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ORIGINAL PAPER

Thermally induced polymerization and copolymerization with styrene of diazoketones in the presence of benzoquinone

Eiji Ihara · Hironori Nishida · Mototaka Fujii · Tomomichi Itoh · Kenzo Inoue

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Abstract Thermally induced polymerization of diazoketones, (*E*)-1-diazo-3-nonen-2-one **1** and (*E*)-1-diazo-4-phenyl-3-buten-2-one **2**, is described. Heating **1** and **2** in a solvent at 60–100 °C afforded polymers, where all the main chain carbons bear acyl groups derived from the monomers and the main chain contains ca. 25–35 mol% of azo group. Molecular weight of the resulting polymers increased up to $M_n = 8{,}400$ by the addition of benzoquinone to the reaction mixtures. The polymerization was supposed to proceed via radical propagating chain end and copolymerization of **1** with styrene gave copolymers ($M_n = 11{,}000$–$15{,}000$) having acylmethylene, azo group, and repeating unit from styrene in their main chains.

Keywords Diazoketone · Radical polymerization · Copolymerization · Styrene

Introduction

Recently, we and other groups have been developing polymerization of diazocarbonyl compounds (For a recent review on the reactions of diazocarbonyl compounds, see [1]) such as diazoacetates and diazoketones, which are basically stable compounds, in sharp contrast to highly explosive diazoalkanes (For polymerization of diazoalkanes, see [2]). For example, whereas Cu- [3], Pd- [4], and B-mediated [5] polymerization of alkyl diazoacetate afforded low molecular weight poly(alkoxycarbonylmethylene)s, high molecular weight polymers ($M_n > 200{,}000$) from ethyl diazoacetate were obtained in a stereospecific manner by using some Rh–diene

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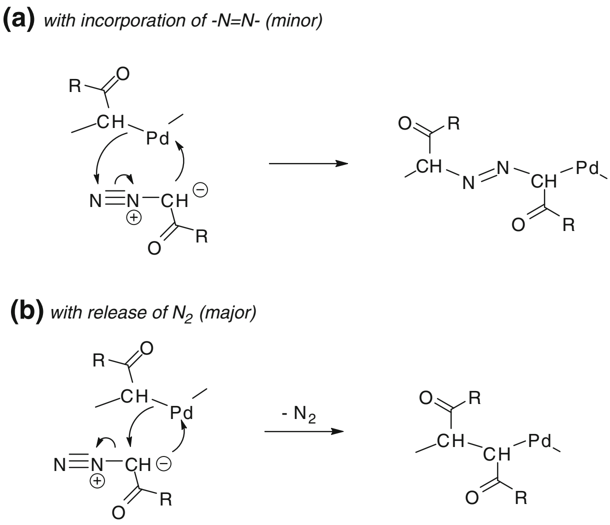
E. Ihara (✉) · H. Nishida · M. Fujii · T. Itoh · K. Inoue
Department of Material Science and Biotechnology, Graduate School of Science and Engineering, Venture Business Laboratory, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan
e-mail: ihara@eng.ehime-u.ac.jp



Scheme 1 Propagation mechanism for Pd-mediated polymerization of diazoketones

complexes [6, 7]. The polymerization is a new method for preparing C–C main chain polymers with polar substituents on all the main chain carbon atoms [8], whereas the polymers with the same structure can be prepared by the radical polymerization of dialkyl fumarate or maleate [9]. Similarly, Pd- [10, 11] and Al-mediated [12] polymerization of diazoketones has been reported to give polymers, whose all the main chain carbons bear acyl groups, although the molecular weights of the polymers are rather low (M_n = ca. 2,000). Interestingly, in the polymerization of diazoketones [10–12], incorporation of azo group (–N=N–) in the main chain of the products has been observed, where the azo content depends on the kinds of monomer, mediator, and solvent. The incorporation of azo group indicates that the insertion of the monomer into the propagating metal–carbon bond should occur in a mode without release of N_2 as shown in Scheme 1a in a certain extent, along with the dominant mode of the insertion with release of N_2 in Scheme 1b.

Based on these results, we can expect that the reactivity of diazoketones is somewhat different from that of diazoacetates and diazoketones would be able to be polymerized via other mechanism than those we have demonstrated. Actually, we have found that diazoketones can be polymerized by heating alone to give polymers with rather high content of azo group, probably via propagation with radical species at active chain ends. The detail of this unique polymerization will be described in this article.

Experimental

Materials

Toluene and THF were dried over sodium and Na/K alloy, respectively, and distilled before use. Anisole (Wako, 99.0%) was dried over molecular sieves 4 Å and used without further purification. V-70 (Wako, 95%), AIBN (Nacalai, 98%), VAZO (Wako, 95%), VAm-110 (Wako, 95%), BPO (Kishida chemical), benzoquinone (BQ) (Nacalai, 98%), naphthoquinone (NQ) (Nacalai, 98%), and galvinoxyl (GX) (Aldrich) were used as received. Styrene (Aldrich, 99%) was dried over CaH_2 and distilled before use. Diazoketone monomers **1** [10], **2** [13], and $PdCl_2(MeCN)_2$ [14], were prepared according to the literatures.

