Polymer 51 (2010) 397–402

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Radical copolymerization of methyl 2-norbornene-2-carboxylate and 2-phenyl-2-norbornene with styrene, alkyl acrylate, and methyl methacrylate: Facile incorporation of norbornane framework into polymer main chain and its effect on glass transition temperature

Eiji Ihara [a,*], Shingo Honjyo [a], Koh Kobayashi [a], Satoru Ishii [a], Tomomichi Itoh [a], Kenzo Inoue [a,*], Hikaru Momose [b], Mitsufumi Nodono [c]

[a] *Department of Material Science and Biotechnology, Graduate School of Science and Engineering, Venture Business Laboratory, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan*

[b] *Research and Development Administration Department, Mitsubishi Rayon Co. Ltd., 1-6-41 Konan, Minato-ku, Tokyo 108-8506, Japan*

[c] *Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd. Otake, Hiroshima 739-0693, Japan*

ARTICLE INFO

Article history:
Received 3 August 2009
Received in revised form
28 November 2009
Accepted 6 December 2009
Available online 16 December 2009

Keywords:
2-Substituted norbornene
Radical copolymerization
T_g-raising effect

ABSTRACT

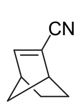
Radical copolymerization behavior of methyl 2-norbornene-2-carboxylate **1** and 2-phenyl-2-norbornene **2** was investigated. Radical copolymerization of **1** and **2** with styrene, alkyl acrylate, and methyl methacrylate in a variety of monomer combinations afforded copolymers, whose main chains consisted of norbornane framework. Relative monomer reactivity ratios for the copolymerization of **1** and **2** with *n*-butyl acrylate (*n*-BA) were determined by the Fineman–Ross method. Temperature-modulated DSC analysis for poly(**1** or **2**-*co*-*n*-BA)s revealed remarkable T_g-raising effect of incorporation of norbornane framework into the polymer main chain, compared to that effect of styrene repeating unit.

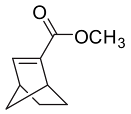
1. Introduction

Incorporation of norbornane framework into polymer main chains by vinyl polymerization of norbornene [1] is a highly effective method for improving physical properties of polymers, such as thermal stability, transparency, and birefringence, etc. For example, the strategy has been executed by copolymerization of norbornene with ethylene [2] and propylene [3] initiated by Ti-complexes, with alkyl acrylates mediated by Cu-complexes [4], and with styrene initiated by Ni- and Pd-complexes [5], resulting in the formation of copolymers with norbornane framework in their main chains. Whereas an unsubstituted C=C in norbornene was polymerized in the above examples, a patent [6] reported that a CN-substituted C=C in a norbornene derivative (2-norbornene-2-carbonitrile) can be radically copolymerized with methyl methacrylate (MMA) to give polyMMA-based copolymers bearing norbornane framework in the main chain. In 2-norbornene-2-carbonitrile, the reactivity of C=C is fundamentally altered by the direct substitution by the electron-withdrawing cyano group, resulting in the higher radical polymerizability of the monomer.

In that context, we have been interested in modifying the reactivity of norbornene by attaching other substituents than CN directly to its C=C, and have found that an ester-substituted norbornene, methyl 2-norbornene-2-carboxylate **1**, can be copolymerized with alkyl acrylates, to afford poly(alkyl acrylate)-based copolymers having norbornane framework in their main chains [7].

In this paper, we will report copolymerization of **1** with a variety of new comonomer combinations with styrene, alkyl acrylate, and methyl methacrylate, and similar copolymerization of a phenyl-substituted norbornene, 2-phenyl-2-norbornene **2** (Chart 1). In addition, the effect of incorporating norbornane framework into the


2-norbornene-2-carbonitrile


1

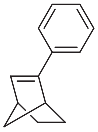

2

Chart 1. 2-Substituted Norbornene Derivatives.

---

* Corresponding authors. Tel./fax: +81 89 927 8547.
E-mail address: ihara@eng.ehime-u.ac.jp (E. Ihara).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.12.008

main chain of poly(*n*-butyl acrylate) is investigated by comparing T_g of the copolymers determined by temperature-modulated DSC.

2. Experimental section

2.1. Materials

Toluene and Et_2O were dried over sodium and CaH_2, respectively, and distilled before use. Styrene (Nacalai, 99%) and MMA (Nacalai, >99.0%) were dried over CaH_2 and distilled before use. Alkyl acrylates (EA and *n*-BA, Nacalai, 99%) were treated with 1 N NaOH aqueous solution, dried over Na_2SO_4, and used without further purification. 1,1′-azobis(cyclohexanecarbonitrile) (VAZO-88, Wako, 95%), dicumyl peroxide (DCPO, Nacalai, 98%), norcamphor (Aldrich, 98%), and $KHSO_4$ (Kanto Chemical, 98%) were used as received. PhBr (Nacalai, 99%) was dried over CaH_2 and used without further purification. Methyl 2-norbornene-2-carboxylate **1** was prepared by a procedure reported in our previous publication [7].

