Synthesis and Polymerization of Poly(*N*-substituted maleimide) Macromonomers

Tsutomu OISHI,[†] Yong-Kyung LEE, Akira NAKAGAWA, Kenjiro ONIMURA,
and Hiromori TSUTSUMI

Department of Applied Chemistry, Faculty of Engineering,
Yamaguchi University
2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

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ABSTRACT: Four new types of poly(*N*-substituted maleimide) macromonomers (RMI, R = *N*-substituent, phenyl and cyclohexyl) were synthesized from methacryloyloxyethyl isocyanate (MOI) and oligomaleimides. The obtained macromonomers were polymerized in tetrahydrofuran (THF) to afford the corresponding polymacromonomers with degradation temperature of 266–272°C in high yields. The radical polymerizations of the macromonomers with styrene (ST) or methyl methacrylate (MMA) were performed in THF at 60°C to give the corresponding copolymers. The obtained copolymers exhibited higher glass transition temperatures than those of poly(ST) and poly(MMA).

KEY WORDS Macromonomer / Maleimide Polymer / Radical Polymerization / Glass Transition Temperature / Thermal Stability /

Since Searle¹ first reported on synthesis of *N*-substituted maleimide (RMI) in 1948, a large number of investigators have extensively synthesized and polymerized many kind of RMI.² RMI implies characteristic polymerizability and copolymerizability because RMI is one of 1,2-disubstituted ethylene type monomers, and has a cyclic structure with two carbonyl groups. In particular, the main chain of RMI polymer is so rigid that RMI can become important reagents to improve thermal stability for common vinyl polymers and resins.³ In all poly(RMI)s, poly(*N*-cyclohexylmaleimide), poly(CHMI) is useful an additive to improve heat resistance common vinyl polymers.⁴ *N*-Phenylmaleimide (PhMI) and *N*-(*p*-hydroxyphenyl)maleimide are applied to ABS⁵ and phenol resin,⁶ respectively. RMI bearing functional groups, *i.e.*, a carboxyl group,⁷ perfluoroalkyl groups⁸ and long chain alkyl groups,⁹ cyclododecyl,¹⁰ aryl with amide groups¹¹ as *N*-substituent have been investigated. However, there have been no reports on synthesis and polymerizabilities of macromonomers derived from poly(RMI)s.

Generally, macromonomers are polymerized and copolymerized with ordinary vinyl monomers to form the corresponding star-like or comb-like polymers and graft copolymers, respectively. Particularly synthesis of graft-type polymers by use of macromonomer methods is useful for controlled side chain length of graft units. Generally, macromonomers are synthesized from polymers with a reactive group at the chain end and compounds with a polymerizable double bond and reactive functional group such as methacryloyl chloride and glycidyl methacrylate. From this point of view, many papers were reported so far.^{12–16}

This paper describes synthesis of macromonomers derived from methacryloyloxyethyl isocyanate (MOI) and poly(CHMI) and poly(PhMI). The poly(RMI) macromonomers are radically polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) to afford

the corresponding graft copolymers, as shown in Scheme 1. Thermal stability for the graft polymers and copolymers are discussed, as compared with those for poly(RMI) and RMI copolymers reported previously.^{11,17}

There are some articles on polymerizations of monomers prepared from MOI and alcohol and amine derivatives.^{18,19} Lately we prepared macromonomers from MOI and methacryloyloxyethyl phosphorylcholine (MPC).²⁰

EXPERIMENTAL

Poly(RMI) Macromonomer. Poly(RMI) macromonomers were synthesized from MOI and poly(RMI), as shown in Scheme 2. A typical procedure of macromonomer is as follows.

CHMI Prepolymers (PreCH-1 and PreCH-2). Radical polymerization of CHMI (1.0 g, 5.58 mmol) was performed in a sealed glass tube under nitrogen atmosphere using 4,4'-azobis(cyanopentanoic acid) (ACPA, 0.079 g, 0.28 mmol) in tetrahydrofuran (THF) (3 mL) for 24 h at 60°C to give CHMI prepolymer. The product was filtered and reprecipitated from the THF solution into excess methanol twice. The resulting product was collected and dried under reduced pressure for two days to afford CHMI prepolymer containing a carboxylic acid group at the chain end (PreCH-1). The polymerization of CHMI was carried out with azobisisobutyronitrile (AIBN) and 3-mercaptopropionic acid (3-MPA) as a chain transfer reagent in THF at 60°C for 24 h to give CHMI prepolymer with a thioethylcarboxylic acid group (PreCH-2).

