaOAc and 3·91 g (24 mmol) of N(OH)Ph. An N_2 blanket was provided by means of tubing in the opening of the flask and the contents were stirred for 10 min. A dark-maroon solution resulted. Next, 2·67 ml (24 mmol) of BrCH(CH$_3$)(CO$_2$CH$_3$) were added and stirring and cooling were continued for 2 h. A cloudy light-yellow solution resulted. In a separating funnel was placed 200 ml of ice-cold water, 50 ml of $CHCl_{13}$ and the reaction mixture. The contents of the funnel were shaken, then allowed to stand for a few minutes to let the two phases separate. The upper phase was discarded. The lower ($CHCl_3$) phase was extracted once more with 100 ml of ice-cold water and the upper phase discarded. The lower phase was poured into a flask containing $MgSO_4$ and the contents were allowed to stand for about 15 minutes to dry the $CHCl_3$ phase. The dried $CHCl_3$ phase was collected by filtration and was stripped to about 2–5 ml and was combined with 50 ml of pentane. The white product was collected by filtration, vacuum dried and weighed, giving 3·65 g (61% yield).

Procedure, using N(OCH(CH$_3$)CO$_2$CH$_3$)Ph, to prepare PBA–PMA a block copolymer. In a N_2-filled dry-box, a 6 ml crimp cap vial with a stir bar was charged with 0·0567 g (0·23 mmol) of N(OCH(CH$_3$)CO$_2$CH$_3$)Ph, 1 ml (11·2 mmol) of MA and 2 ml of THF. The vial was capped and the contents were stirred at 50 °C for 4 h using an aluminium block heater. The product solution was stripped in the dry-box and resulted in 0·40 g (36% conversion) of PMA. Next, also in a dry-box, a 6 ml septum-capped vial was charged with 0·0343 g of PMA, 0·25 ml (1·8 mmol) of BA and 0·75 ml of THF. The vial contents were stirred and heated at 50 °C for 17 h. Following stripping of the final product solution, 0·354 g of PBA–PMA were obtained (Table 6, run 2). A ^{1}H NMR spectrum of the product gave a PBA–PMA ratio of 4·2. Samples of the PMA and PBA–PMA polymers were analysed by GPC: PMA, $M_w = 46{,}900$, $M_n = 21{,}500$, P/D = 2·18; PBA–PMA, $M_w = 18{,}500$, P/D 5·48.

A sample of the PBA–PMA copolymer was analyzed by LC and showed the presence of a major peak (97·3 area%) eluting at 5·60 min and a minor peak (2·7 area%) eluting at 25·9 min (retention time of PMA). A reference ligand chromatogram of PBA gave a retention time of 5·47 min.

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