Measurements

^{1}H-NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($CDCl_3$) at 50 °C. IR spectra were recorded on a JASCO FT/IR spectrometer.

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) 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). The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 600 K for polystyrene) and Styragel HR2 (Waters; 300 × 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, $M_n = 200{,}000$, $M_w/M_n = 1.05$, $M_n = 47{,}300$, $M_w/M_n = 1.02$, $M_n = 21{,}700$, $M_w/M_n = 1.02$, $M_n = 5{,}220$, $M_w/M_n = 1.06$, $M_n = 2{,}190$, $M_w/M_n = 1.08$) and dibutyl sebacate ($M_w = 314.5$) were used for the calibration.

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 × 20 mm i.d., exclusion molecular weight of 70 K for polystyrene) and a JAIGEL-2H (600 × 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.

Thermal properties of the polymers were measured using a differential scanning calorimeter (DSC), Seiko DSC 6200, under nitrogen atmosphere at a 10 °C/min heating rate. Thermogravimetric analyses of the polymers were carried out using a Seiko TG/DTA 6200 under nitrogen atmosphere at a 10 °C/min heating rate.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University.

Thermally induced polymerization of diazocarbonyl compounds

As a typical procedure for the thermally induced polymerization of diazocarbonyl compounds, the procedure for run 14 in Table 1 is described as follows.

Under a nitrogen atmosphere, BQ (48.4 mg, 0.447 mmol) was placed in a Schlenk tube. After a toluene (10 mL) solution of **1** (294.7 mg, 1.773 mmol) was added at room temperature, the mixture was degassed three times by

Table 1 Thermally induced polymerization of (*E*)-1-diazo-3-nonen-2-one (**1**)

Run	Additive (A)[a]	[**1**]:[A]	Solvent	Temp. (°C)	Yield (%)[b]	M_n[c]	M_w/M_n[c]	Elemental analysis C%:N% (mol% of –N=N–)[d]
1	–	–	Toluene	40	4.4	1,040	1.25	
2	–		Toluene	60	26.2	2,210	1.65	
3	–	–	Toluene	80	27.3	2,610	1.47	66.98:8.64 (33.2)
4	–	–	Toluene	100	41.2	2,290	1.53	
5	–	–	Anisole	130	62.1	780	1.30	
6	AIBN	100:5	Toluene	80	26.4	1,040	1.38	
7	BPO	100:5	Toluene	100	74.8	1,060	1.62	
8	BQ	100:2	Toluene	80	27.3	1,140	1.66	
9	BQ	100:10	Toluene	80	32.2	5,500	1.59	65.30:8.56 (33.6)
10	BQ	100:25	Toluene	80	39.2	7,600	2.21	66.22:9.18 (34.9)
11	BQ	100:40	Toluene	80	38.0	6,300	2.15	66.18:9.05 (34.5)
12	NQ	100:40	Toluene	80	45.5	2,090	1.37	69.59:6.30 (25.9)
13	BQ	100:25	Toluene	100	27.7	8,400	1.31	
14	BQ	100:40	Toluene	100	48.3	7,300	2.95	
15	GX	100:25	Toluene	80	38.5	1,290	1.60	
16	GX	100:50	Toluene	80	17.1	1,770	1.30	
17	–	–	THF	60	8.5	1,060	1.39	
18	BQ	100:40	THF	60	14.5	6,200	2.37	66.00:9.47 (33.6)
19	$PdCl_2$	100:2	Toluene	80	55.1	1,590	1.60	73.73:1.09 (5.41)

Solvent = 10 mL; polymerization period = 18 h; **1** = 1.74–1.85 mmol

[a] *V-70* 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile), *AIBN* 2,2′-azobisisobutyronitrile, *BPO* benzoyl peroxide, *VAZO* 1,1′-azobis(cyclohexane-1-carbonitrile), *VAm-111* 2,2′-azobis(*N*-cyclohexyl-2-methylpropionamide), *BQ* benzoquinone, *NQ* naphthoquinone, *GX* galvinoxyl

[b] Yield (%) = 100 × (the weight of the product after purification with the recycling GPC − the weight of N contained in the product calculated from the result of elemental analysis)/(the weight of **1** − the weight of N contained in **1**)

[c] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solutions

[d] The mol% of –N=N– in the copolymer was calculated on the assumption that all the C content from EA derives from the repeating unit of **1**, without considering the polymer chain ends

freeze–thawing, and stirred for 18 h at 80 °C. The volatiles were removed under reduced pressure and 20 mL of chloroform was added to remove insoluble solid by filtration. The chloroform solution was concentrated to give a crude product, which was purified by using preparative recycling GPC to afford the polymer as a reddish-brown solid (90.8 mg, 39.2%). With the purification using preparative recycling GPC, unidentified low molecular weight products were removed, which was a significant reason for the low polymer yields in these polymerizations, along with the formation of uncharacterized insoluble materials removed by filtration as described above.