PhMI Prepolymers (PrePh-1 and PrePh-2). PhMI prepolymers with a carboxylic acid group (PrePh-1) and with a thioethylcarboxylic acid group (PrePh-2) at the chain end were prepared, according to the same method as that of preCH-1 and PreCH-2.

Poly(CHMI) Macromonomer (PCH-1 and PCH-2). A mixture of the prepolymer (PreCH-1 or PreCH-2) (2.5 g), MOI (0.5 g, 3.2 mmol) and di-*n*-butyltindilaurate

[†]To whom correspondence should be addressed (Tel & Fax: +81-836-85-9281, E-mail: oishi@po.cc.yamaguchi-u.ac.jp).

Scheme 1.

Scheme 2.

(DBTDL) (20 mg) in THF (25 mL) was stirred for 24 h at 30°C. The reaction mixture was concentrated, followed by pouring excess methanol to precipitate a crude macromonomer, which was purified by reprecipitation from the THF solution to excess methanol twice to obtain

pure poly(CHMI) macromonomers (PCH-1 and PCH-2). *PCH-1*: $M_n = 2200$, $M_w/M_n = 1.08$, yield 93%, ^1H NMR (δ , ppm from TMS in CDCl_3): 6.11 (s, 1H, (*trans*) $\text{CH}_2=\text{C}$), 5.64 (s, 1H, (*cis*) $\text{CH}_2=\text{C}$), 4.77 (s, 1H, HN-CO), 4.32 (t, $J = 5.60$ Hz, 2H, $\text{H}_2\text{C}-\text{O}$), 4.18–2.50 (1H, HC-C in polymer unit and 2H, CH-CH in polymer unit), 3.60 (q, $J = 6.93$ Hz, 2H, $\text{H}_2\text{C}-\text{NH}$), 2.35–0.75 (10H, cyclohexyl group in polymer unit), 2.05 (s, 3H, $=\text{C}(\text{CH}_3)-$). ^{13}C NMR (δ , ppm from TMS in CDCl_3): 177.8–175.9 (N-C=O in polymer unit), 167.9 (O=C-O), 158.5 (O=C-NH), 136.3 ($=\text{C}<$), 125.9 ($\text{CH}_2=$), 64.4 ($\text{H}_2\text{C}-\text{O}$), 53.2–52.2 (HC in cyclohexyl group in polymer unit), 46.5–42.6 (HC-CH in polymer unit), 39.8 ($\text{H}_2\text{C}-\text{NH}$), 30.0–25.4 (cyclohexyl group in polymer unit), 18.8 ($=\text{C}(\text{CH}_3)-$). *PCH-2*: $M_n = 1980$, $M_w/M_n = 1.13$, yield 90%. ^1H NMR (δ , ppm from TMS in CDCl_3): 6.11 (s, 1H, (*trans*) $\text{CH}_2=\text{C}$), 5.69 (s, 1H, (*cis*) $\text{CH}_2=\text{C}$), 4.88 (s, 1H, HN-CO), 4.35 (t, $J = 5.60$ Hz, 2H, $\text{H}_2\text{C}-\text{O}$), 4.20–2.60 (1H, HC-C in polymer unit and 2H, CH-CH in polymer unit), 3.60 (q, $J = 6.93$ Hz, 2H, $\text{H}_2\text{C}-\text{NH}$), 2.38–0.85 (10H, cyclohexyl group in polymer unit), 2.05 (s, 3H, $=\text{C}(\text{CH}_3)-$). ^{13}C NMR (δ , ppm from TMS in CDCl_3): 177.7–175.5 (N-C=O in polymer unit), 167.9 (O=C-O), 158.7 (O=C-NH), 136.4 ($=\text{C}<$), 126.3 ($\text{CH}_2=$), 64.3 ($\text{H}_2\text{C}-\text{O}$), 52.7–52.2 (HC in cyclohexyl group in polymer unit), 46.5–42.6 (HC-CH in polymer unit), 39.5 ($\text{H}_2\text{C}-\text{NH}$), 29.4–25.4 (cyclohexyl group in polymer unit), 18.8 ($=\text{C}(\text{CH}_3)-$).

