

Synthesis of an Azo Macromolecular Initiator Composed of Polyamide 4 and Its Initiation Activity for the Radical Polymerization of Vinyl Monomers

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ABSTRACT: Polyamide 4 containing an azo group (azo-PA4) was synthesized by the ring-opening polymerization of 2-pyrrolidone when 4,4'-azobiscyanopentanoyl chloride was used as an initiator. It was possible to control the molecular weight (MW) of the azo-PA4s through the concentration of the initiator to some extent, and the highest weight-average MW obtained was 35×10^3 . To assess the initiation activity of the azo-PA4 for radical polymerization, styrene (St) was used as a vinyl monomer. The azo-PA4 was found to initiate the radical polymerization of St to produce polymers. Analyses by FT-IR

spectroscopy, $^1\text{H-NMR}$, and differential scanning calorimetry after the homopolymers [polyamide 4 (PA4) and polystyrene (PSt)] were removed by Soxhlet extraction showed that the remaining polymer was PA4-*block*-PSt. Azo-PA4 was also found to have an initiation activity for other vinyl monomers (methyl methacrylate, vinyl acetate, etc.). © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: biodegradable; block copolymers; 2-pyrrolidone; polyamides; radical polymerization

INTRODUCTION

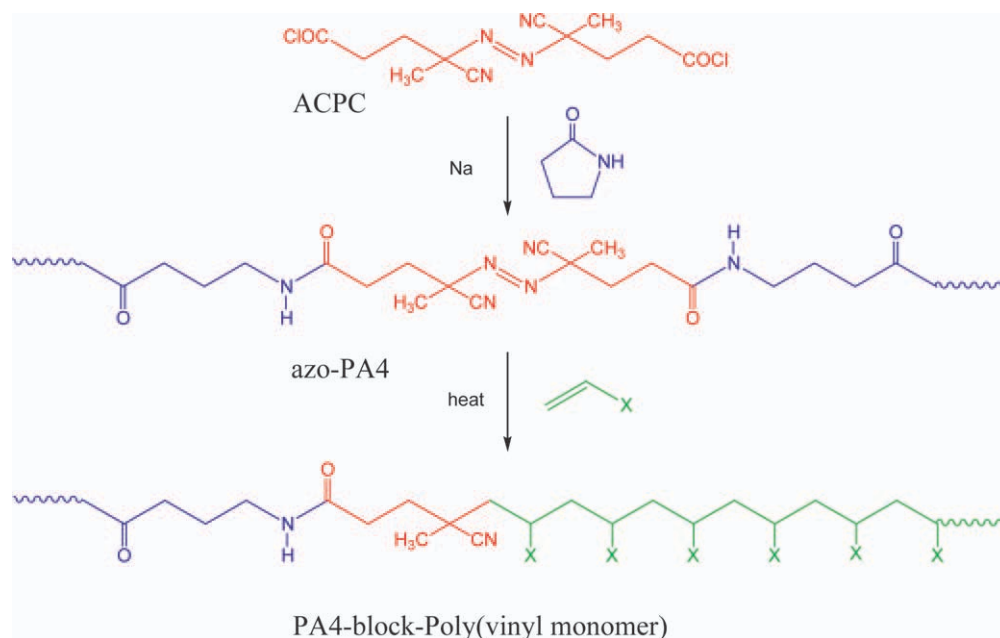
The synthesis of polyamide 4 (PA4) by the ring-opening polymerization of 2-pyrrolidone was first reported by Ney et al.¹ in 1953. Since then, the syntheses and properties of PA4 have been investigated intermittently;^{2–6} however, this topic has received very little attention, and so far, no processes have been developed to realize a practical use of PA4. Nevertheless, some researchers have shown interest in PA4 because of its unique properties, and a few articles on this compound have been published in recent years.^{7–11}

Under these circumstances, we focused our attention on the environmental sustainability of PA4. That is, PA4 was synthesized by 2-pyrrolidone, which can be easily prepared from biomass. Specifically, 2-pyrrolidone can be obtained via the decarboxylation of glutamic acid derived from glucose into γ -aminobutyric acid by a biological process and via the cyclization of γ -aminobutyric acid into 2-pyrrolidone by a chemical process. The use of biomass provides one promising solution to the depletion of fossil resources (petroleum, etc.) from the viewpoint of green sustainable chemistry. Additionally, PA4