Table 2 Thermally induced polymerization of (*E*)-1-diazo-4-phenyl-3-buten-2-one (**2**)

Run	Additive (A)	[**2**]:[A]	Solvent	Temp. (°C)	Yield (%)[a]	M_n[b]	M_w/M_n[b]	Elemental analysis C%:N% (mol% of –N=N–)[c]
1	–	–	Toluene	40	1.2	760	1.54	
2	–	–	Toluene	60	7.5	840	1.21	
3	–	–	Toluene	80	37.2	760	1.68	73.35:8.17 (32.3)
4	–	–	Toluene	100	65.4	1,050	1.45	
5	BQ	100:10	Toluene	80	15.4	2,310	1.48	73.92:8.43 (32.9)
6	BQ	100:25	Toluene	80	44.9	2,030	1.38	71.84:9.06 (35.1)
7	BQ	100:40	Toluene	80	43.6	2,000	1.96	71.48:8.11 (32.8)
8	BQ	100:100	Toluene	80	56.3	1,410	1.51	
9	NQ	100:40	Toluene	80	55.4	1,130	1.33	74.64:6.69 (27.8)
10	BQ	100:40	Toluene	100	51.1	3,140	1.53	
11	–	–	THF	60	6.8	790	1.40	
12	BQ	100:40	THF	60	17.4	1,160	1.26	71.86:6.56 (28.3)
13	$PdCl_2$	100:2	Toluene	80	42.8	1,760	1.27	79.14:0.32 (1.64)

Solvent = 10 mL; polymerization period = 18 h; **2** = 1.72–1.78 mmol

[a] Yield (%) = 100 × (the weight of the product after purification with the recycling GPC − the weight of N contained in the product calculated from the result of elemental analysis)/(the weight of **2** − the weight of N contained in **2**)

[b] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solutions

[c] The mol% of –N=N– in the copolymer was calculated on the assumption that all the C content from EA derives from the repeating unit of **2**, without considering the polymer chain ends

Other polymerizations in Tables 1, 2 were carried out in a similar manner. ^{1}H-NMR spectra for these polymers are identical with those of the products of the Pd-mediated polymerization of **1** and **2**.

Thermally induced copolymerization of 1 with styrene

As a typical procedure for the thermally induced copolymerization of **1** with styrene, the procedure for run 3 in Table 3 is described as follows.

Under a nitrogen atmosphere, BQ (74.5 mg, 0.689 mmol) was placed in a Schlenk tube. After a mixture of **1** (289.3 mg, 1.740 mmol) and styrene (1.00 mL, 8.75 mmol) was added at room temperature, the mixture was degassed three times by freeze–thawing, and stirred for 18 h at 80 °C. The volatiles were removed under reduced pressure and 20 mL of chloroform was added to remove insoluble solid by filtration. The chloroform solution was concentrated to give a crude product, which was purified by using preparative recycling GPC to afford the copolymer as a reddish-brown solid (102 mg, 26.3%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.0–8.0 (C_6H_5 [styrene], $-C(=O)-CH=CH-$), 1.7–2.4 ($-CH=CH-CH_2-$, main chain CH from styrene), 1.0–1.7 ($CH_2-[CH_2]_3-CH_3$, main chain CH_2 from styrene), 0.4–1.0 (CH_3). The signal for main chain CH from **1′** could not be identified.

Table 3 Thermally induced copolymerization of **1** with styrene

Run	[**1**]:[St]:[BQ]	Yield (%)[a]	M_n[b]	M_w/M_n[b]	Composition[c] [**1′**]:[St]	T_g	Elemental analysis C%:N% (100 × [–N=N–])/{[–N=N–] + [**1′**]}[d]
1	100:200:0	20.1	2,710	1.56	1:0.49		
2	100:200:40	12.4	15,200	5.78	1:0.32	n.o.[e]	68.24:8.28 (37.6)
3	100:500:40	26.3	11,100	4.95	1:0.73	79	74.76:6.65 (36.1)
4	100:1,000:40	16.0	13,200	5.59	1:1.69	88	79.36:4.91 (37.4)
5	100:2,000:40	16.1	13,300	5.27	1:5.94	97	86.32:2.30 (39.3)
6	100:4,000:40	21.9	21,400	2.46	PolySt		
7	0:1,000:0	33.5	419,000	1.13	PolySt		
8	0:1,000:40	Trace	–	–			

Bulk polymerization except for runs 1 and 2, where 2 mL of toluene was used as solvent; polymerization temperature = 100 °C; polymerization period = 18 h; for runs 1 and 2, **1** = 1.74–1.84 mmol and for runs 3–8, St = 17.5 mmol

[a] Yield (%) = 100 × (the weight of the product after purification with the recycling GPC − the weight of N contained in the product calculated from the result of elemental analysis)/(total amount of both monomers − the weight of N contained in **1**)

[b] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solutions

[c] Determined by ^{1}H-NMR

[d] The 100 × [–N=N–]/([–N=N–] + [**1′**]) values in the copolymer was calculated on the assumption that all the C content from EA derives from the repeating unit of **1** and styrene and the NMR-determined [**1′**]:[St] was correct, without considering the polymer chain ends

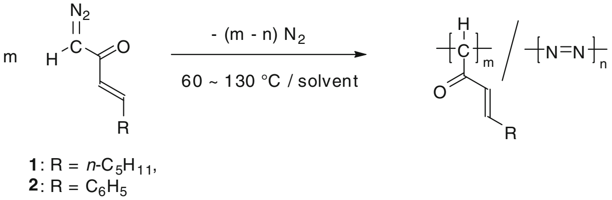
[e] Not observed

Results and discussion

Thermally induced polymerization of (*E*)-1-diazo-3-nonen-2-one (**1**) and (*E*)-1-diazo-4-phenyl-3-buten-2-one (**2**)

In the course of investigating polymerization of diazocarbonyl compounds, we found that diazoketones **1** and **2** can be spontaneously polymerized by heating alone (Scheme 2, Tables 1, 2).