Poly(PhMI) Macromonomer (PPh-1 and PPh-2). poly-(PhMI) macromonomers (PPh-1 and PPh-2) were synthesized by the same procedure as that of PCH-1 and PCH-2. *PPh-1*: $M_n=1900$, $M_w/M_n=1.20$, yield 90%, ^1H NMR (δ , ppm from TMS in CDCl_3): 7.98–6.35 (5H, phenyl group in polymer unit), 6.11 (s, 1H, (*trans*) $\text{CH}_2=$), 5.64 (s, 1H, (*cis*) $\text{CH}_2=\text{C}$), 4.80 (s, 1H, HN-CO), 4.50

Table I. Polymerizations of CHMI and PhMI at 60 °C for 24 h^a

Run	Monomer	Initiator ^b	Chain transfer ^c agent	Yield ^d	M_n^e	M_w/M_n^e
		mol%	mol%	%		
1	CHMI	ACPA(5)	None	80	1900	1.33
2	CHMI	AIBN(5)	3-MPA(10)	95	1760	1.27
3	PhMI	ACPA(5)	None	85	1750	1.25
4	PhMI	AIBN(5)	3-MPA(10)	85	1010	1.46

^a CHMI, cyclohexylmaleimide; PhMI, phenylmaleimide; monomer, 1.0 g; solv., THF, 3 mL. ^b ACPA, 4,4'-azobiscyanopentanoic acid; AIBN, 2,2'-azobisisobutyronitrile. ^c 3-MPA, 3-mercaptopropionic acid. ^d Methanol insoluble. ^e By GPC with polystyrene standard.

Table II. Syntheses of macromonomers^a

Run	Prepolymer ^b	Macromonomer ^c	Yield ^d	M_n^e	M_w/M_n^e	Vinyl group ^f
			%			
1	PreCH-1	PCH-1	93	2200	1.08	1.15
2	PreCH-2	PCH-2	90	1980	1.13	1.26
3	Pre Ph-1	PPh-1	90	1900	1.20	1.13
4	Pre Ph-2	PPh-2	93	1240	1.38	1.10

^a MOI, 2-methacryloyloxyethyl isocyanate, 0.5 g; Prepolymer, 2.5 g; di-*n*-butyltin dilaurate(DBTDL), 20 mg; solv., THF, 25 mL. ^b See Table I. ^c See Scheme 2. ^d Methanol insoluble. ^e By GPC with polystyrene standard. ^f Piece of vinyl group per a polymer chain, calculated by ¹H NMR.

—2.80 (1H, HC—C in polymer unit and 2H, CH—CH in polymer unit), 4.32 (t, J = 5.60 Hz, 2H, H₂C—O), 3.60 (q, J = 6.93 Hz, 2H, H₂C—NH), 2.05 (s, 3H, =C(CH₃)—). ¹³C NMR (δ , ppm from TMS in CDCl₃): 176.4—175.2 (N—C = O in polymer unit), 167.4 (O=C—O), 158.2 (O=C—NH), 135.9 (=C<), 131.4—126.1 (phenyl group in polymer unit), 125.9 (CH₂=), 63.7 (H₂C—O), 39.8 (H₂C—NH), 18.8 (=C(CH₃)—). *PPh-2*: M_n = 1240, M_w/M_n = 1.38, yield 93%, ¹H NMR (δ , ppm from TMS in CDCl₃): 7.98—6.35 (5H, phenyl group in polymer unit), 6.11 (s, 1H, (*trans*) CH₂ =), 5.64 (s, 1H, (*cis*) CH₂ = C), 4.80 (s, 1H, HN—CO), 4.50—2.80 (1H, HC—C in polymer unit and 2H, CH—CH in polymer unit), 4.32 (t, J = 5.60 Hz, 2H, H₂C—O), 3.60 (q, J = 6.93 Hz, 2H, H₂C—NH), 2.05 (s, 3H, =C(CH₃)—). ¹³C NMR (δ , ppm from TMS in CDCl₃): 176.4—174.2 (N—C = O in polymer unit), 168.0 (O=C—O), 158.1 (O=C—NH), 136.4 (=C<), 131.4—126.5 (phenyl group in polymer unit), 126.3 (CH₂=), 64.6 (H₂C—O), 40.2 (H₂C—NH), 18.8 (=C(CH₃)—).

Comonomer and Other Materials

PhMI and CHMI were synthesized from maleic anhydride and the corresponding amine, according to the usual method.^{1,21} PhMI mp 91.0 °C and CHMI mp 89.0 °C. ST and MMA were purified by the usual methods.²² AIBN and ACPA were purified by usual methods. Solvents, THF and methanol were purified by usual methods.