2.2. Measurements

^1H (400 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($CDCl_3$) at 50 °C. For the measurement, 5 mg of a sample was dissolved in 0.6 mL of $CDCl_3$. For quantitative determination of copolymer compositions from the signal intensity, the longitudinal relaxation time (T_1) of major signals was determined for representative samples in Table 1–6, and the repetition delay was set to more than 5 times of the longest T_1 observed in each sample; the actual repetition delay was 8 s for the samples in Tables 1, 3, and 5, 12 s for those in Table 2 and runs 1–4 in Table 6, and 15 s for those in Table 4 and runs 5–7 in Table 6. The details for calculation of copolymer composition from signal intensity are described in Supplementary Contents.

Molecular weights (M_n) and molecular weight dispersities (M_w/M_n) were measured by means of size exclusion chromatography (SEC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(MMA) standards. The column used for the SEC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 600 K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20 K for polystyrene), and poly(MMA) standards (Shodex M-75, $M_p = 212000$, $M_w/M_n = 1.05$, $M_p = 50000$, $M_w/M_n = 1.02$, $M_p = 22600$, $M_w/M_n = 1.02$, $M_p = 5720$, $M_w/M_n = 1.06$, $M_p = 2400$, $M_w/M_n = 1.08$) and dibutyl sebacate (MW = 314.5) were used for the calibration.

Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70 K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 20 K for polystyrene), using $CHCl_3$ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

Table 1
Radical Copolymerization of Methyl 2-Norbornene-2-carboxylate (**1**) with Styrene[a].

Run	Feed ratio [**1**]/[St]	Temp °C	Yield (%)	M_n[b]	M_w/M_n[b]	Composition of **1** (mol%)[c]
1	1:3	100	33.3	6000	1.73	14
2	1:3	85	25.6	7400	1.64	15
3	1:2	100	26.6	4400	1.65	21
4	1:1	100	18.1	2600	1.62	33
5	2:1	100	13.3	2000	1.55	43

[a] Bulk for 13.5 h; initiator (I) = VAZO-88; total amount of monomers = 8.19 mmol, ([**1**] + [St])/[I] = 200.
[b] M_n and M_w/M_n were obtained by SEC calibration using standard PMMAs in THF solutions.
[c] Determined by ^1H NMR.

Table 2
Ternary Radical Copolymerization of Methyl 2-Norbornene-2-carboxylate (**1**), Styrene, and *n*-Butyl Acrylate (*n*-BA)[a].

Run	Feed ratio [**1**]/[St]/[*n*-BA] (mol% of **1**)	Yield (%)	M_n[b]	M_w/M_n[b]	Copolymer composition[c] [**1**]/[St]/[*n*-BA] (mol% of **1**)
1	1:3:1 (20%)	27.0	15500	1.67	0.02:2.3:1.0 (1%)
2	3:3:1 (43%)	21.6	3000	2.26	0.2:1.7:1.0 (7%)
3	1:1:1 (33%)	25.0	7900	1.76	0.1:1.2:1.0 (4%)
4	3:1:1 (60%)	15.2	3100	1.91	0.3:1.0:1.0 (13%)
5	1:1:3 (20%)	42.1	26100	1.72	0.3:1.0:1.8 (10%)
6	3:1:3 (43%)	28.8	6000	1.52	0.4:1.0:1.9 (12%)

[a] Bulk at 85° for 13.5 h; initiator (I) = VAZO-88; total amount of monomers = 8.19 mmol, ([**1**] + [St] + [*n*-BA])/[I] = 200.
[b] M_n and M_w/M_n were obtained by SEC calibration using standard PMMAs in THF solutions.
[c] Determined by ^1H NMR.

Temperature-modulated DSC analyses for poly(**1** or **2**-*co*-*n*-BA)s were carried out using TA Instruments DSC Q-100, under nitrogen atmosphere at a 4 °C/min heating rate with a modulating rate of 0.64 °C/60 s. T_gs for poly(St-*co*-*n*-BA)s in Table 6 were measured using Seiko DSC 6200, under nitrogen atmosphere at a 10 °C/min heating rate.

2.3. Preparation of 2-phenyl-2-norbornene (2)

This compound was prepared by following the procedure reported for the synthesis of 7-*syn*-chloro-2-phenylnorbornene from 7-*syn*-chloro-2-phenylnorbornene and PhLi [8]. Norcamphor and PhMgBr were used as starting materials for the preparation of **2**.

Under a nitrogen atmosphere, an Et_2O (20 mL) solution of norcamphor (5.00 g, 45.4 mmol) was placed in a round bottomed flask and cooled to 0 °C. After an Et_2O solution of PhMgBr (0.88 M, 56.7 ml, 49.9 mmol) was added to the solution, the mixture was stirred at 0 °C for 30 min and refluxed for 2 h. A cooled HCl aqueous solution (1 N, 60 mL) was added dropwise at room temperature, and the mixture was extracted with 50 mL of Et_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude 2-phenylnorbornanol (7.87 g), which was used for the next step without purification.

