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High-Molecular-Weight Alternating Copolymers from Thermal Copolymerizations of *N*-Alkylcitraconimides with Styrene

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HIGH-MOLECULAR-WEIGHT ALTERNATING COPOLYMERS FROM THERMAL COPOLYMERIZATIONS OF *N*-ALKYLCITRACONIMIDES WITH STYRENE†

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ABSTRACT

Radical copolymerizations of eight *N*-alkylcitraconimides (**1**) and styrene (**2**) were carried out in the presence or absence of a radical initiator. Alternating copolymers with number-average molecular weights higher than 7 × 10^5 were obtained from the thermal copolymerizations (monomer molar ratio = 1:1) in bulk at 60°C. The spontaneous copolymerization is considered to be by induced radicals produced via an intermediate Diels-Alder dimer and minary a contact-type charge transfer complex between *N*-alkylcitraconimide and styrene. Thermogravimetric analyses indicate the resulting copolymers have high thermal stabilities.

INTRODUCTION

The radical copolymerizations of *N*-substituted maleimides with styrene have been well known to result in alternating copolymers, which show relatively high thermal stabilities [1–5].

Recently, we studied the radical homopolymerization of various *N*-substituted citraconimides, α-methyl-substituted derivatives of *N*-substituted maleimides, and

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†Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

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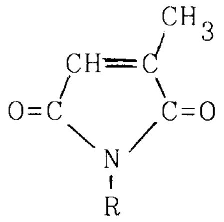
found that *N*-alkylcitraconimides **(1)** undergo homopolymerization in the presence of a radical initiator, to give polymers with molecular weights up to 10,000 [6]. The polymers obtained were also found to show high thermal stabilities comparable to that of poly(*N*-alkylmaleimide)s [7, 8].

Copolymerization parameters of **1** other than *N*-methylcitraconimide **(1a)** with styrene **(2)** were reported by Oishi [9]; a high alternating tendency was observed, $0 < r_1 < 0.07$ and $0.18 < r_2 < 0.46$. Cowie et al. [10] studied the effect of side chain length on the glass transition temperature of these copolymers. However, the molecular weights of the resulting copolymers were rather low. There are no data on the thermal stability of the copolymers. Radical copolymerization of **1a** with **2** was also reported [11].

To clarify further the copolymerization behavior of **1a** and **2**, radical copolymerization of these two monomers was carried out. In the course of the study, we found that **1a** undergoes alternating copolymerization with styrene even in the absence of a radical initiator to give high-molecular-weight copolymer. Therefore, thermal copolymerizations of some other **1** with **2** were investigated to obtain high-molecular-weight alternating copolymers. Monomers, **1**, used in this paper are listed below.



(1)

R	CH_3	C_2H_5	$CH_2CH_2CH_3$	$CH(CH_3)_2$	$CH_2(CH_2)_2CH_3$	$CH_2CH(CH_3)_2$	$CH(CH_3)CH_2CH_3$	$C(CH_3)_3$
1	1a	1b	1c	1d	1e	1f	1g	1h

EXPERIMENTAL

Materials

1 were prepared according to the method reported by Oishi [9]; i.e. citraconic anhydride was allowed to react with the corresponding monoalkylamines in diethyl ether at 0–5°C, followed by dehydration in the presence of *p*-toluenesulfonic acid as a catalyst in refluxing xylene. The monomers thus obtained were confirmed to be pure by ^{1}H NMR spectroscopy.

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2 was distilled before use. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from methanol. Other reagents and solvents were used after ordinary purifications.

Copolymerization Procedure

Copolymerizations were carried out in a sealed glass tube under shaking. After polymerization for a given time, the mixture was poured into a large amount of hexane to isolate the copolymer. The copolymer was filtered, washed with hexane, and then dried in vacuum. The purification of the copolymers obtained was performed by repeating reprecipitation. The yield of polymers was determined gravimetrically. The composition of the copolymers was determined by measuring the intensity of the specific resonances for the respective monomer units in the ^{1}H NMR spectra. The monomer reactivity ratios, r_1 and r_2, were calculated by a nonlinear least-squares procedure [12].

Measurements

^{1}H NMR spectra were taken on a JEOL-GX 400 spectrometer in $CDCl_3$ at 27°C. Number-average molecular weight ($\overline{M}_n$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes at 38°C using tetrahydrofuran (THF) as an eluent. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream with a heating rate of 10°C/min. UV spectra were measured by SHIMADZU UV-160 ultraviolet spectrometer in benzene at room temperature using 1-cm quartz cells.