Polymerization

Radical polymerizations of the macromonomers were carried out with the initiator in a sealed glass tube at 60 °C. After polymerization for given time, precipitating product in the tube was filtered off and washed with THF to exclude the monomer completely. The polymer was filtered, purified by reprecipitation from the THF solution into excess mixture of methanol and THF (8/2: v/v), and dried under reduced pressure for 2 days.

Radical copolymerization of the macromonomer with ST or MMA was performed with AIBN at 60 °C similarly.

The composition of the copolymer was determined from ¹H NMR spectra.

Measurements

Gel permeation chromatography (GPC) measurement of polymers was accomplished on a LC-10 AS (Shimadzu) equipped with UV detector SPD-A (Shimadzu) using THF as eluent at 50 °C. Four GPC columns HSG-10, 15, 20, 40H (Shimadzu) were connected in series, and molecular weight was calibrated with standard polystyrene. ¹H and ¹³C NMR spectra of polymers were measured in chloroform-*d* at room temperature in the presence of tetramethylsilane (TMS) as an internal standard using a JEOL EX-270 (¹H, 270 MHz, ¹³C, 68.7 MHz) spectrometer. IR spectra were recorded using Shimadzu FT-IR 8100 A. Thermal stability was measured by a differential scanning calorimeter with a SSC/5200 (Seiko) and Shimadzu DSC-50.

RESULTS AND DISCUSSION

Synthesis of Poly(RMI) Macromonomers

Table I summarizes the result of the polymerization of CHMI and PhMI in THF at 60 °C for 24 h. The polymerizations proceeded homogeneously throughout. Methanol-insoluble poly(CHMI) and poly(PhMI) were obtained in high yields and had number-average molecular weight (M_n) of 1010—1900 and polydispersity (weight-average-molecular weight (M_w)/ M_n) 1.25—1.46, respectively. These M_w/M_n 's were relatively small. It is difficult to explain the reason clearly. But it is considered that THF is good solvent for the polymerization of RMI and that a mixture of THF and methanol is effective for purification of oligo(RMI) using reprecipitation method.

Table II depicts the result of the synthesis of poly-(RMI) macromonomer. No reaction occurred without di-*n*-butyltin dilaurate (DBTDL) as catalyst. The macromonomers were obtained in quantitative yields and exhibited M_n of 1240 to 2200, which were almost equal

Table III. Polymerizations of macromonomer^a

Run	Macromonomer	Yield ^d	T_g^c	T_d^c
		%	°C	°C
1	PCH-1	96.0	—	268
2	PCH-2	92.6	—	266
3	PPh-1	98.5	—	270
4	PPh-2	94.0	—	272

^a Monomer, 0.5 g; solv., THF, 3 mL; initiator, AIBN, 0.03 mol L⁻¹; time, 24 h; temp, 60°C. ^b THF insoluble. ^c By TG-DSC; under N₂.

Figure 1. ¹H NMR spectrum of PCH-1 in CDCl₃.

to the sum of M_n for carboxyl group-terminated poly(RMI) ($M_n = 1010$ to 1900) and MOI ($M_w = 155.15$). M_w/M_n of 1.08–1.38 became smaller than those of prepolymers. This may be due to further removal of oligomers with lower M_n since the macromonomers were recovered by reprecipitation method. Figure 1 shows typical ¹H NMR spectrum of macromonomer.

The number of vinyl groups in the macromonomers was 1.10 to 1.26, as shown in Table II, which were calculated from the ratios of integration values for vinyl protons and alkyl protons in ¹H NMR spectra of poly(CHMI) macromonomers (PCH-1 and PCH-2). That is, the macromonomers contains a little amount of oligomer with two MOI units. In IR charts of poly(CHMI) macromonomers, new peaks due to amide groups formed from isocyanate in MOI and COOH in poly(CHMI) were observed at 1620 and 3420 cm⁻¹, and the peaks due to OH at 3600 cm⁻¹ of carboxylic acid disappeared, as shown in Figure 2.