Under a nitrogen atmosphere, the crude 2-phenylnorbonanol (7.87 g) and $KHSO_4$ (6.29 g, 46.2 mmol) were placed in a round bottomed flask and was heated to 100 °C, at which temperature the mixture became viscous oil. After the mixture was stirred at 100 °C for 30 min, it was cooled to room temperature and 50 mL of cold water was added. The mixture was extracted with 50 mL of hexane and the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product, which was purified by column chromatography (eluent = hexane)

Table 3
Ternary Radical Copolymerization of Methyl 2-Norbornene-2-carboxylate (**1**), Methyl Methacrylate (MMA), and Ethyl Acrylate (EA)[a].

Run	Feed ratio [**1**]/[MMA]/[EA] (mol% of **1**)	Yield (%)	M_n[b]	M_w/M_n[b]	Copolymer composition[c] [**1**]/[MMA]/[EA] (mol% of **1**)
1	1:1:1 (33%)	32.9	18400	2.25	0.1:1:0.5 (6%)
2	1.5:1:2 (33%)	46.4	13600	2.53	0.8:1:1.2 (27%)
3	2:1:3 (33%)	39.6	19000	2.19	0.6:1:1.9 (17%)

[a] Bulk at 85° for 13.5 h; initiator (I) = VAZO-88; total amount of monomers = 8.19 mmol, ([**1**] + [MMA] + [EA])/[I] = 200.
[b] M_n and M_w/M_n were obtained by SEC calibration using standard PMMAs in THF solutions.
[c] Determined by ^1H NMR.

Table 4
Radical Copolymerization of 2-Phenyl-2-Norbornene (**2**) with Alkyl Acrylates (AA) by Azo-initiators[a].

Run	AA	Feed ratio [**2**]/[AA]	Initiator	Solvent	Temp °C	Yield (%)	M_n[b]	M_w/M_n[b]	Composition of **2**[c] (mol%)
1	*n*-BA	1:3	VAZO-88	bulk	110	51.4	8600	2.01	30
2	*n*-BA	1:2	VAZO-88	bulk	110	52.4	7400	1.97	32
3	*n*-BA	1:3	VAZO-88	bulk	100	37.5	9300	1.87	32
4	*n*-BA	1:3	VAZO-88	bulk	85	23.4	9600	1.72	35
5	EA	1:3	VAZO-88	bulk	85	32.6	4500	1.92	39
6	*n*-BA	1:5	DCPO	bulk	110	59.2	11400	2.01	18
7	*n*-BA	1:4	DCPO	bulk	110	60.3	12100	2.20	25
8	*n*-BA	1:3	DCPO	bulk	110	59.8	8000	2.27	30
9	*n*-BA	1:2	DCPO	bulk	110	42.7	8000	1.91	38
10	*n*-BA	1:1	DCPO	bulk	110	30.0	5200	1.91	48
11	*n*-BA	2:1	DCPO	bulk	110	34.0	1400	2.17	60

[a] For 13.5 h; total amount of monomers = 7.40 – 8.19 mmol, ([**2**] + [AA])/[I] = 200.
[b] M_n and M_w/M_n were obtained by SEC calibration using standard PMMAs in THF solutions.
[c] Determined by ^{1}H NMR.

afforded **2** as colorless liquid in a 58.2% total yield from norcamphor (4.49 g, 26.5 mmol). Spectral data for **2** have been reported in a literature [9].

2.4. General procedure for radical copolymerization

Under a nitrogen atmosphere, a mixture of monomers and an initiator was placed in a Schlenk tube. After the mixture was degassed by freeze-thaw three times, it was heated to 85, 100, or 110 °C and stirred at that temperature for 13.5 h. After volatiles were removed under reduced pressure, CHCl$_3$ (20 mL) and 1 N HCl aqueous solution was added, and the organic layer was separated by using a separatory funnel and washed with H$_2$O (50 mL). The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated to give a crude product, which was purified by using preparative recycling SEC to give a copolymer. Poly(**1**-*co*-St); ^{1}H NMR (400 MHz, CHCl$_3$) δ 6.0–7.5 (Ph), 0.2–4.0 (OCH$_3$, CH$_2$, CH in styrene main chain and norbornane framework); poly(**1**-*co*-St-*co*-*n*-BA); ^{1}H NMR (400 MHz, CHCl$_3$) δ 6.4–7.6 (Ph), 3.2–4.3 (O*CH$_2$*CH$_2$CH$_2$CH$_3$ and OCH$_3$ in **1**), 1.0–3.1 (CH$_2$, CH in styrene and *n*-BA main chain, OCH$_2$*CH$_2$CH$_2$*CH$_3$, and CH$_2$, CH in norbornane framework), 0.7–1.0 (OCH$_2$CH$_2$CH$_2$*CH$_3$*); poly(**1**-*co*-MMA-*co*-EA); ^{1}H NMR (400 MHz, CHCl$_3$) δ 3.9–4.3 (O*CH$_2$*CH$_3$), 3.4–3.8 (OCH$_3$ in MMA and **1**), 0.7–2.8 (CH$_2$, C–CH$_3$ in MMA, CH$_2$, CH in EA main chain, OCH$_2$*CH$_3$*, and CH$_2$, CH in norbornane framework); poly(**2**-*co*-*n*-BA); ^{1}H NMR (400 MHz, CHCl$_3$) δ 6.8–7.6 (Ph), 3.1–4.4 (O*CH$_2$*CH$_2$CH$_2$CH$_3$), 1.1–3.1 (CH$_2$, CH in *n*-BA main chain, OCH$_2$*CH$_2$CH$_2$*CH$_3$, and CH$_2$, CH in norbornane framework), 0.6–1.0 (OCH$_2$CH$_2$CH$_2$*CH$_3$*); poly(**2**-*co*-MMA-*co*-EA); ^{1}H NMR (400 MHz, CHCl$_3$) δ 6.8–8.1 (Ph), 3.8–4.5 (O*CH$_2$*CH$_3$), 3.2–3.8 (OCH$_3$), 0.3–3.2 (CH$_2$, C–CH$_3$ in MMA, CH$_2$, CH in EA main chain, OCH$_2$*CH$_3$*, CH$_2$, CH in norbornane framework).