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RESULTS AND DISCUSSION

Copolymerization of 1a with 2 in the Presence of AIBN

At first, radical copolymerization of **1a** (M_1) with **2** (M_2) was performed in bulk at 60°C with 0.02 mol·dm^{-3} AIBN. The copolymerizations proceeded rapidly to give a copolymer with $\overline{M}_n$ in the range of (4.4–28.0) × 10^4, as indicated in Table 1.

TABLE 1. Radical Copolymerization of **1a** (M_1) with **2** (M_2) in Bulk at 60°C; [AIBN] = 0.02 mol·dm^{-3}

M_1 in feed (mol%)	Polymn. time (min)	Yield of copolymer (%)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	M_1 in copolymer (mol%)
10.0	30	4.2	4.4	2.8	35.8
30.0	30	6.2	22.5	1.6	46.7
50.0	45	14.4	28.0	1.6	50.2
70.0	30	9.7	25.8	1.8	50.9
90.0	30	4.0	12.4	1.8	55.9

Based on the data in Table 1, the relationship of the initial rate of copolymerization and $\overline{M}_n$ of the copolymers with monomer feed molar ratio are obtained (shown in Fig. 1). The initial copolymerization rate and $\overline{M}_n$ of the copolymers are observed to have a maximum at about 1:1 monomer feed composition, as has been reported for many other alternating copolymerization systems.

The copolymer composition curve plotted in terms of the mol% of M_1 in the copolymer against that in the monomer feed is illustrated in Fig. 2, from which a highly alternating tendency is observed over a wide range. In this figure, the open circles represent the experimental points, and the solid line is calculated by using a nonlinear least-squares procedure. The monomer reactivity ratios, r_1 and r_2, for the copolymerization of **1a** with **2** are calculated as 0.032 and 0.080, respectively. These values are somewhat different from those reported in the literature ($r_1 = 0.24$ and $r_2 = 0.14$) [11], but they are in agreement with the results reported by Oishi [9] for other monomers **1** with **2**.

Spontaneous Thermal Copolymerization of 1 with 2

The copolymerization of **1a** with **2** (monomer feed molar ratio = 1:1) was found to occur slowly even in the absence of AIBN at 60°C to give higher-molecular-weight copolymer compared with those obtained in the presence of AIBN, as shown in Table 2. Furthermore, the spontaneous thermal copolymerizations of **1** other than **1a** with **2** were also investigated under similar conditions. Copolymers consisting of almost 1:1 alternating composition were obtained from

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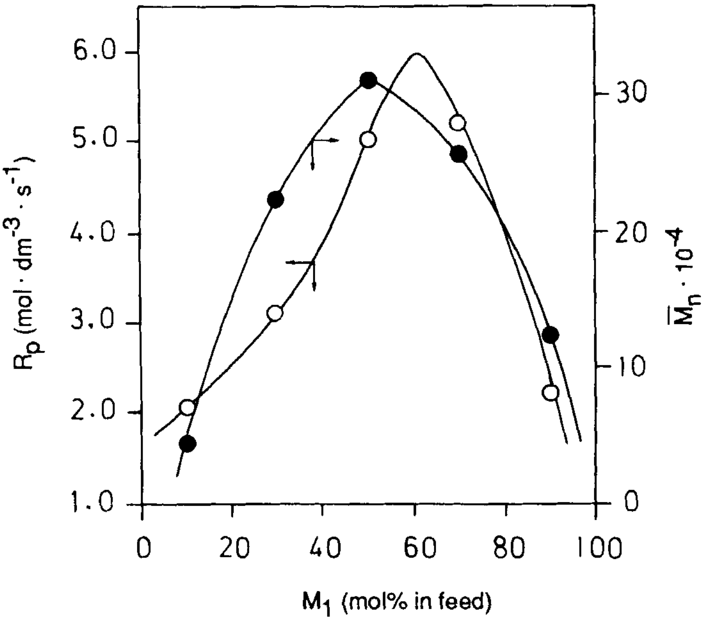

FIG. 1. Initial copolymerization rate (○) and number-average weight of the copolymer (●) vs. monomer feed molar ratio for copolymerization of **1a** (M_1) with **2** (M_2). Copolymerization conditions: see Table 1.