Polymerization of Poly(RMI) Macromonomers

The results of the polymerization of poly(RMI) macromonomers are summarized in Table III. The polymerization of poly(RMI) macromonomers proceeded heterogeneously, that is, homogeneous polymerization solution became heterogeneous and some of polymers were precipitated while the polymerization proceeded. The polymers were quantitatively obtained and not soluble in any solvents, suggesting that the polymers were network structures, *i.e.*, three-dimension polymer. This indicates that some of macromonomers consist of poly(RMI) with two vinyl groups in the polymer chain, as shown in Table II. In addition, filtrate after collecting the polymers was concentrated with an evaporator to afford nothing. Thus, the macromonomers gave quantitatively corresponding polymers.

Figure 2. IR spectra of PreCH-1 and PCH-1.

Tables IV and V summarize the results of radical copolymerizations of poly(CHMI) and poly(PhMI) macromonomers (PCH-1, PPh-1, M_1) with ST (M_2) or MMA (M_2) in THF at 60°C. The polymerization proceeded homogeneously throughout. When the polymerization time was short (0.5 to 2 h), polymer yields were low, but the contents of the macromonomer (M_1 units) increased with the macromonomer feed (runs 1–6, 13–18 in Tables IV and V). The copolymer-composition curves are shown in Figure 3, according to the composition of copolymer in low yield (runs 1–6 and 13–18 in Tables IV and V). When the polymerization time was long (24 h, runs 7–12, 19–24 in Tables IV and V), the polymer yields enhanced but the content of M_1 units was scarcely varied by the monomer feeds. This suggests that the vinyl monomer, ST and MMA, was polymerized itself after the macromonomer (M_1) was completely consumed.

Tables VI and VII show the result of the polymerization of PCH-2 (M_1) and PPh-2 (M_1) with ST (M_2) and MMA (M_2) in THF at 60°C, respectively. The copolymerization proceeded homogeneously throughout. When the concentration of M_1 macromonomers varied from 0.3 to 4.3 mol% (5 to 30 wt%), the M_1 macromonomer content in the copolymer were 0.9 to 7.8 mol%. Generally, the M_1 contents in the ST systems were higher than those in MMA systems.

Table IV. Radical copolymerizations of PCH-1 (M_1) with ST (M_2) and MMA (M_2) in THF (4 mL) at 60 °C^a

Run	M_2	M_1 in monomer	Polym. time	Yield ^b	M_1 in copolymer ^c	T_g^d	T_d^d
		mol% (wt%)			mol%	°C	°C
1	ST	0.2 (5)	2	4	3.1	82	258
2	ST	0.4 (10)	2	7	4.1	98	270
3	ST	0.7 (15)	2	11	7.0	136	270
4	ST	1.0 (20)	0.5	10	9.3	172	272
5	ST	1.4 (25)	1	14	16.2	—	266
6	ST	1.8 (30)	0.5	15	26.7	—	268
7	ST	0.2 (5)	24	36	2.8	105	266
8	ST	0.4 (10)	24	40	2.6	150	270
9	ST	0.7 (15)	24	43	2.3	140	264
10	ST	1.0 (20)	24	47	2.6	128	264
11	ST	1.4 (25)	24	51	2.5	154	260
12	ST	1.8 (30)	24	50	2.8	164	260
13	MMA	0.2 (5)	4	35	0.6	136	262
14	MMA	0.4 (10)	2	33	1.2	148	264
15	MMA	0.7 (15)	2	29	2.1	190	264
16	MMA	1.0 (20)	1	22	6.8	210	266
17	MMA	1.3 (25)	1	27	8.9	224	266
18	MMA	1.7 (30)	1	29	10.3	252	266
19	MMA	0.2 (5)	24	61	0.2	138	246
20	MMA	0.4 (10)	24	51	0.2	144	246
21	MMA	0.7 (15)	24	62	0.3	144	254
22	MMA	1.0 (20)	24	81	0.4	144	250
23	MMA	1.3 (25)	24	93	0.6	148	258
24	MMA	1.7 (30)	24	61	0.7	192	260

^a Initiator, 2,2'-azobisisobutyronitrile, 0.03 mol L⁻¹. ^b Methanol/THF(8/2) insoluble. ^c By ¹H NMR. ^d By TG-DSC; under N₂.