Table 5
Ternary Radical Copolymerization of 2-Phenyl-2-Norbornene (**2**), Methyl Methacrylate (MMA), and Ethyl Acrylate (EA)[a].

Run	Feed ratio [**2**]/[MMA]/[EA] (mol% of **2**)	Yield (%)	M_n[b]	M_w/M_n[b]	Copolymer composition[c] [**2**]/[MMA]/[EA] (mol% of **2**)
1	1:1:1 (33%)	8.3	3400	1.76	0.7:1:0.7 (29%)
2	1.5:1:2 (33%)	13.0	4600	1.82	0.9:1:1.0 (31%)
3	2:1:3 (33%)	15.3	4400	1.84	1.3:1:1.4 (35%)

[a] Bulk at 85 °C for 13.5 h; initiator (I) = DCPO; total amount of monomers = 7.40 mmol, ([**2**] + [MMA] + [EA])/[I] = 200.
[b] M_n and M_w/M_n were obtained by SEC calibration using standard PMMAs in THF solutions.
[c] Determined by ^{1}H NMR.

3. Results and discussion

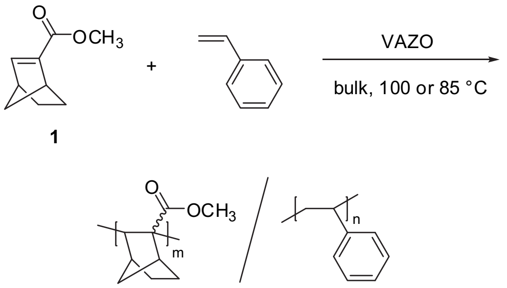
*3.1. Radical copolymerization of methyl 2-norbornene-2-carboxylate (**1**) with styrene*

In addition to the copolymerization of **1** with alkyl acrylates reported in our previous publication [7], we have found that radical copolymerization of **1** with styrene (St) proceeds by using 1,1′-azobis(cyclohexanecarbonitrile) (VAZO-88) as an initiator as summarized in Table 1. As described previously [7], the propagation of **1** should proceed in a normal 1,2-addition mode (Scheme 1), because the propagation at 2,7-positions reported for radical polymerization of unsubstituted-norbornene [10] should have an energetically unfavorable intermediate. For example, when the bulk copolymerization was conducted with a feed ratio of [**1**]/[St] = 1:3 at 100 °C, poly(**1**-*co*-St) with $M_n = 6000$ was obtained in a 33.3% yield (run 1). As shown in Fig. 1 for the sample obtained in run 4, very broad signals derived from both repeating units of **1** and styrene appear in its ^{1}H NMR, reflecting the highly rigid main chain structure partly due to the incorporation of the norbornane framework. In addition, probably because of ring current effect of phenyl groups in styrene repeating units, OCH$_3$ signals derived from **1** show complex appearance in a rather wide range of chemical shift, as usually observed in the case of poly(MMA-*co*-St)s obtained by conventional radical copolymerization. The composition of the repeating units can be estimated from the signal intensity ratio between the signals in aromatic region for Ph

Table 6
Glass Transition Temperature of Poly(M-*co*-*n*-BA) Measured by Temperature-modulated DSC.

Sample	Copolymer	M_n[a]	M_w/M_n[a]	Composition[b] (mol% of M)	T_g (°C)
1	poly(**1**-*co*-*n*-BA)	16900	2.73	22	−10
2	poly(**1**-*co*-*n*-BA)	12300	2.64	27	3
3	poly(**1**-*co*-*n*-BA)	6400	2.21	39	39
4	poly(**1**-*co*-*n*-BA)	7200	1.88	43	51
5	poly(**2**-*co*-*n*-BA)	29400	5.07	14	−18
6	poly(**2**-*co*-*n*-BA)	13100	1.92	31	37
7	poly(**2**-*co*-*n*-BA)	10500	1.46	44	110
8	poly(St-*co*-*n*-BA)	35900	8.82	21	−38[c]
9	poly(St-*co*-*n*-BA)	35300	13.4	30	−26[c]
10	poly(St-*co*-*n*-BA)	202000	6.33	56	12[c]

[a] M_n and M_w/M_n were obtained by SEC calibration using standard polyPMMAs in THF solutions.
[b] Determined by ^{1}H NMR.
[c] T_gs for samples 8–10 were determined by DSC measurement without temperature modulation.