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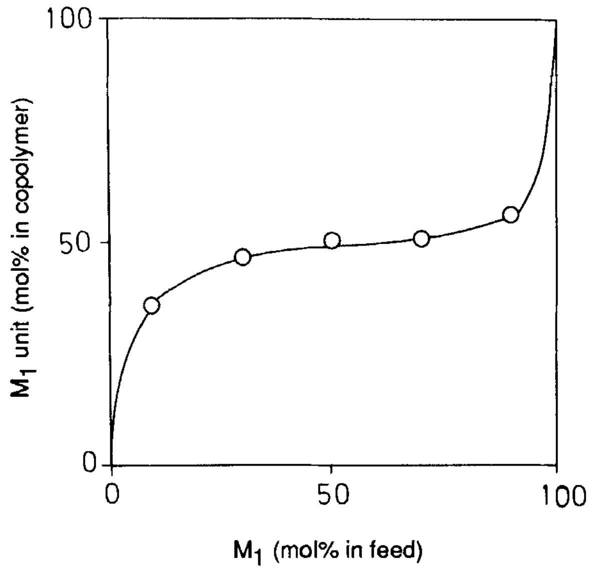

FIG. 2. Copolymer composition curve for copolymerization of **1a** (M_1) with **2** (M_2). Copolymerization conditions: see Table 1.

these systems. The number-average molecular weights of these copolymers (determined by GPC) were considerably high ($>7 \times 10^5$).

The GPC elution curves of the copolymers were observed to be unimodal without a shoulder. From Table 2, the rate of the spontaneous thermal copolymerizations seems to be dependent on the *N*-alkyl substituents of **1**; i.e., it decreases with increasing bulkiness of the *N*-alkyl substituents. Characterizations of these

TABLE 2. Spontaneous Copolymerization of **1** (M_1) with **2** (M_2) in Bulk at 60°C; $[M_1]:[M_2]$ = 1:1 Molar Ratio[a]

M_1	Polymn. time (h)	Yield (%)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	M_1 in copolymer (mol%)
1a	5	2.3	90.5	1.9	49.8
1b	24	8.7	80.1	1.6	46.8
1c	16	4.2	77.9	2.2	45.8
1d	24	3.6	71.3	1.5	47.6
1e	24	6.3	80.5	1.8	46.2
1f	16	3.3	96.3	2.5	43.8
1g	24	4.5	76.5	1.7	47.0
1h	24	3.5	68.9	1.7	46.9

[a] Polymerizations were carried out in the dark without AIBN.

copolymers were carried out by means of IR and NMR. Figure 3 depicts the ^1H NMR spectra of poly(**1d**-co-**2**) from which resonances at 4.0 ppm due to **1d** unit (NCH proton) and at 7.7 ppm due to **2** unit (C_6H_5 protons) are observed.

The resulting copolymers are colorless powders, soluble in many organic solvents, e.g., benzene, acetone, dioxane, chloroform, THF, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, and insoluble in hexane, methanol, and water.

Mechanism of the Spontaneous Copolymerization

To determine the mechanism of the initiation reaction in these spontaneous thermal copolymerizations, the interaction between **1a** and **2** was investigated spectroscopically. It has been well known that electron donor-acceptor complexes exist in many of the copolymerization systems, e.g., maleic anhydride/styrene, vinyl ethers, and vinyl sulfides [13]. In some of these systems, radical alternating copolymerization has been known to be induced spontaneously. In order to clarify whether such a complex exists in the 1 and 2 system, a UV spectroscopic study was performed for the system **1a** and **2**.

Figure 4 shows the UV spectra of the benzene solution of **1a** and **2** changing in various molar ratios. From this figure, no evidence for the formation of a charge transfer complex between **1a** and **2** was obtained. Yamada et al. [14] reported that no CT complex was found in the case of *N*-alkylmaleimides and **2**, either. However, from these observations, the formation of a contact-type CT complex may be not eliminated. In fact, although the system isobutyl vinyl sulfide, a strong electron-donating monomer, and acrylonitrile or methyl acrylate, a weak electron-accepting