has excellent thermal and mechanical properties because of the strong hydrogen bonds among its polymer chains. Furthermore, various structures of PA4 can easily be designed because of a polymerization mechanism in which the initiators are attached to the polymer chains. This polymerization mechanism plays a key role in the development of novel PA4s containing unique structures that differ from conventional linear PA4. Specifically, when a base is used as a catalyst and a carboxylic acid derivative is used as an initiator, an amide anion of 2-pyrrolidone forms and reacts with the carboxylic acid derivative to produce acylated 2-pyrrolidone. Because the acylated 2-pyrrolidone has a high reactivity, the ring-opening polymerization of 2-pyrrolidone proceeds through an activated monomer mechanism.² When initiators having various structures or functional groups are used, the characteristic structure or functionality from the initiators is incorporated into the PA4 chains. Consequently, the utilization of the activated monomer mechanism mentioned previously enables the modification of the physical properties or the introduction of functionality into the polymer. For example, when a polybasic acid chloride was used as an initiator, a branched structure was formed in PA4. The branched PA4 showed superior tensile strength to that of linear PA4 (e.g., four-branched type, 72 MPa).⁸

On the other hand, we selected an azo group that exhibited polymerization activity toward vinyl

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Scheme 1 Synthesis of the azo-PA4 macromolecular initiator and PA4-*block*-poly(vinyl monomer). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomers to provide functionality to PA4. When 2-pyrrolidone was polymerized with an initiator containing an azo group, the resulting polyamide 4 containing an azo group (azo-PA4) was a radical producer and an initiator for the PA4-*block*-polyvinyl monomer (Scheme 1). Over the last few decades, numerous investigations have been carried out on azo macromolecular initiators synthesized by polycondensation or polyaddition.^{12–22} Two types of synthetic pathways can be used to synthesize block copolymers: vinyl polymerization followed by ring-opening polymerization and vice versa. However, to the best of our knowledge, very few azo macromolecular initiators have been synthesized with the ring-opening polymerization in the first step.^{23,24} The advantages of the latter synthetic path (the synthesis of an azo-PA4 macromolecular initiator with the ring-opening polymerization in the first step) are as follows:

1. The molecular weight (MW) of the azo-PA4 macromolecular initiator can be controlled.
2. The method can be applied to vinyl monomers that have polar groups (polar groups suppress the polymerization of 2-pyrrolidone; therefore, the polymerization of the vinyl monomers should be conducted after the synthesis of PA4^{25–27}).
3. The macromolecular initiator can be synthesized directly from the azo reagent with 2-pyrrolidone (the synthesis of the initiator by ring-opening polymerization requires only one step, whereas the synthesis by polycondensation requires the

formation of a PA4 chain first and the subsequent introduction of azo groups.).

The purposes of this study were to synthesize an azo-PA4 and to determine if the azo-PA4 was applicable to the radical polymerization of vinyl monomers as azo macromolecular initiators.

EXPERIMENTAL

Materials

2-Pyrrolidone (Kishida Chemical, Osaka, Japan) was distilled under reduced pressure. Sodium (Wako Pure Chemical Industries, Osaka, Japan) was used after impurities were removed from the surface. 4,4'-Azobiscyanopentanoic acid (Wako Pure Chemical), thionyl chloride (Kishida Chemical), *n*-hexane (Wako Pure Chemical), tetrahydrofuran (Wako Pure Chemical), 2,2,2-trifluoroethanol (Kishida Chemical), and formic acid (Wako Pure Chemical) were used as received. Styrene (St), methyl acrylate (MA), methyl methacrylate (MMA), vinyl acetate (VA), acrylic acid (AA), and *N*-vinyl-2-pyrrolidone (NVP) (Wako Pure Chemical) were purified by distillation.

Synthesis of 4,4'-azobiscyanopentanoic chloride (ACPC)

4,4'-Azobiscyanopentanoic acid (5.00 g; 17.8 mmol) was dispersed in thionyl chloride (60 mL; 823 mmol) in an ice-water bath under an argon atmosphere, after which it was incubated at room temperature

TABLE I
Results of the Polymerization of 2-Pyrrolidone with ACPC as an Initiator

Run	Initiator (mol %) ^a	Catalyst (mol %) ^b	Yield (%)	$M_n \times 10^{-3}$ ^c	$M_w \times 10^{-3}$ ^c	M_w/M_n
1	0.5	3.5	4	8.3	13.4	1.62
2	1.0	4.0	7	8.1	12.0	1.48
3	1.5	4.5	37	22.1	35.3	1.59
4	2.0	5.0	48	15.3	29.0	1.89
5	3.0	6.0	55	14.0	22.4	1.61
6	4.0	7.0	78	12.6	21.4	1.69
7	6.0	9.0	70	11.1	16.9	1.52

^a ACPC; Converted concentration from quantities of chlorocarboxyl groups in the initiator.

^b Na; Calculated from quantities of sodium.