Table V. Radical copolymerizations of PPh-1 (M_1) with ST (M_2) and MMA (M_2) in THF (4 mL) at 60 °C^a

Run	M_2	M_1 in monomer	Polym. time	Yield ^b	M_1 in copolymer ^c	T_g^d	T_d^d
		mol% (wt%)			mol%	°C	°C
1	ST	0.3 (5)	2	6	1.3	90	264
2	ST	0.7 (10)	2	7	2.1	160	272
3	ST	1.1 (15)	2	10	7.2	168	272
4	ST	1.5 (20)	1	12	9.7	190	262
5	ST	2.0 (25)	0.5	11	15.0	—	270
6	ST	2.6 (30)	0.5	13	20.1	—	268
7	ST	0.3 (5)	24	40	1.8	115	280
8	ST	0.7 (10)	24	43	2.4	130	282
9	ST	1.1 (15)	24	40	2.6	138	280
10	ST	1.5 (20)	24	25	3.0	132	278
11	ST	2.0 (25)	24	33	5.6	—	270
12	ST	2.6 (30)	24	41	5.0	—	268
13	MMA	0.3 (5)	3	27	0.8	105	264
14	MMA	0.7 (10)	3	40	1.2	144	268
15	MMA	1.0 (15)	3	36	1.4	145	266
16	MMA	1.5 (20)	2	34	2.0	196	266
17	MMA	1.9 (25)	2	42	2.2	196	268
18	MMA	2.5 (30)	0.5	35	6.6	222	262
19	MMA	0.3 (5)	24	60	2.0	146	262
20	MMA	0.7 (10)	24	65	2.6	142	268
21	MMA	1.0 (15)	24	69	2.3	150	270
22	MMA	1.5 (20)	24	67	2.3	130	262
23	MMA	1.9 (25)	24	66	3.2	138	270
24	MMA	2.5 (30)	24	90	2.8	130	268

^a Initiator, 2,2'-azobisisobutyronitrile, 0.03 mol L⁻¹. ^b Methanol/THF(8/2) insoluble. ^c By ¹H NMR. ^d By TG-DSC; under N₂.

Thermal Property of the Polymers

Figure 4 depicts typical TG and DSC curves of poly(PCH-1) (run 1 in Table III). Only initial decomposition temperature (T_d) was observed at 268 °C and no glass transition temperature (T_g) was detected in the curves. Other poly(macromonomer)s exhibited similar tendency. T_d was 266 to 272 °C, which were relatively low, as compared with over 360 °C for poly(PhMI).^{23,24}

Figure 5 shows typical TG and DSC curves of poly-

(PCH-1-co-ST) (run 12 in Table IV). There was little difference between DSC and TGA curves for ST and MMA copolymers. T_g for poly(PCH-1-co-ST) and poly(PCH-1-co-MMA) were 82 to 172 °C and 136 to 252 °C, respectively. T_d for all copolymers was approximately 260 °C. T_d for poly(ST) and poly(MMA) were 282 and 214, respectively.¹¹ Thus, thermal stability for poly(MMA) was improved by the copolymerization with macromonomers. T_g for poly(PCH-2-co-ST) and poly(PCH-2-co-MMA)

Table VI. Radical copolymerizations of PCH-2 (M_1) with ST (M_2) and MMA (M_2) in THF (4 mL) at 60°C^a

Run	M_2	M_1 in monomer mol% (wt%)	Polym. time h	Yield ^b %	M_1 in copolymer ^c mol%	T_g^d °C	T_d^d °C
1	ST	0.3 (5)	24	39	3.2	146	290
2	ST	0.7 (10)	24	39	3.2	139	280
3	ST	1.1 (15)	24	40	3.5	142	272
4	ST	1.5 (20)	24	40	3.6	140	270
5	ST	2.0 (25)	24	44	3.6	150	262
6	ST	2.6 (30)	24	50	4.3	168	272
7	MMA	0.3 (5)	24	55	1.2	138	242
8	MMA	0.7 (10)	24	60	1.2	140	252
9	MMA	1.0 (15)	24	67	0.9	140	258
10	MMA	1.4 (20)	24	65	5.6	155	265
11	MMA	1.9 (25)	24	50	3.7	148	258
12	MMA	2.5 (30)	24	52	2.3	132	262

^a Initiator, 2,2'-azobisisobutyronitrile, 0.03 mol L⁻¹. ^b Methanol/THF(8/2) insoluble. ^c By ¹H NMR. ^d By TG-DSC; under N₂.