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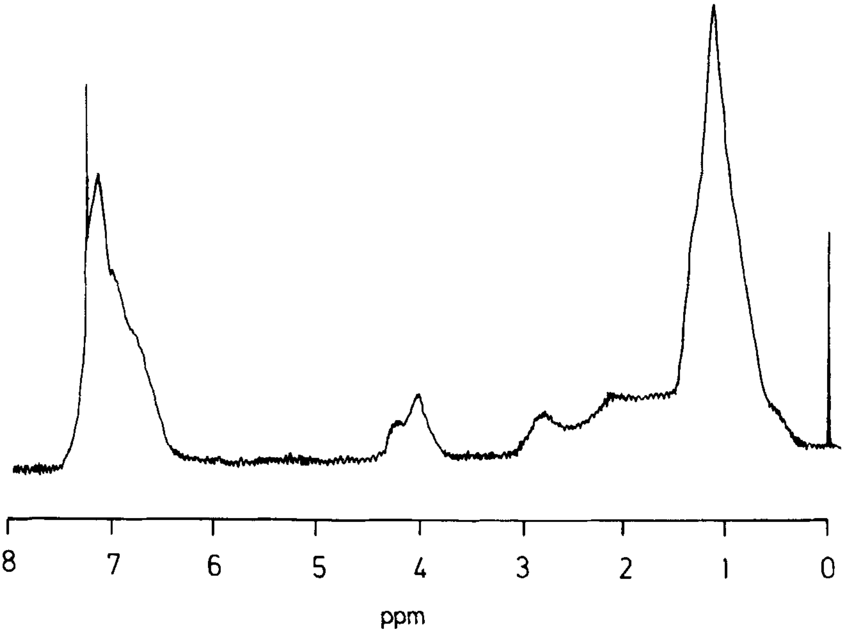

FIG. 3. ^1H NMR (400 MHz) spectrum of poly (**1d**-co-**2**) in $CDCl_3$ at 27 °C.

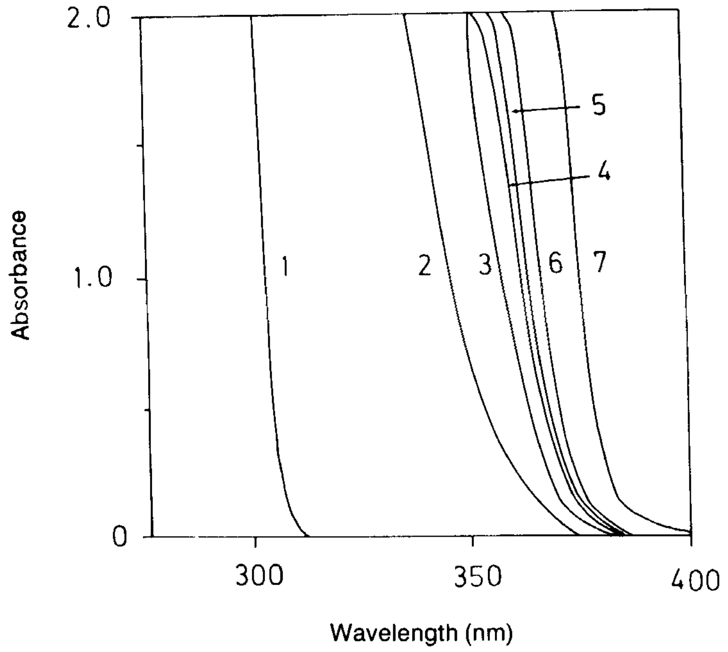

FIG. 4. UV absorption spectra of **1a**-**2** system in benzene at room temperature. [**1a**] + [**2**] = 1.0 mol·dm^{-3}. (1), [**1a**] = 0; (2), [**1a**] = 10; (3), [**1a**] = 30; (4), [**1a**] = 50; (5), [**1a**] = 70; (6), [**1a**] = 90; (7), [**1a**] = 100 mol%.

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monomer, did not show any evidence for the CT complex formation spectroscopically, the spontaneous copolymerization was found to occur [15].

On the other hand, **2** has been well known to homopolymerize spontaneously when heated. In fact, the spontaneous polymerization of **2** occurs under conditions similar to those of the copolymerizations in the present study (yield 1.1% for 10 h). Therefore, the spontaneous thermal copolymerization of **1** with **2** in the absence of initiator is considered to be induced by a mechanism close to the thermal polymerization mechanism proposed for **2** by Mayo [16], Pryor [17], and Sato-Otsu [15, 18-20]; i.e., initiating radicals are produced mainly through a molecule (*M*)-assisted termolecular mechanism between intermediate Diels-Alder adduct of **2** with **1** and free monomers [16-19]. However, some initiating radicals may also be produced even in a minor way by an intramolecular proton transfer in the contact-type CT complex, as proposed by Sato and Otsu [20] (Scheme 1).

Thermal Stability of the Copolymers

TGA analyses for some of the poly(**1**-alt-**2**)s obtained by the thermal copolymerization were carried out to evaluate their thermal stabilities. Figure 5 shows the TGA curves obtained for copolymers of **1a**, **1c**, and **1f** with **2**. Initial decomposition temperature (T_{init}) and maximum decomposition temperature (T_{max}) and residue at 500°C are summarized in Table 3, from which it can be observed that the thermal stabilities of the poly(**1**-alt-**2**)s are quite high.