For example, as shown in runs 2–4 in Table 1, heating **1** at 60–100 °C in toluene or anisole resulted in the formation of polymeric products, whose GPC-estimated



Scheme 2 Thermally induced polymerization of diazoketones

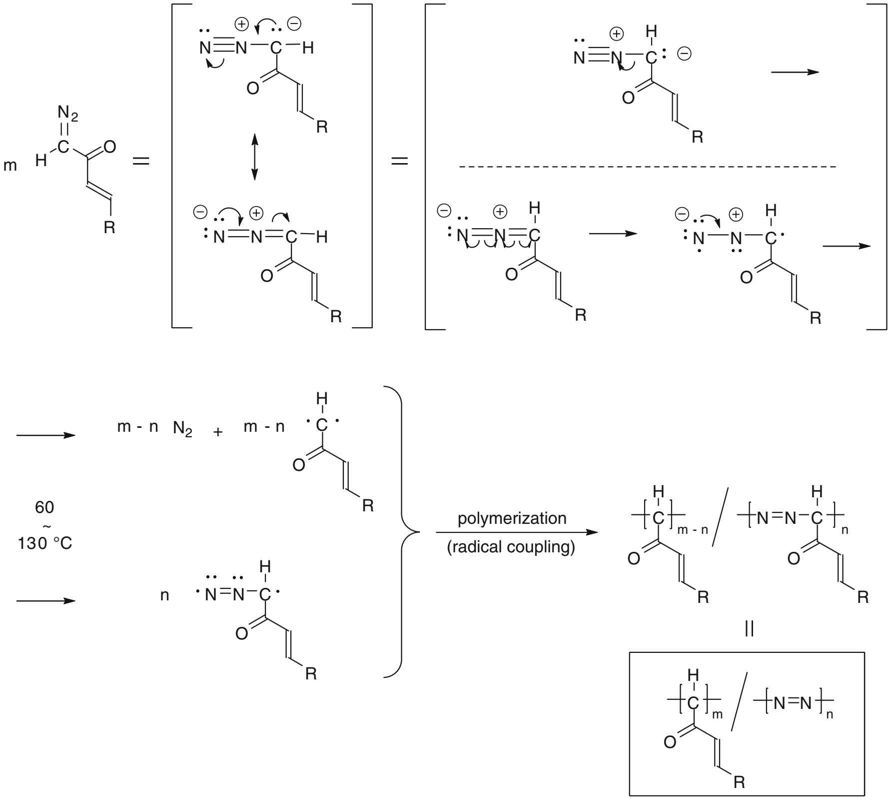
M_ns (based on PMMA standards) were 2,200–2,600 and ^{1}H-NMR spectra were almost identical with those of polymers obtained by the Pd-mediated polymerization of **1**. Whereas heating at 130 °C in anisole afforded a lower molecular weight product ($M_n = 780$) in a higher yield (run 5), the yield significantly decreased when the reaction was conducted at 40 °C (run 1). Similar thermally induced polymerization behavior was observed for **2** as summarized in runs 1–4 in Table 2, although the M_ns of the products were much lower than those of the products obtained from **1** under the same condition in Table 1.

On the assumption that the polymerization was initiated by some radical species generated by the heating, **1** was heated in the presence of radical initiators (runs 6 and 7, Table 1). As a result, increase of polymer yield (run 7) and decrease of M_n (runs 6 and 7) were observed, which supports the idea of the initiation by radical species.

Results of elemental analyses listed in Tables 1, 2 reveal the structural feature of the polymers obtained by the thermally induced polymerization, compared to those obtained by the Pd-mediated polymerization. As we have demonstrated in our previous publications [10, 11, 15], N-content in the polymers obtained from the Pd-mediated polymerization of diazoketones should be ascribed to the incorporation of azo group in the main chain (Scheme 1b). In particular, in the case of the Pd-mediated polymerization of phenyldiazomethane, the incorporation of the azo group was confirmed by a Raman spectrum of a product [15]. Although the degree of the azo group incorporation depends on the reaction condition, the content for a polymer obtained by the Pd-mediated polymerization of **1** was rather low (1.09%) as demonstrated in run 19 in Table 1. On the other hand, run 3 in Table 1 indicates a much higher N-content (8.64%), which corresponds to the azo content of 33.2 mol% ($100 \times [\text{–N=N–}]/\{[\mathbf{1'}] + [\text{–N=N–}]\}$), if we simply assume that all the C content of the sample comes from the acylmethylene repeating unit **1′**. The same calculation resulted in an azo content of 5.41 mol% for the sample obtained by the Pd-mediated polymerization in run 19. Similar trend was observed for the thermally induced polymerization of **2**, by comparing the results in the runs 3 (thermally induced polymerization, azo content = 32.3 mol%) and 13 (Pd-mediated polymerization, azo content = 1.64 mol%) in Table 2.