Table VII. Radical copolymerizations of PPh-2 (M_1) with ST (M_2) and MMA (M_2) in THF (4 mL) at 60°C^a

Run	M_2	M_1 in monomer mol% (wt%)	Polym. time h	Yield ^b %	M_1 in copolymer ^c mol%	T_g^d °C	T_d^d °C
1	ST	0.5 (5)	24	61	4.1	110	268
2	ST	1.1 (10)	24	60	5.3	150	280
3	ST	1.8 (15)	24	57	6.5	142	260
4	ST	2.5 (20)	24	58	6.6	146	260
5	ST	3.4 (25)	24	54	7.8	162	258
6	ST	4.3 (30)	24	60	7.4	160	262
7	MMA	0.5 (5)	24	38	1.3	138	262
8	MMA	1.1 (10)	24	38	2.2	136	264
9	MMA	1.7 (15)	24	39	3.8	142	260
10	MMA	2.4 (20)	24	39	1.9	146	260
11	MMA	3.2 (25)	24	39	2.7	162	258
12	MMA	4.1 (30)	24	48	2.8	160	258

^a Initiator, 2,2'-azobisisobutyronitrile, 0.03 mol L⁻¹. ^b Methanol/THF(8/2) insoluble. ^c By ¹H NMR. ^d By TG-DSC; under N₂.

Figure 3. Copolymer composition curves for (○) poly(PCH-1-co-ST), (●) poly(PCH-1-co-MMA), (▽) poly(PPh-1-co-ST), and (▼) poly(PPh-1-co-MMA).

were 139 to 168°C and 132 to 155°C, respectively. T_d for both systems was similar to those for PCH-1 systems. In general, T_g is relatively low because polymer with sul-

Figure 4. TG and DSC curves of poly(PCH-1) (run 1 in Table III).

fide bond is flexible.²⁵ In this study, T_g for poly(CH-2) were similar to those for poly(PCH-1) though copolymer obtained from PCH-2 contains sulfide bond. T_g for poly(PPh-1-co-ST) and poly(PPh-1-co-MMA) were 90 to 190 and 105 to 222°C, respectively. T_d for both systems was approximately 270°C. T_g for poly(PPh-2-co-ST) and poly(PPh-2-co-MMA) were 110 to 162 and 136 to 162, respectively, and T_d for both systems was about 260°C. PCH and PPh systems exhibited similar results. Accordingly, no large difference was observed for use of PCH and PPh.

Figure 5. TG and DSC curves of poly(PCH-1-co-ST) (run 12 in Table IV).

Figure 6. Relationship between T_g of copolymer and content (mol%) of macromonomer in copolymer: (○) poly(PCH-1-co-ST)s, (●) poly(PCH-1-co-MMA)s, (▽) poly(PPh-1-co-ST)s, (▼) poly(PPh-1-co-MMA)s, (□) poly(ST), and (■) poly(MMA).

Figure 6 depicts relationship between T_g of copolymer and contents of the monomeric units of macromonomer in copolymer. In ST and MMA systems, T_g of the copolymers increased with increase of macromonomer units.

Figure 7 shows relationships between T_g of copolymer and contents of the RMI units in copolymer. T_g for poly(ST) and poly(CHMI) reported previously^{17,25} are also indicated. In the ST systems, T_g for poly(PCH-1-co-ST) were lower than those for poly(CHMI-co-ST), and poly(PPh-1-co-ST) showed similar tendency. However, in the MMA systems, poly(PCH-1-co-MMA) exhibited higher T_g than poly(CHMI-co-MMA). Furthermore, poly(PPh-1-co-MMA) showed similar tendency. Our macromonomers were found to be efficient reagent for improvement of thermal stability for poly(MMA).

CONCLUSIONS

1. Poly(RMI) macromonomers were first successful to be synthesized from poly(CHMI) and poly(PhMI).

Figure 7. Relationship between T_g of copolymer and content (mol%) of RMI unit in copolymer: (○) poly(PCH-1-co-ST)s, (●) poly(PCH-1-co-MMA)s, (▽) poly(PPh-1-co-ST)s, (▼) poly(PPh-1-co-MMA)s, (◇) poly(CHMI-co-ST)s, (◆) poly(CHMI-co-MMA)s, (□¹¹, □¹⁷) poly(PhMI-co-ST)s, and (■¹¹, ■¹⁷) poly(PhMI-co-MMA)s.

2. Polymerizations of poly(RMI) macromonomers were carried out to obtain the corresponding polymers, which were insoluble in organic solvents.
3. Copolymerizations of poly(RMI) macromonomers with ST and MMA were performed to give corresponding copolymers with thermal stability.

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