^c Determined by GPC. The eluent was HFIP, and the standard was poly(methyl methacrylate).

overnight. The reaction product was then passed through a glass filter to remove the insoluble fraction. The filtrate was subsequently concentrated by the evaporation of thionyl chloride *in vacuo* to give a white solid.¹⁴ The yield was 62%.

Synthesis of azo-PA4

A typical procedure was as follows. 2-Pyrrolidone (4.26 g, 50 mmol) and sodium (0.069 g, 3 mmol) were placed in a round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was then heated to 50°C under reduced pressure. After the sodium reacted completely with 2-pyrrolidone, *n*-hexane (5 mL) was added to the flask; we took care not to raise the temperature during polymerization. The reaction mixture was then cooled in an ice–water bath carefully in a manner that prevented the 2-pyrrolidone from solidifying, after which ACPC (0.238 g, 0.75 mmol) dissolved in tetrahydrofuran (1 mL) was added to the flask. The reaction mixture was kept in the ice–water bath until the viscosity increased greatly, at which point it was brought to room temperature. After the *n*-hexane was evaporated under reduced pressure, the mixture was maintained at room temperature for approximately 20 h to complete polymerization. The polymerization mixture was subsequently dissolved in 2,2,2-trifluoroethanol (50 mL) containing formic acid (0.14 g, 3 mmol) and passed through a filter paper. The filtrate was concentrated by evaporation under reduced pressure and precipitated in acetone, after which it was washed with water followed by methanol and then dried. The yield was 55%.

Polymerization of vinyl monomers by azo-PA4

The following procedure was generally used. In a 50-mL recovery flask equipped with a vacuum adapter and a magnetic stirrer, azo-PA4 (M_n 6900, 0.5 g, 0.072 mmol) was dissolved in 5 mL of 2,2,2-

fluoroethanol, after which St (1.20 g, 11.5 mmol) was added. The reaction mixture was subsequently frozen by the immersion of the reaction vessel in a dry ice–ethanol bath and then degassed *in vacuo*. Argon was passed through the vessel to displace the air by three freeze–thaw cycles. After the vessel was filled with argon, the mixture was maintained at 60°C for approximately 24 h. The polymerization mixture was then poured into acetone to form a precipitate, which was subsequently dried. To remove the homopolymer polystyrene (PSt), the polymerization product was washed with 150 mL of chloroform for 24 h with a Soxhlet extractor. The yield was 83%.

Characterization

Fourier transform infrared spectra were recorded on a Nicolet AVATAR360 FT-IR spectrophotometer (Thermo Fisher Scientific K.K., Yokohama, Japan) with KBr-pellet-containing samples. ¹H-NMR spectra were measured with a JEOL (Tokyo, Japan) JNM-ECA-500 NMR spectrometer (500 MHz). A mixture of formic acid-*d*₂ and chloroform-*d* (1/9 v/v) was used as the solvent. The MWs were determined by gel permeation chromatography (GPC) with a Tosoh (Tokyo, Japan) HLC-8220 GPC system. Two columns (TSK gel Super HM-N, TSK gel Super H-RC, Tosoh) were used with hexafluoroisopropyl alcohol (HFIP; Central Glass Co., Tokyo, Japan) as an eluent (0.2 mL/min) at 40°C. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC3100S calorimeter (Bruker AXS K. K., Yokohama, Japan). All scans were carried out from 30 to 300°C at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of azo-PA4

Azo-PA4 was synthesized from 2-pyrrolidone with ACPC as the initiator. The optimum temperature for

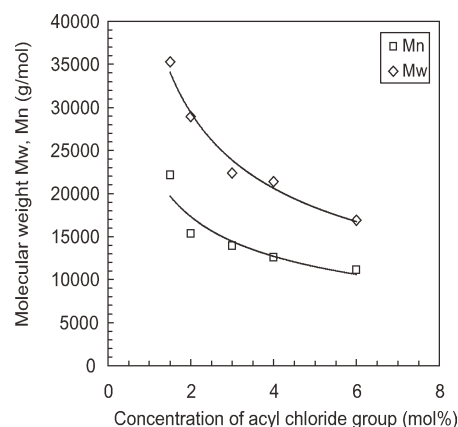


Figure 1 Relationship between M_w of azo-PA4 and the concentration of acylchloride groups in ACPC.