Scheme 1. Radical Copolymerization of Methyl 2-Norbornene-2-carboxylate (**1**) with styrene.

group and those in 0.2–4.0 ppm for all the aliphatic Hs (See Supplementary Contents for the detail.). The thus determined composition of **1** in run 1 was 14 mol%. The copolymerization of **1** with styrene at 85 °C afforded a copolymer with a slightly higher M_n in a lower yield (run 2). When the feed ratio of [**1**]/[St] was changed from 1:2 to 2:1, the composition of **1** in the resulting copolymers increased from 21 to 43 mol%, with the decrease of yield and M_n (runs 3–5), which suggested that propagating chain end derived from **1** would be susceptible to termination and/or chain transfer although the exact mechanisms for the side reactions are unclear at present.

3.2. *Ternary radical copolymerization of methyl 2-norbornene-2-carboxylate (**1**), styrene, and n-butyl acrylate*

Because we have revealed that **1** can be copolymerized with both *n*-butyl acrylate (*n*-BA) [7] and styrene, we examined ternary radical copolymerization of **1**, styrene, and *n*-BA, by which incorporation of norbonane framework into poly(St-*co*-*n*-BA) would be achieved (Scheme 2). As summarized in Table 2, the ternary copolymerization was conducted, with the two different relative feed ratios of [**1**] to ([St] + [*n*-BA]) for three [St]/[*n*-BA] ratios of 3:1 (runs 1 and 2), 1:1 (runs 3 and 4), and 1:3 (runs 5 and 6). In each run, a copolymer consisting of the three repeating units was obtained in a rather low yield. The ^{1}H NMR-determined compositions of the copolymers indicated that whereas the [St]/[*n*-BA] ratio in the copolymer roughly corresponded to the feed ratio, the composition of **1** in the products was much lower than the feed ratio of **1**. In particular, reflecting the aforementioned low copolymerizability of **1** with styrene, the composition of **1** in run 1 is quite low. In addition, higher feed ratios of **1** brought about significant diminishing of both copolymer yield and M_n, as observed in the copolymerization of **1** with *n*-BA [7] and with styrene.

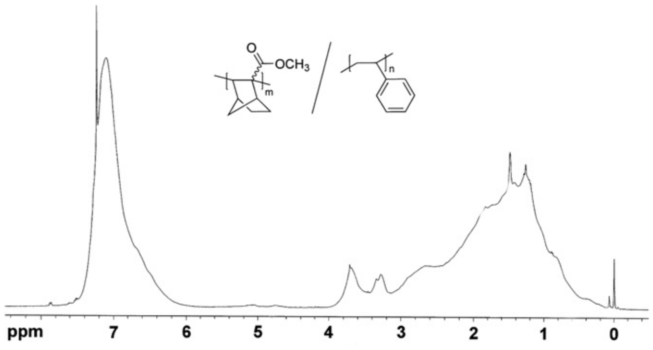
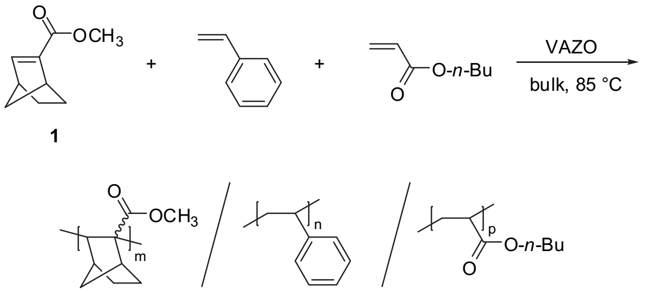


Fig. 1. ^{1}H NMR spectrum for poly(**1**-*co*-St) (run 4 in Table 1).



Scheme 2. Radical Copolymerization of Methyl 2-Norbornene-2-carboxylate (**1**), Styrene, and *n*-Butyl Acrylate.