From these results, it is apparent that the thermally induced polymerization of **1** and **2** proceeds in a different mechanism than that operates in the Pd-mediated polymerization of these monomers. One of the possible mechanisms is shown in Scheme 3, where the propagation is a radical coupling of two types of biradical species (with or without N_2) generated from the diazoketones by heating (We do not have any information with respect to the multiplicity (singlet or triplet) of the carbene species generated from 1 to 2. For theoretical studies on the multiplicity of carbenes derived from various diazo compounds, see [16]). Although the biradicals should be very unstable and easily form dimers and low molecular weight cyclic oligomers, some parts of the coupling products would lead to the polymer formation. The observed high azo contents in the products suggest that the presence of the azo containing biradical might play an important role for the linear polymer chain to extend.

As alternate polymerization mechanisms, cyclopropanation and/or radical vinyl polymerization of the C=C might be considered. However, although we do not have



Scheme 3 Proposed mechanism for the thermally induced polymerization of diazoketones

a definitive evidence at present, we assume that such possibilities would be ruled out from the following reasons: (1) the reactivity of diazocarbonyl compounds for cyclopropanation toward electron-deficient C=Cs is basically low even in the presence of metal catalysts [17], (2) polymerizability of 1,2-disubstituted olefins except for cyclic compounds such as maleic anhydride and maleimide analogs is also generally low. For example, it was reported that methyl crotonate cannot be polymerized by radical initiators (For polymerization of methyl crotonate, see [18]). Indeed, we did not obtain polymeric products by heating starting materials for **1** and **2**, *trans*-3-nonen-2-one and 4-phenyl-3-buten-2-one, respectively, with AIBN at 80 °C. In addition, the observation of IR absorption of C=O stretch of polymers from **1** at the same wavelength (1,660 cm^{-1}) as that of monomer **1** indicated that the α,β-unsaturated carbonyl group in **1** was intact during the polymerization procedure.

Thermally induced polymerization of diazoketones in the presence of benzoquinone

Next, in order to check the effect of addition of an inhibitor on the thermally induced polymerization, diazoketone **1** was heated at 80 °C in toluene with BQ in various [**1**]:[BQ] ratios as shown in runs 8–11 in Table 1. Contrary to our initial expectation, the polymerization was not inhibited and M_ns of the resulting polymers increased with the increase of [BQ], reaching up to 7,600 in run 10 with the ratio of [**1**]:[BQ] = 100:25. The M_n slightly increased when the polymerization was conducted at 100 °C (runs 13 and 14) up to 8,400. On the other hand, NQ did not show the M_n elongation effect, although the polymerization was not suppressed by its addition (run 12). When GX was used as an inhibitor instead of the quinones, although the polymerization was not inhibited, M_n became lower than those of polymers obtained without any additive (runs 15–16, Table 1). Similar effect of the addition of BQ and NQ was observed for the thermally induced polymerization of **2**, even in a lesser extent (runs 5–10, Table 2).

As a mechanism for the M_n elongation effect of BQ, we at first assumed the incorporation of BQ in a biradical form in the main chain with the radical coupling propagation for the polymerization. However, ^{1}H-NMR spectra of the products obtained in the presence of BQ did not exhibit signals assignable to the incorporated BQ as shown in Fig. 1a, although a very small signal derived from BQ moiety attached at both chain ends would overlap with the broad signal at 6.7–7.2 ppm (The signal for BQ in ^{1}H-NMR in $CDCl_3$ appears at 6.79 ppm).

Thus, as another possibility, we can suppose that the propagating chain ends of this polymerization would have BQs as described in Scheme 4. Then, the resulting C–O bond would stabilize the radial chain end, preventing unfavorable side reactions such as formation of cyclic oligomers. However, the C–O bond would be cleaved reversibly by heating, regenerating the radical chain end that can react with the biradicals formed from the monomers. This mechanism should be reminiscent us of the one demonstrated in TEMPO-mediated living radical polymerization [19], and suggests that the use of excess BQ could be one of the reasons for the low polymer yields. However, the reason why BQ is not incorporated into the main chain and the nature of the other group (denoted as X in Scheme 4) attached to BQ is not clear at present.

In accord with the proposed mechanism, the ^{1}H-NMR spectrum in Fig. 1b for the sample obtained with NQ ([**1**]/[NQ] = 100:40, M_n = 1,200, M_w/M_n = 1.28 [GPC based on PMMA standards]) exhibits the signals for aromatic-Hs assignable to NQ units at the polymer chain ends: signals at 7.9–8.4, 7.3–7.8, and 6.7–7.2 ppm correspond to the NQ signals at 8.1, 7.7, and 7.0 ppm (Fig. 1c), respectively. A somewhat reasonable value (M_n = 1,830) was obtained from the calculation using the integral ratio between the peaks at 7.9–8.4 ppm for NQ and 0.8 ppm for CH_3 of **1′** unit on the assumption that the NQ-moiety was attached to both chain ends of the polymer. Considering the polymerization mechanism described above, the lower M_n elongation effect of NQ could be ascribed to the more stable radical species derived from NQ, resulting in the higher concentration of radical polymer chain end in the equilibrium between active and dormant species.