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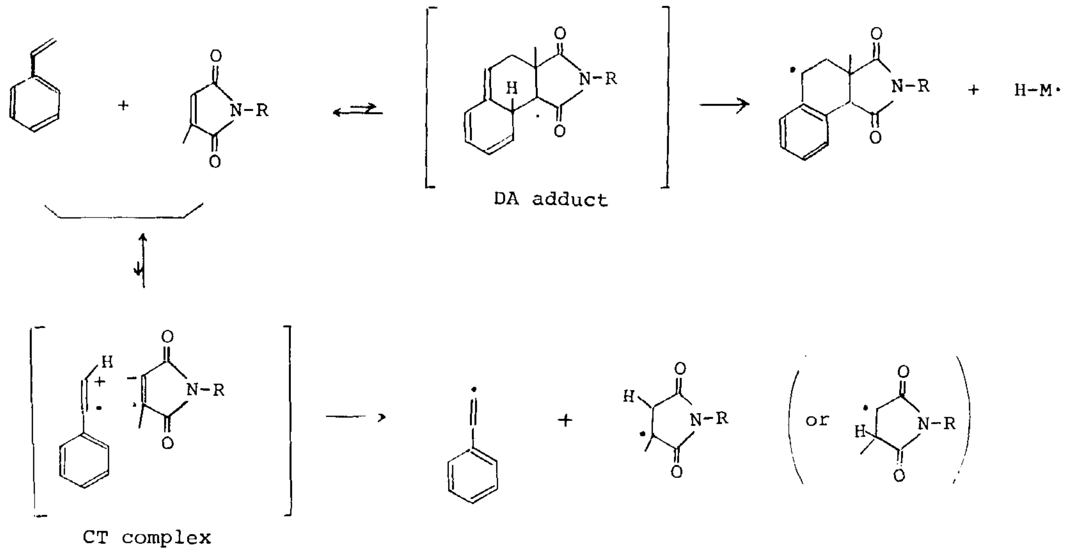

SCHEME 1.

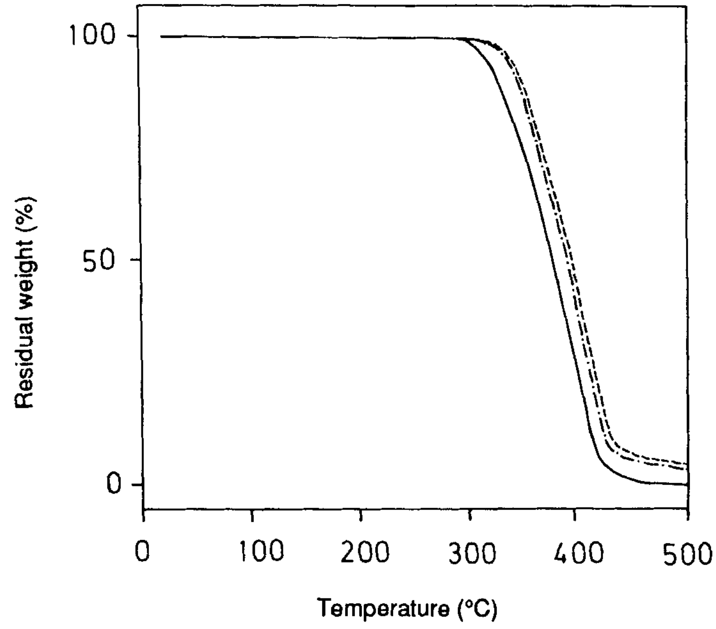

FIG. 5. TGA curves of poly(**1a**-alt-**2**) (——), poly(**1c**-alt-**2**) (- - -), and poly(**1f**-alt-**2**) (-·-·-). Analyses were performed in a nitrogen stream with a heating rate of 10°C·min^{-1}.

TABLE 3. Thermogravimetric Analysis for Poly (**1**-alt-**2**)s

Polymer	T_{init} (°C)	T_{max} (°C)	Residue at 500°C (%)
Poly(**1a**-alt-**2**)	282	335, 390	0
Poly(**1c**-alt-**2**)	298	405	3.0
Poly(**1f**-alt-**2**)	297	403	3.7

CONCLUSION

The alternating copolymers having high molecular weights and considerable thermal stabilities have been synthesized through thermal copolymerizations of various **1** with **2**. Recently, radical copolymerizations of **1** with some derivatives of **2** such as α-methylstyrene were also found to give alternating copolymers [21].

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