TABLE II
Results of the Polymerization of St by Azo-PA4 as an Initiator

Run	<i>I</i> of azo-PA4 (g; mmol) ^a	<i>M</i> of St (g; mmol)	<i>M/I</i> feed ratio (mol/mol)	<i>P</i> yield (g; %) ^e	<i>P - I</i> (= ΔM ; increments of St unit; g; mmol)	$(P - I)/I$ ($\Delta M/I$; mol/mol)	Calcd. MW (g/mol) ^f
1	0.50; 0.051 ^b	0.25; 2.4	47	0.50; 66.7	0; 0	0	4.9×10^3
2	1.00; 0.079 ^c	1.00; 9.6	122	1.18; 59.0	0.18; 1.72	21.8	8.6×10^3
3	0.50; 0.072 ^d	1.20; 11.5	160	1.41; 82.9	0.91; 8.74	121.4	16.1×10^3
4	0.50; 0.051 ^b	2.00; 19.2	376	1.99; 79.6	1.49; 14.31	280.6	34.1×10^3
5	0.25; 0.026 ^b	5.00; 48.0	1846	4.87; 92.8	4.62; 44.36	1706.2	182.6×10^3

^a Mole of azo-PA4 calculated from measured value (M_n) by GPC. For example, for run 2, $1.00/(12.7 \times 10^3) = 0.079$ mmol.

^b $M_n = 9.8 \times 10^3$, $M_w = 19.0 \times 10^3$.

^c $M_n = 12.7 \times 10^3$, $M_w = 24.6 \times 10^3$.

^d $M_n = 6.9 \times 10^3$, $M_w = 10.9 \times 10^3$.

^e Soxhlet extraction with only chloroform.

^f For example, MW of run 2 = 21.8×104.15 (formula weight of St) + $12,700 (M_n \text{ of azo-PA4})/2 = 8.6 \times 10^3$.

the polymerization of 2-pyrrolidone was 40–60°C. However, ACPC was thermally unstable. Therefore, polymerization was carried out at a lower temperature [in the vicinity of the melting temperature (T_m) of 25°C] with a longer polymerization time. After purification, azo-PA4 was obtained as a white powder or granule.

The products were mainly characterized by IR and ¹H-NMR spectroscopy to confirm the production of azo-PA4. The IR spectra revealed amide I (1636 cm⁻¹) and amide II (1541 cm⁻¹) absorptions related to PA4. However, no absorption band derived from the nitril group in the ACPC portion of the azo-PA4 was observed (2240–2260 cm⁻¹).²⁸ This absence may have occurred because the relative concentration of the ACPC portion of azo-PA4 was present at exceedingly low levels, and the nitril absorption of the azobiscyanopentanoate was very weak.

¹H-NMR signals corresponding to the methylene protons from the PA4 portion were observed at 1.83, 2.26, and 3.25 ppm, which were assigned to the β , α , and γ positions, respectively. Furthermore, a weak signal reflecting the methyl proton of the azobiscyanopentanoate portion was clearly observed at 1.68 ppm. On the basis of the intensity ratio of the methyl proton (1.68 ppm) to the methylene proton (1.83 ppm), the content of azobiscyanopentanoate portion was estimated to be 2 mol % when 2 mol % of the initiator ACPC was used for polymerization.

The results of synthesis of azo-PA4 are given in Table I. Sodium metal was used to generate 2-pyrrolidone anion. During this reaction, a lower concentration of the initiator (ACPC) was used to keep 2-pyrrolidone anion to some extent. When a high concentration of initiator was used, a polymer with a low weight-average molecular weight (M_w) was obtained in high yield (run 6 and 7). Run 3 (initiator = 1.5 mol % and catalyst = 4.5 mol %) showed the highest number-average molecular weight (M_n) and

M_w . Figure 1 provides a plot of MW against the concentration of the initiator (runs 3–7, Table I). The MWs of azo-PA4 tended to increase with decreasing concentration of the initiator. Taken together, these findings indicate that control of the PA4 chain length in the block polymer was possible. To maintain a high MW and yield, it was important to use a balanced concentration of the initiator.

Radical polymerization of vinyl monomers with azo-PA4

The results of the polymerization of St by azo-PA4s are summarized in Table II. Three kinds of azo-PA4s with different MWs were used. To clarify the relationship between the polymerization increment of St ($P - I$) and the quantity of St monomer (M), ($P - I$) and M were normalized against quantity of initiator (I). This normalization can be understood with ease. When the feed ratio (M/I) was small, St was not polymerized

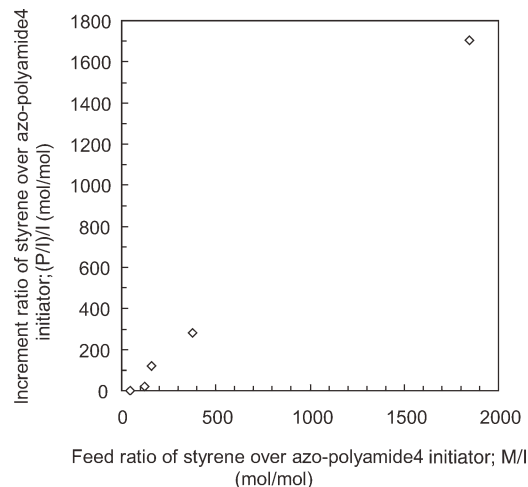


Figure 2 Relationship between the increment ratio and feed ratio.