To confirm the presence of BQ unit at polymer chain ends, after **1** and BQ ([**1**]/[BQ] = 100:40) was reacted at 80 °C for 3 h in toluene and the resulting polymer was isolated, second stage polymerization was conducted by adding an equal amount of **1** to a toluene solution of the polymer and heating the mixture at 80° for 12 h. As a result, elongation of M_n was attained by the second stage polymerization

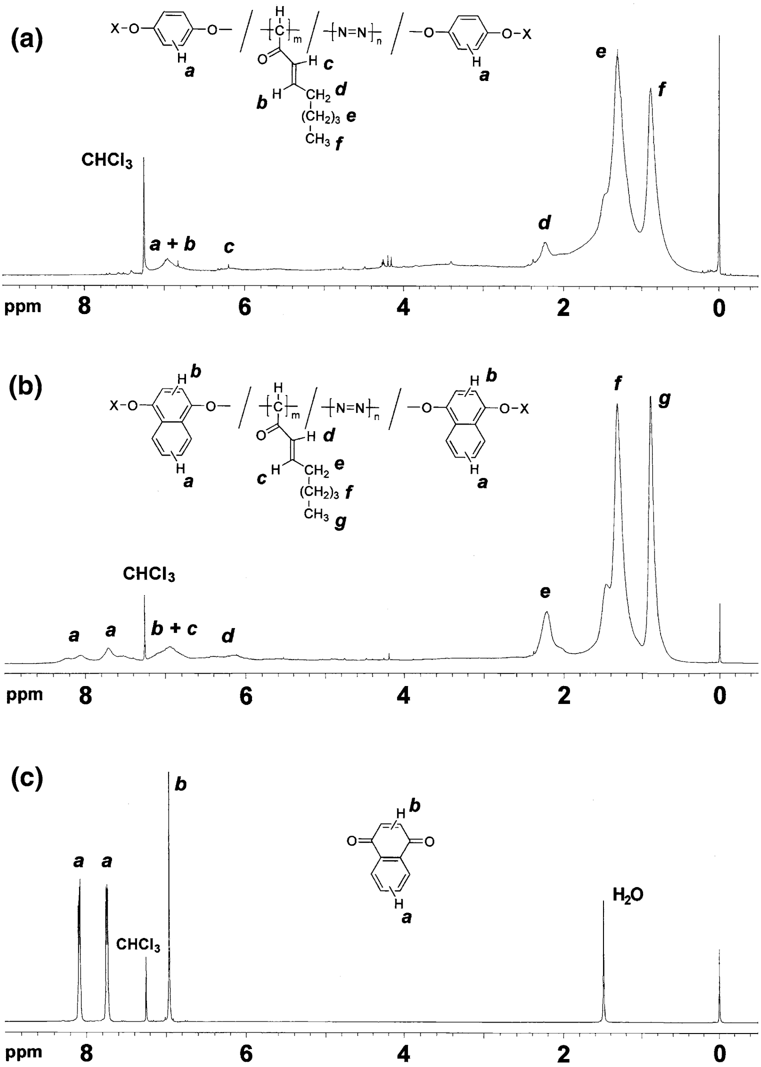
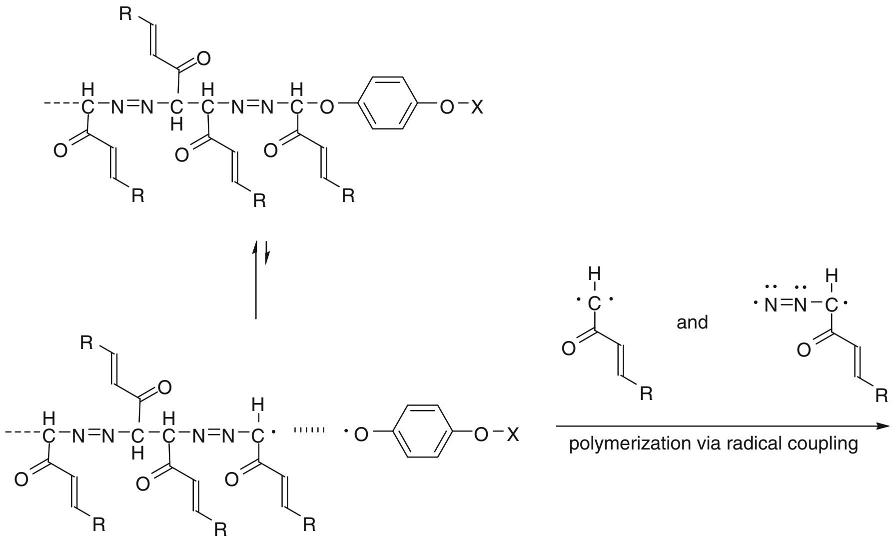


Fig. 1 ^{1}H-NMR spectra of polymers obtained from **1** in the presence of BQ (**a**) and NQ (**b**), and a spectrum of NQ (**c**)

from $M_n = 1{,}700$ to $M_n = 2{,}620$, indicating that the propagating ability still remained at the BQ-attached polymer chain end.