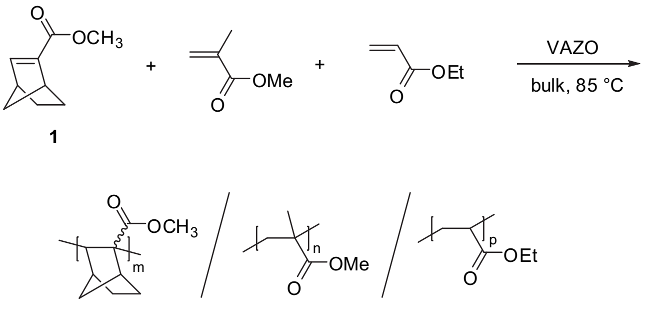
3.3. *Ternary radical copolymerization of methyl 2-norbornene-2-carboxylate (**1**), MMA, and ethyl acrylate*

Although copolymerization of **1** with MMA failed to afford copolymers probably because of steric reasons as described in our previous paper [7], the aforementioned results prompted us to examine ternary copolymerization of **1**, MMA, and ethyl acrylate (EA), in order to prepare copolymers of MMA bearing norbornane uframework in the main chain (Scheme 3). Because EA can copolymerize with both **1** and MMA, poly(**1**-*co*-MMA-*co*-EA) would be obtained even without **1**-MMA sequence in the main chain. As shown in run 1 in Table 3, the bulk ternary copolymerization with a feed ratio of [**1**]/[MMA]/[EA] = 1:1:1 at 85 °C gave a terpolymer, whose composition determined by ^{1}H NMR was 0.1:1:0.5 and M_n was 18400. By increasing the relative feed ratio of ([**1**] + [EA]) to [MMA], the composition changed as shown in runs 2 and 3. As an example, the ^{1}H NMR spectrum for the sample obtained in run 2 is shown in Fig. 2. Compared to the spectra of poly(**1**-*co*-St) in Fig. 1, because the copolymer does not contain a phenyl group, OCH_2 and OCH_3 signals appear much simpler as a broad signal at 3.9–4.3 ppm and a peak cluster at 3.4–3.8 ppm, being assignable to OCH_2 from EA and OCH_3 from both **1** and MMA, respectively.

For quantitative evaluation of the reactivity of **1** in radical copolymerization, monomer reactivity ratios (r_1 and r_2) were determined by using the Fineman–Ross method for copolymerization of **1** with *n*-BA (bulk, at 85 °C, [**1**]/[*n*-BA] = 2.5:1–1:3, conversion < 2.7%; see Supplementary Contents for the details.). As a result, r_1 (**1**) and r_2 (*n*-BA) turned out to be 0.023 and 1.33, respectively. The very small r_1 value indicates that the probability for the formation of **1**-**1** sequence is very low in the copolymerization, and also agrees with the fact that **1** does not homopolymerize.

3.4. *Radical copolymerization of 2-phenyl-2-norbornene (**2**) with alkyl acrylates*

The successful incorporation of norbornane framework into various polymer main chains using **1** prompted us to use 2-phenyl-



Scheme 3. Radical Copolymerization of Methyl 2-Norbornene-2-carboxylate (**1**),MMA, and Ethyl Acrylate.

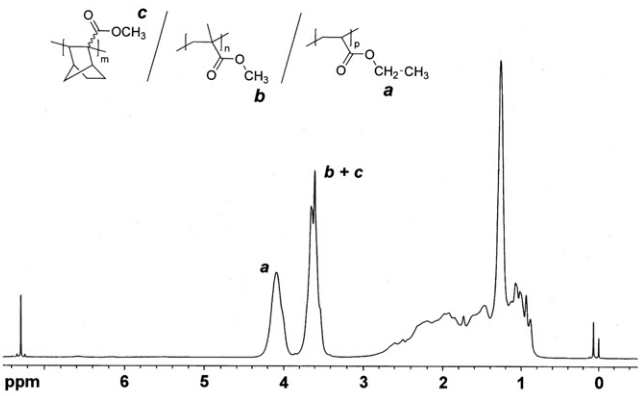
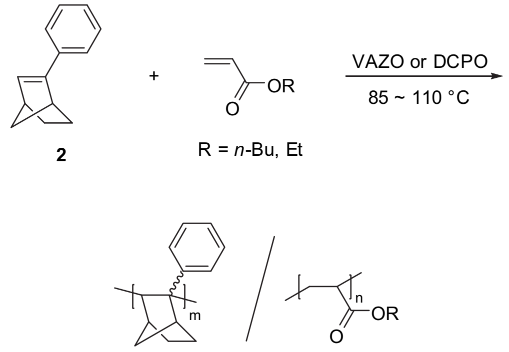


Fig. 2. ^{1}H NMR spectrum for poly(**1**-*co*-MMA-*co*-EA) (run 2 in Table 3).

2-norbornene **2**, which had a Ph group instead of methyl ester on the 2-positon of norbornene, as another type of a radically polymerizable norbornene-based monomer. Although the synthesis of **2** via Pd-catalyzed coupling of 2-bromonorbornene with iodobenzene has been reported in a literature [9], we have found that **2** was obtained efficiently by the reaction of norcamphor with PhMgBr, which was a modified procedure of the preparation of 7-*syn*-chloro-2-phenylnorbornene in another literature [8] and whose synthetic procedure is described in Experimental Section.