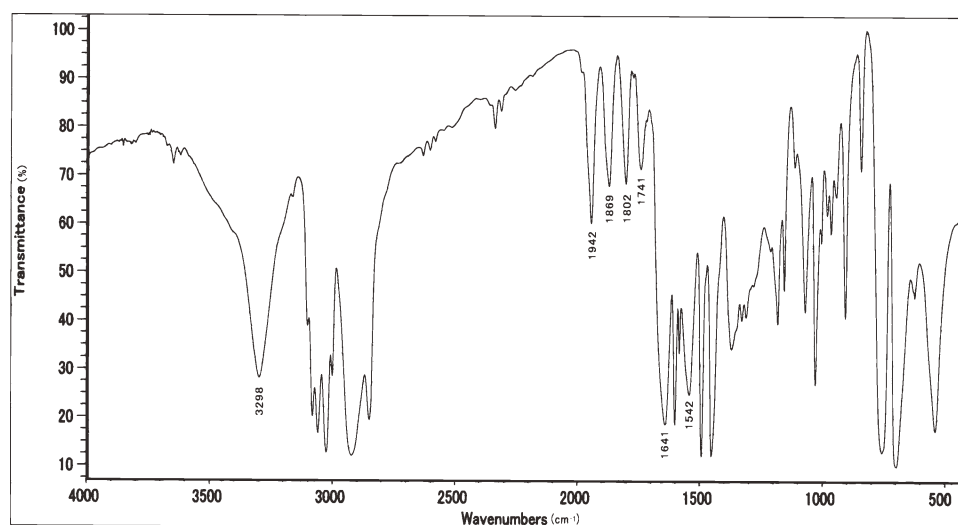


Figure 3 IR absorption spectrum of PA4-block-PSt (run 3 in Table II).

(run 1, Table II). In situations in which M/I ranged from approximately 50 to 1800; $(P - I)/I$ was proportional to M/I (Fig. 2). The St conversion did not reach 100% because a solvent was used for polymerization. Suitable amounts of 2,2,2-trifluoroethanol were used for dissolving azo-PA4 completely in runs 1–5. Among these runs, the initial St concentration of run 5 was the highest and resulted in a high conversion of the monomer. The MWs of these polymerization products could not be measured by GPC because the products were not dissolved in common GPC eluents, even in HFIP. However, we could estimate the calculated MW of the products with increments of St units per azo-PA4 initiator molecule.

To confirm initiation activity of azo-PA4, the polymerization of St was attempted according to the procedure described in the Experimental section. To remove the homopolymers (PSt and PA4) from the

crude polymer, Soxhlet extraction was carried out separately with chloroform (PSt was soluble, and PA4 was insoluble) and 2,2,2-trifluoroethanol (PSt was insoluble, and PA4 was soluble) as extracting solvents for each 24 h. The products obtained from the extraction were purified to give a white powder. As a control, the polymerization of St was attempted with a PA4 free of azo groups. In this experiment, the polymerization of St did not occur.

Figure 3 shows the IR absorption spectrum of the purified polymerization product (run 3 in Table II). In addition to the NH stretching vibrations (3298 cm^{-1}) and carbonyl stretching vibrations (1641 and 1542 cm^{-1}) caused by the PA4 portion, the vibrational bands of an aromatic ring in the PSt portion were observed at 1942 , 1869 , 1802 , and 1741 cm^{-1} . These characteristic absorption peaks suggested

TABLE III
Polymer Composition of PA4-block-PSt for the Feed Ratio of Azo-PA4 to St after Purification by Soxhlet Extraction

Run	[PA4] (units of azo-PA4 g; mmol) ^a	[PSt] (g; mmol)	[PA4]/[PSt] (feed ratio; mol/mol)	[PA4]/[PSt] (polymer composition; mol/mol) ^e
2	1.00; 11.8 ^c	1.00; 9.6	55/45	5/95
3	0.50; 5.9 ^d	1.20; 11.5	34/66	4/96
4	0.50; 5.9 ^b	2.00; 19.2	24/76	4/96
5	0.25; 2.9 ^b	5.00; 48.0	6/94	6/94

^a Moles of the feed amounts were calculated from the formula weight of constitutional repeating units of azo-PA4 (formula weight = 85.10). For example, for run 2, $1.00/85.10 = 11.8\text{ mmol}$.