When THF was employed as a solvent for the thermally induced polymerization of **1** and **2** at 60 °C, the similar M_n elongation effect of BQ was observed, although the polymer yield became much lower (runs 17 and 18 in Table 1, and runs 11 and 12 in Table 2). The high azo contents observed in the products obtained in THF suggest that the polymerization proceeded in the same mechanism as that in toluene.



Scheme 4 Proposed mechanism for propagation in the presence of benzoquinone

Thermally induced copolymerization of **1** with styrene

Assuming that the thermally induced polymerization of **1** proceeds via radical propagating species, copolymerization of **1** with styrene (St) was examined. When the copolymerization was conducted with the feed ratio of [**1**]:[St] = 100:200 in the absence of BQ, we obtained a polymeric product, whose GPC chart was unimodal and ^{1}H-NMR spectrum exhibits signals derived from both repeating units (run 1 in Table 3). The results suggested that the radical copolymerization actually occurred, although the M_n (2,710) of the product was rather low.

On the other hand, when 40 equiv of BQ with respect to [**1**] was employed for the copolymerization, M_n of the copolymers drastically increased. For example, the copolymerization with a feed ratio of [**1**]:[St]:[BQ] = 100:200:40 gave a copolymer whose M_n was 15,200 and composition was [**1′**]:[St] = 1:0.32 based on its ^{1}H-NMR spectrum (run 2). Increase of the relative St feed ratio resulted in the gradual increase of St composition, as demonstrated in runs 2–6, eventually giving polystyrene with the ratio of [**1′**]:[St] = 100:4,000 in run 6. Although the copolymers have broad molecular weight distributions, their GPC traces are unimodal. As shown in Fig. 2, ^{1}H-NMR spectrum for the sample in run 5 exhibits signals derived from both repeating units, and the composition can be calculated from the integral ratio of signals at 6.2–7.4 ppm (C_6H_5– for St and CH=CH for **1′**) and 0.5–1.0 ppm (CH_3 for **1′**). The N-content of the copolymers determined by elemental analysis can be interpreted as 36–39 mol% of azo group with respect to the acylmethylene unit as listed in Table 3, based on the calculation using C and N % and ^{1}H-NMR-estimated composition of [**1′**]:[St]. Each copolymer sample in runs 3–5 in Table 3 exhibits only one glass transition temperature (T_g), and the T_g increased with the increase of styrene composition approaching the T_g of

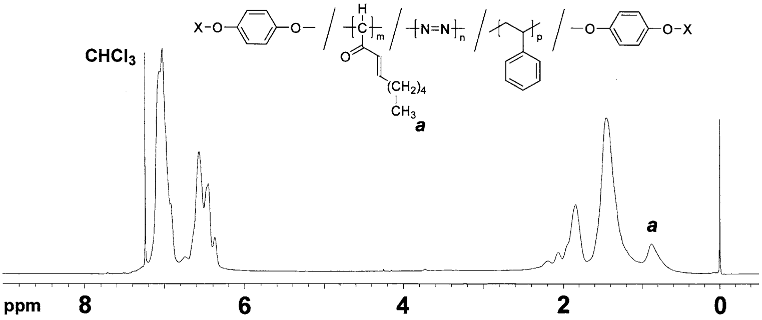
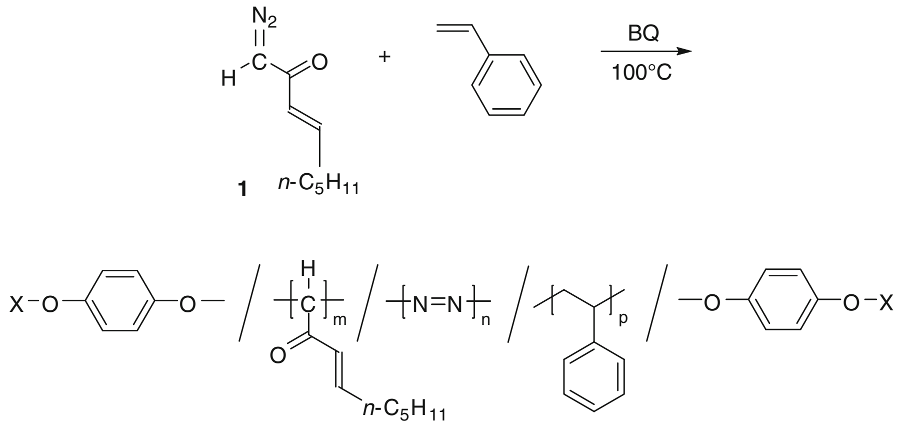


Fig. 2 ^{1}H-NMR spectrum of a sample obtained in run 5 in Table 3

polystyrene (100 °C), as expected for the flexibility imparted by the presence of alkyl side chain derived from **1**. TGA analysis under N_2 for the sample obtained in run 4 in Table 3 showed 5 and 20% weight losses at 261 and 358 °C, respectively, and 25% of the original weight remained after heating at 500 °C.