In the same manner as **1**, homopolymerization and copolymerization with MMA of **2** failed to afford polymeric products. However, because **2** has inherent homopolymerizability as its reactivity ratio in the copolymerization with *n*-BA mentions (*vide infra*), very low solubility owing to the high rigidity of successive sequence of **2** could prevent the progress of homopolymerization of **2**. On the other hand, when bulk copolymerization of **2** with *n*-BA was conducted with a feed ratio of [**2**]/[*n*-BA] = 1:3 at 110 °C for 13.5 h, a copolymer was obtained in a 51.4% yield (run 1, Table 4, Scheme 4). Whereas the M_n (8600) was relatively low, the ^{1}H NMR-determined composition of **2** was 30 mol%, which was close to the feed ratio of **2** (25 mol%). Increase of the relative feed ratio of **2** to [**2**]/[*n*-BA] = 1:2 resulted in a slight increase in **2** composition to 32 mol% (run 2). By decreasing polymerization temperature to 100 and 85 °C, slight increase of M_n was observed, while yields diminished significantly (runs 3 and 4). Copolymerization of **2** with EA with a feed ratio of [**2**]/[EA] = 1:3 at 85 °C proceeded in a similar manner as that with *n*-BA, except for the lower M_n and higher **2** incorporation (run 5). In the ^{1}H NMR spectrum for the sample obtained in run 4 shown in Fig. 3, the integral ratio between the signals in aromatic region and the rest of the signals allows us to estimate the composition (See Supplementary Contents).



Scheme 4. Radical Copolymerization of 2-Phenyl-2-norbornene (**2**) with Alkyl Acrylate.

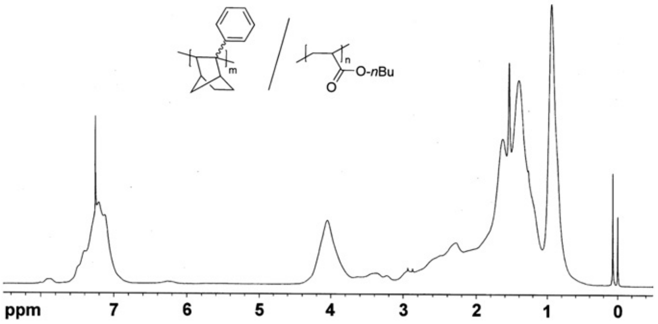


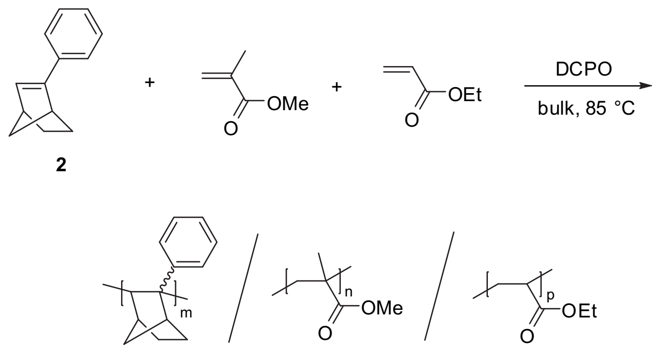
Fig. 3. ^{1}H NMR spectrum for poly(**2**-*co*-*n*-BA) (run 4 in Table 4).

Runs 6–11 in Table 4 summarize the copolymerization of **2** with *n*-BA initiated with dicumyl peroxide (DCPO), where the feed ratio of [**2**]/[*n*-BA] was varied from 1:5 to 2:1. With the increase of the relative feed ratio of **2**, the **2** content increased, whereas both M_n and copolymer yield decreased drastically, which suggested the instability of the growing chain end derived from **2**. The 60 mol% composition of **2** in run 11 with the feed ratio of [**2**]/[*n*-BA] = 2:1 indicates that the growing radical chain end from **2** can actually react with **2** to form **2**–**2** sequence.

The monomer reactivity ratios [r_1 (**2**) and r_2 (*n*-BA)] were determined to be $r_1 = 0.24$ and r_2 0.11 for the copolymerization of **2** with *n*-BA (bulk, at 85 °C, [**2**]/[*n*-BA] = 1:3–1:1, conversion < 6.7%) by the Fineman–Ross method (See Supplementary Contents for the details.). Interesting to note is that the r_1 value is much higher than that observed for **1** as described above [r_1 (**1**) = 0.023], indicating the higher probability of **2**–**2** sequence in poly(**2**-*co*-*n*-BA) probably because of the lower steric congestion of the propagating end derived from **2** than that from **1**. The reactivity ratios are also consistent with the formation of poly(**2**-*co*-*n*-BA) with the **2** composition of 60 mol% in run 11 in Table 4.

*3.5. Ternary radical copolymerization of phenyl-2-norbornene (**2**), MMA, and ethyl acrylate (EA)*

In a similar manner as that for the aforementioned copolymerization of **1**, MMA, and EA, ternary copolymerization of **2**, MMA, and EA was examined as summarized in Table 5, where the similar feed ratios as those in Table 3 were employed (Scheme 5). As a result, copolymers with a lower M_n were obtained in lower yields compared to those obtained in Table 3. However, as expected from the higher incorporation efficiency of **2**, the composition of **2** in the copolymers was higher than those of **1** in Table 3.



Scheme 5. Radical Copolymerization of 2-Phenyl-2-norbornene (**2**), MMA, and Ethyl Acrylate (EA).