^b $M_n = 9.8 \times 10^3$, $M_w = 19.0 \times 10^3$.

^c $M_n = 12.7 \times 10^3$, $M_w = 24.6 \times 10^3$.

^d $M_n = 6.9 \times 10^3$, $M_w = 10.9 \times 10^3$.

^e Soxhlet extraction with chloroform and 2,2,2-trifluoroethanol separately.

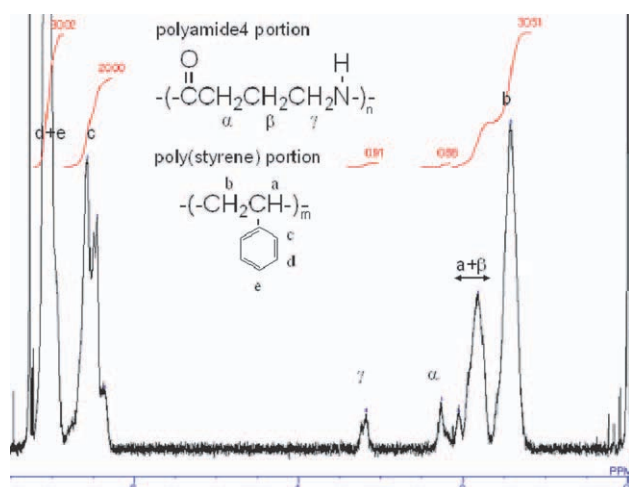


Figure 4 $^1\text{H-NMR}$ spectrum of PA4-block-PSt (run 3 in Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

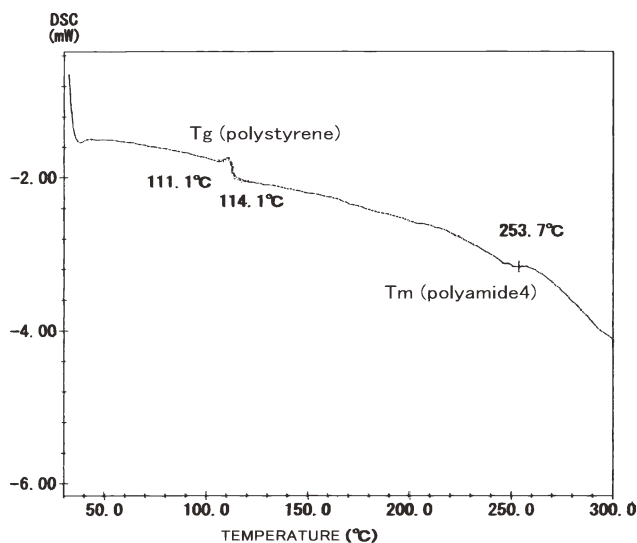


Figure 5 DSC thermogram of PA4-*block*-PSt (run 3 in Table II).

copolymer formation; therefore, it can be stated that azo-PA4 had polymerization activity for St.

Figure 4 shows an example of the $^1\text{H-NMR}$ spectrum of the purified polymerization product that did not contain homopolymers (run 3, Table II). However, signals based on both the PA4 portion and the PSt portion were observed. These results indicate that the product was a block polymer of PA4 and PSt. The assignments are described in Figure 4. $^1\text{H-NMR}$ was also used to determine the polymer composition in molar percentage by calculation of the peak areas of the PA4 and the PSt portions. The ratio of this polymer ($[\text{PA4}]/[\text{PSt}]$) was 4/96. The symbols $[\text{PA4}]$ and $[\text{PSt}]$ represent constitutional repeating units of PA4 and PSt, respectively.

Table III summarizes the polymer compositions of PA4-*block*-PSt for various feed ratios of azo-PA4 to St after purification by Soxhlet extraction. Despite variations in the feed ratio, the polymer compositions were approximately constant ($[\text{PA4}]/[\text{PSt}] = 4/96\text{--}6/94$). These results show that these copolymers had rich St in the polymer chains compared to the feed ratio. For the purpose of analyzing the components of the polymerized products, the products were separated into the chloroform-soluble, 2,2,2-trifluoroethanol-soluble, and insoluble fractions by stepwise Soxhlet extraction. The mass fractions of each component were found to be dependent on the polymerization conditions. For example, in the case of run 2 (Table II), the $(P - I)/I$ values were low; that is, the value for the insoluble fraction (block copolymer) was only 33%, and those for the chloroform-soluble and 2,2,2-trifluoroethanol-soluble fractions were 6 and 61%, respectively. On the other hand, run 4 had a high $(P - I)/I$, and the insoluble fraction (block copolymer) comprised 67%, whereas

chloroform accounted for 13%, and 2,2,2-trifluoroethanol accounted for 20%. The samples that had a large $(P - I)/I$ contained more insoluble than soluble portions. These findings indicate that the PA4-rich copolymer fraction might have been removed from the products by the Soxhlet extraction step, whereas these show bonding between the PSt chain and PA4 chain to form block copolymers.