In the absence of the diazoketone **1**, a high molecular weight polySt was obtained by thermally induced radical polymerization (run 7), and the polymerization was inhibited in the presence of BQ (run 8). It is noteworthy that copolymers were actually obtained in runs 2–6, although spontaneous polymerization of styrene was inhibited in the presence of BQ as demonstrated in run 8. Based on the mechanism described in Scheme 5, we tentatively assume the presence of BQ-capped styryl radical as a propagation chain end after propagation with styrene. We, thus, suppose that the BQ-capped styryl radical should be activated in the presence of **1** to propagate with **1** and styrene, although the exact mechanism for the process is not clear at present.



Scheme 5 Thermally induced copolymerization of **1** with styrene in the presence of benzoquinone

Conclusions

We have demonstrated that thermally induced polymerization of diazoketones can afford polymers with high azo content in their main chains. The copolymerization of diazoketones with styrene in the presence of BQ proceeded to give polymers with unique structure. The new polymerization mode for diazoketones presented here will extend the utility of the monomers for polymer synthesis.

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References

1. Zhang Z, Wang J (2008) Recent studies on the reactions of α-diazocarbonyl compounds. Tetrahedron 64:6577–6605
2. Smets G, Bourtembourg A (1970) Copolymerization of aryldiazomethanes. J Polym Sci A-1 8:3251–3258 (and references therein)
3. Liu L, Song Y, Li H (2002) Carbene polymerization: characterization of poly(carballyloxycarbene). Polym Int 51:1047–1049
4. Ihara E, Haida N, Iio M, Inoue K (2003) Palladium-mediated polymerization of alkyl diazoacetates to afford poly(alkoxycarbonylmethylene)s. First synthesis of polymethylenes bearing polar substituents. Macromolecules 36:36–41
5. Bai J, Burke LD, Shea KJ (2007) BH_3-catalyzed oligomerization of ethyl diazoacetate: the role of C-boron enolates. J Am Chem Soc 129:4981–4991
6. Hetterscheid DGH, Hendriksen C, Dzik WI, Smits JMM, van Eck ERH, Rowan AE, Busico V, Vacatello M, Van Axel Castelli V, Segre A, Jellema E, Bloemberg TG, de Bruin B (2006) Rhodium-mediated stereoselective polymerization of "carbenes". J Am Chem Soc 128:9746–9752
7. Jellema E, Budzelaar PHM, Reek JNH, de Bruin B (2007) Rh-mediated polymerization of carbenes: mechanism and stereoregulation. J Am Chem Soc 129:11631–11641
8. Noels AF (2007) Carbene chemistry: stereoregular polymers from diazo compounds. Angew Chem Int Ed 46:1208–1210
9. Otsu T, Shiraishi K, Matsumoto A (1993) Monomer-isomerization radical polymerization of di-tert-butyl maleate and preparation of poly(fumaric acid) via pyrolysis. J Polym Sci A 31:885–890 (and references therein)
10. Ihara E, Fujioka M, Haida N, Itoh T, Inoue K (2005) First synthesis of poly(acylmethylene)s via palladium-mediated polymerization of diazoketones. Macromolecules 38:2101–2108
11. Ihara E, Hiraren T, Itoh T, Inoue K (2008) Palladium-mediated polymerization of cyclic diazoketones. J Polym Sci A 46:1638–1648
12. Ihara E, Kida M, Itoh T, Inoue K (2007) Organoaluminum-mediated polymerization of diazoketones. J Polym Sci A 45:5209–5214
13. Danheiser RL, Miller RF, Brisbois RG, Park SZ (1990) An improved method for the synthesis of α-diazo ketones. J Org Chem 55:1959–1964
14. Hegedus LS (2002) Organopalladium chemistry. In: Schlosser M (ed) Organometallics in synthesis. A manual. Wiley, West Sussex, p 1126
15. Ihara E, Kida M, Fujioka M, Haida M, Itoh T, Inoue K (2007) Palladium-mediated copolymerization of diazocarbonyl compounds with phenyldiazomethane. J Polym Sci A 45:1536–1545
16. Scott AP, Platz MS, Radom L (2001) Singlet-triplet splittings and barriers to Wolff rearrangement for carbonyl carbenes. J Am Chem Soc 123:6069–6076
17. Davies HML (1991) Addition of ketocarbenes to alkenes, alkynes and aromatic systems. In: Trost BM (ed) Comprehensive organic synthesis, chapter 4.8, vol 4. Pergamon Press, Oxford, pp 1031–1067
18. Ute K, Tarao T, Hongo S, Ohnuma H, Hatada K, Kitayama T (1999) Preparation of disyndiotactic poly(methyl crotonate) by stereospecific group transfer polymerization. Polym J 31:177–183 (and references therein)
19. Georges MK, Veregin RPN, Kazmaier PM, Hamer GK (1993) Narrow molecular weight resins by a free-radical polymerization process. Macromolecules 26:2987–2988