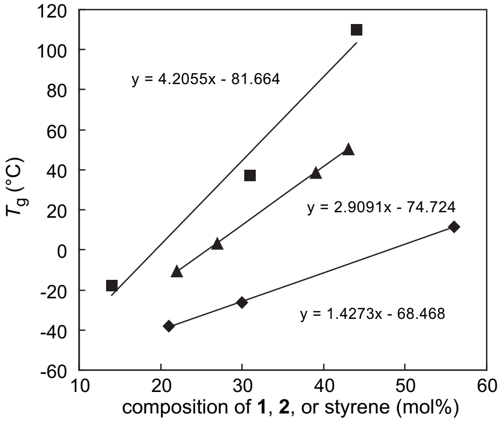


Fig. 4. Relationship between T_g and composition of **1** (▲), **2** (■), and styrene (◆) in poly(**1**, **2**, or St-*co*-*n*-BA).

3.6. *Effect of the main chain norbornane unit on glass transition temperature*

In our previous publication where we reported the synthesis of poly(**1**-*co*-alkyl acrylate) [7], the effect of the incorporation of norbornane framework into the copolymers on their glass transition temperatures could not be clearly demonstrated, because we could not observe T_g for copolymers with a relatively higher **1** content by normal DSC measurement. On the other hand, we have found that T_gs for copolymers obtained from **1** and **2** with *n*-BA can be clearly observed by using temperature-modulated DSC (TM DSC) [11], and the results for the T_g measurement are summarized in Table 6, which also contains related data for poly(St-*co*-*n*-BA) samples observed by normal DSC measurement without temperature modulation. In spite of the M_n difference for the samples, increase of T_g was clearly observed with the increase of **1**, **2**, and St content in the copolymers.

The observed T_gs were plotted against **1**, **2**, or styrene contents in Fig. 4. While linear relationship was clearly observed for each copolymer, interesting to note is that each plot has a different slope, whose value should be related to the T_g-raising ability of the repeating unit of **1**, **2**, and styrene. The slope values (4.2 for **2**, 2.9 for **1**, and 1.4 for styrene) clearly show higher T_g-raising effect of **1** and **2** compared to that of styrene, derived from the high rigidity imparted by the norbornane framework. In addition, the higher slope value of **2** than that of **1** shows that, as a substituent on the norbornane framework, the Ph group is more effective than the ester group in raising T_g.

4. Conclusions

We have demonstrated that radical copolymerizations of 2-substituted norbornenes **1** and **2** with a variety of comonomer combinations with styrene, MMA, and alkyl acrylate are possible to give copolymers consisting of norbornane framework in the main chains. A remarkable T_g-raising effect of the incorporated norbornane framework was revealed by quantitative evaluation using temperature-modulated DSC. We believe that the strategy would be very useful for improving physical properties of polymers obtained by conventional radical polymerization of common monomers such as alkyl (meth)acrylates and styrene, leading to production of a variety of new polymeric materials.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2009.12.008.

References

[1] Janiak C, Lassahn PG. Macromol Rapid Commun 2001;22:479–92.
[2] For example, see (a) Nomura K, Tsubota M, Fujiki M. Macromolecules 2003;36:3797–9;
(b) Hasan T, Ikeda T, Shiono T. Macromolecules 2004;37:8503–9. and refereneces cited there in.
[3] For example, see (a) Hasan T, Ikeda T, Shiono T. Macromolecules 2005;38:1071–4;
(b) Cai Z, Nakayama Y, Shiono T. Macromolecules 2006;39:2031–3. and refereneces cited there in.
[4] Elyashiv-Barad S, Greinert N, Sen A. Macromolecules 2002;35:7521–6.
[5] (a) Peruch F, Cramail H, Deffieux A. Macromol Chem Phys 1998;199:2221–7;
(b) Mi X, Ma Z, Wang L, Ke Y, Hu Y. Macromol Chem Phys 2003;204:868–76;
(c) Gao H, Chen Y, Zhu F, Wu Q. J Polym Sci Part A Polym Chem 2006;44:5237–46.
[6] Nozaki K. (Fujitsu Co.). Jpn Kokai Tokkyo Koho 3476783; 2003.
[7] Ihara E, Honjyo S, Itoh T, Inoue K, Nodono M. J Polym Sci Part A Polym Chem 2007;45:4597–605.
[8] Kleinfelter DC, Dye TE, Mallory JE, Trent ES. J Org Chem 1967;32:1734–41.
[9] Mayo P, Tam W. Tetrahedron 2002;58:9527–40.
[10] Gaylord NG, Mandal BM, Martan M. J Polym Sci Polym Lett Ed 1976;14:555–9.
[11] (a) Gill PS, Sauerbrunn SR, Reading M. J Therm Anal Calorim 1993;40:931–9;
(b) Reading M, Luget A, Wilson R. Thermochim Acta 1994;238:295–307;
(c) Reading M, Elliott D, Hill VL. J Therm Anal Calorim 1993;40:949–55.