Thermal analysis of the copolymer was carried out with DSC. Figure 5 shows the DSC thermogram obtained upon the heating of the product. The temperature of the small peak (254°C) was close to the T_m of PA4 ($260\text{--}265^\circ\text{C}$)^{8,29}. As a result, this transition was attributed to the melting of the PA4 segments. The steplike transition, which occurred in the range $111\text{--}114^\circ\text{C}$, likely corresponded to the glass-transition temperature (T_g) of PSt ($91\text{--}128^\circ\text{C}$); therefore, this transition was attributed to the T_g of the PSt segments. The DSC thermogram revealed the expected block nature of the copolymer. Similar thermograms were obtained for other copolymers, such as the values of $112\text{--}116^\circ\text{C}$ (T_g) and 253°C (T_m) in run 2 and $107\text{--}116^\circ\text{C}$ (T_g) and 260°C (T_m) in run 4.

In light of the IR, $^1\text{H-NMR}$, and DSC data, azo-PA4 was found to be an effective initiator for St polymerization.

Several vinyl monomers were also used to confirm the initiation activity of azo-PA4 ($M_n = 6.9 \times 10^3$). The polymerization products were purified as described previously. To remove the vinyl homopolymer, chloroform or methanol was used. The removal of PA4 was difficult because 2,2,2-trifluoroethanol is a good solvent for copolymers and PA4. Therefore, Soxhlet extraction for purification was only carried out with chloroform or methanol.

Figure 6 shows the GPC curves of azo-PA4 and the polymerization products of several vinyl monomers. With the exception of the St copolymers, the

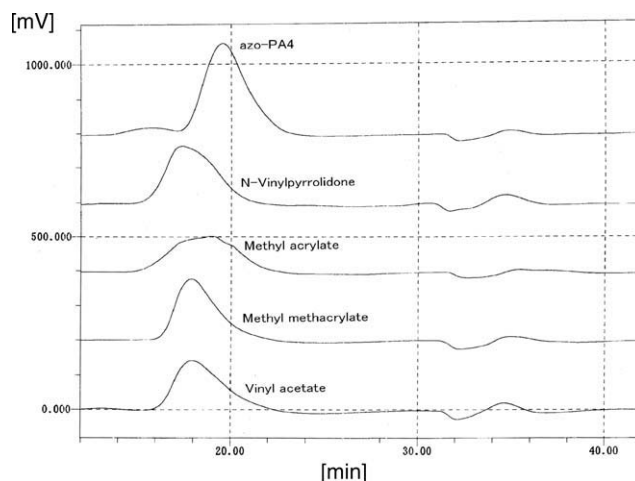


Figure 6 GPC curves of azo-PA4 and the polymerization products of several vinyl monomers.

TABLE IV
Results of the Polymerization of Several Vinyl Monomers by Azo-PA4^a as an Initiator

Run	Vinyl monomer	M (monomer feed; g; mmol)	M/I (feed ratio; mol/mol) ^b	P (yield; g; %)	P - I (= ΔM; increments; g; mmol)	(P - I)/I (ΔM/I; mol/mol)	ΔM/M (%)	M _n × 10 ^{-3c} and M _w × 10 ^{-3c} (g/mol; g/mol)	MW (Calcd; g/mol) ^e
1	St	1.20; 11.5	160	1.41; 82.9	0.91; 8.74	121.4	75.8	— ^d — ^d	16.1 × 10 ³
2	MA	0.99; 11.5	160	1.19; 79.9	0.69; 8.15	113.2	69.7	12.5; 103.5	13.2 × 10 ³
3	MMA	1.15; 11.5	160	0.89; 53.9	0.39; 3.90	54.2	33.9	17.2; 48.7	8.9 × 10 ³
4	VA	0.99; 11.5	160	0.76; 51.0	0.26; 3.02	41.9	26.3	14.1; 49.5	7.1 × 10 ³
5	AA	0.83; 11.5	160	0.73; 54.9	0.23; 3.19	44.3	27.7	8.9; 13.4	6.6 × 10 ³
6	NVP	1.28; 11.5	160	0.58; 32.6	0.08; 0.72	10.0	6.3	23.4; 116.0	4.6 × 10 ³

^a Azo-PA4 = 0.50 g (0.072 mmol). M_n = 6.9 × 10³. M_w = 10.9 × 10³. M_w/M_n = 1.58.

^b 11.5 × 10⁻³/(0.50/6900) = 160.

^c Determined by GPC. The eluent was HFIP. The standard was poly(methyl methacrylate).

^d Not measurable for insolubility in HFIP (GPC eluent).

^e For example, MW of run 2 = 113.2 × 86.09 (formula weight of MA) + 6900 (M_n of azo-PA4)/2 = 13.2 × 10³.

products were soluble in HFIP; therefore, HFIP was used as the eluent for GPC measurement. Obvious increases in the MWs were observed after the polymerization of each vinyl monomer by azo-PA4, and the MW distributions were fairly large (2–8). On the basis of the GPC analysis, the initiation activity of azo-PA4 for radical polymerization was evident.

Table IV summarizes the results of the radical polymerization. The feed amount of vinyl monomers was set to 11.5 mmol, which was approximately 160 times greater than that of azo-PA4. The conversions of vinyl monomer (ΔM/M) were 6–76%, depending on the type of monomer used. St and MA were polymerized especially well. NVP seemed to be a poor monomer for the azo-PA4 initiator. Moles of increments (ΔM) were calculated from the formula weight of each monomer and normalized against the quantity of initiator (ΔM/I). From the ΔM/I, we calculated the MWs for runs 1–6. With the exception of N-vinyl pyrrolidone (run 6), there were not extreme differences between the calculated MWs and the M_n values measured by GPC. The polymerizations proceeded in every run, but the degree of polymerization varied, depending on the vinyl monomers. One of the reasons for this appeared to be differences in

the chain-transfer constants to monomers [C_M (×10⁴)] and to solvents [C_S (×10⁴)] and termination rate constants [k_t (×10⁻⁶)] of individual monomers. The values of C_M, C_S, and k_t reported in the literature were somewhat different from each other.^{30,31} Therefore, the data were selected from the vicinity of the median in the case of wide variations, and the averages were calculated (Table V). For example, the data of St (C_M) were 0.6, 0.6, 0.6, 0.75, 0.79, 0.85, 0.92, 1.1, and 1.37 in the literature. Using these data, we calculated an average of 0.84 and a probable error of 0.06. On the basis of the calculated results, the order of each chain-transfer constant and k_t was as follows: C_M: MMA ≤ MA < St < VA < NVP, C_S (acetone): MMA ≤ MA ≤ St < VA, C_S (ethanol): MMA < St < VA, C_S (toluene): St ≤ MMA < MA < VA, and k_t: AA < St ≤ MMA ≤ MA < VA < NVP.

As judged from the order of values, VA and NVP showed large values of C_M, C_S, and k_t. These findings indicated that VA and NVP suppressed propagation and, thereby, decreased the constitutional repeating unit of vinyl monomer in the block polymer chain. This speculation was in good agreement with the polymerization results presented in Table III.

TABLE V
Average Chain-Transfer Constants and k_t Values by Data Calculated from the Literature

	C _M × 10 ⁴	C _S (acetone) × 10 ⁴	C _S (ethanol) × 10 ⁴	C _S (toluene) × 10 ⁴	k _t × 10 ⁻⁶
St	0.84 ± 0.06	0.41 ± 0.09 ^a	1.47 ± 0.15 ^a	0.14 ± 0.01 ^a	21 ± 3 ^b
MA	0.18 ± 0.12 ^a	0.23 ^a	—	2.7 ^a	31 ± 24 ^b
MMA	0.11 ± 0.02 ^a	0.195 ^a	0.40 ^a	0.27 ± 0.03 ^a	26 ± 2 ^b
VA	2.18 ± 0.07 ^a	11.9 ± 0.15 ^a	25 ^a	23.0 ± 2.06 ^a	70 ± 11 ^b
AA	—	—	—	—	2.6 ^d
NVP	4.0 ^c	—	—	—	600 ± 200 ^b

^a 60°C.

^b 25°C.

^c 20°C.

^d 23°C.

CONCLUSIONS

In this study, it was shown that an azo group could be easily introduced into PA4 chains through an activated monomer mechanism with the ring-opening polymerization of 2-pyrrolidone. Azo-PA4 had an initiation activity for the radical polymerization of a variety of vinyl monomers and could be used as an azo-PA4 macromolecular initiator. Where St was polymerized by azo-PA4, the polymerization products were composed of a PA4 block and PSt block. The resulting block copolymers are expected to be additives that could improve the thermal stability and impact resistance. Furthermore, the block copolymer could also be used as a compatibilizer between PA4 and polyolefins. Because the block copolymer (PA4-*block*-PSt) is composed of PA4 and PSt segments, the block copolymer has miscibility to each homopolymer.

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